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THERMAL AND PHOTODECOMPOSITION OF TWO ORGANOPHOSPHORUS INSECTICIDES

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Abstract

This investigation was carried out to study the influence of different temperature degrees, short ultra-violet and direct sunlight on the rate of decomposition of diazinon and pirimiphosmethyl insecticides, which are widely used in Egypt to protect vegetable crops from economic pest. The results indicated that the increase of temperature degrees means an increase in insecticide residue loss. The percentage loss of diazinon and pirimiphos-methyl insecticides was reached 39.03% and 11.58% at 20 °C; 99.97% and 58.48% at 30 °C; 99.99% and 97.53% at 40 °C and 100%, and 99.90% at 50 °C, respectively after 192 hours of the time exposure . On the other hand, the half life values of the two insecticides were >192 and >192 hours at 20 °C; 70.79 and 158.76 hours at 30 °C ;17.46 and 57.76 hours at 40 °C and 7.78 and 31.94 hours at 50 °C, respectively. In general, increasing temperature degrees and prolongation of exposure increase the percentage loss of insecticide. Pirimiphos-methyl had the highest thermal decomposition during the periods of experiment.

Diazinon was less stable than pirimiphos-methyl when exposed to UV- rays after three hours from application. The percentage loss of diazinon and pirimiphos-methyl insecticides after 24 hours was 61.61 % and 80.53 %, respectively. The half-life values of the two insecticides were 13.59 and 8.77 hours, respectively. The rate of degradation of the two tested insecticides varied according to their chemical structure, time of exposure and the wave length of UV-rays used. Pirimiphos-methyl was the most affected by UV irradiation compared with diazinon insecticide.

The tested insecticides greatly deteriorated when exposed to direct sunlight. The percentage loss of diazinon and pirimiphos-methyl were 100% after 48 hours from exposure.

The half-life values of the diazinon and pirimiphos-methyl were 1.02 and 0.60 hours, respectively. The active ingredient of the two insecticides greatly deteriorated when exposed to direct sunlight. Sunlight was found to be more effective than UV-rays in accelerating the photodecomposition of the insecticides, this could be due to thermal, evaporation and light intensity considerations.

INTRODUCTION

In Egypt, pesticides are applied to control economic pests during the summer season under enormous heat.

The ultraviolet component of sunlight, which varied from 240 to 400 nm, is responsible for pesticide photolysis in the environment. Both heat and light might affect the efficiency of pesticides, as measured by the duration of their residual effect.

The present study was undertaken to investigate the effect of temperature, UV-rays (short waves) and direct sunlight on the stability and degradation of diazinon and pirimiphos-methyl of the active ingredients.

MATERIALS AND METHODS

Pesticides

Diazinon (Baudin, Diazitol, Neocidol, Nucidol): O, O-diethyl-O- (2-isopropyl-4-methyl-6-pyrimidinyl) phosphorothioate.

Pirimiphos-methyl (Actellic, Actellifog, Silo Son, Blex): (0-2diethyl -6-methyl pyrimidin-4yl O, O dimethyl phosphorothioate).

Procedure : Aliquots of each insecticide representing one milliliter ethyl acetate containing 1000 ug (a.i.) was each spread as uniformly as possible on the surface of uncovered petridishs (5 cm i.d.)

The organic solvent (ethyl acetate) was left to dry at room temperature and the resulting deposits were divided and subjected to different treatments.

The 1st set of treatment petridishes was exposed to 20,30,40 and 50 °c for 1, 4, 12, 24, 48, 96 and 192 hours inside a dark electric oven provided with a temperature regulating system.

The 2nd set was exposed to short waves of an ultraviolet lamp (254 nm) at a distance of 12 cm for 1, 2, 4, 8, 12 and 24 hours, Abdel-Baki *et al.* (1999).

The 3rd set was exposed to normal and direct sunlight regime for 1, 4, 12, 24 and 48 hours, maximum temperature ranged between 35 and 37 °C.

The residues which remained on the exposed surfaces were quantitatively transferred to standard glass stopper test tubes with ethyl acetate after which the solvent was evaporated under reduced pressure to dryness and the residues were ready for determination by gas liquid chromatography.

Determination: A Pye Unicam 4500 gas chromatograph equipped with a flame photometric detector operated in the phosphorus mode (526 filter) was used for determination of the tested insecticides. A Pyrex glass column (1.5 m x 4 mm I.D.) was packed with 4% S.E.- 30+6% OV-210 on gas chromosorb Q (60-100 mesh).

Temp degrees and gas flow rates were as follows:

Column temp. 230 °C.
Detector temp. 240 °C.
Injector temp. 235 °C.

Gases flow rates were 30 ml/min. for nitrogen, hydrogen and air. Retention times for diazinon and pirimiphos-methyl under these conditions were 5.25 and 7.64 min., respectively. The half-life time ($t_{1/2}$) for each insecticide was calculated using the equation of Moye (Moye *et al.* ,1987).

$$T_{1/2} = \frac{\ln 2}{k'} = \frac{0.6932}{k'}$$

$$k' = \frac{1}{t_x} \ln \frac{a}{b_x}$$

Where:

k'=rate of decomposition time in days — t_x=time in days

a = initial residue. — b_x = residue at x time

RESULTS AND DISCUSSION

1. Thermal decomposition of tested insecticides

1.1 Diazinon insecticide

Table 1 shows the relationship between the different temperature degrees and the exposure period on the decomposition of diazinon insecticide on glass surface. Percent loss of diazinon residues reached 21.19, 44.83, 91.80, 99.96, 99.98, 99.99 and 100% after 1, 4, 12, 24, 48, 96 and 192 hours of exposure to 50 °C, respectively. The corresponding values when diazinon was exposed to 40 and 30 °C for the same periods were 11.26, 24.36, 44.90, 75.26, 96.90, 99.98 and 99.99% and 7.96, 11.94, 14.37, 24.61, 42.47, 76.03 and 99.97%, respectively. The percent loss of diazinon at 20 °C were 5.71, 10 71, 12.34, 16.43, 20.00, 26.44, and 39.03 % for the same periods, respectively. The calculated residue half-life values of this insecticide were > 192, 70.79, 17.46 and 7.78 hours at 20, 30, 40 and 50 °C, respectively.

1.2. Pirimiphos-methyl insecticide.

Data in Table 1 clearly showed that temperature and the period of exposure were greatly influenced the rate of pirimiphos-methyl persistence on glass surfaces. The percent loss of pirimiphos-methyl residues was being 8.55, 15.21, 31.21, 45.82, 91.17, 96.47 and 99.90% after 1, 4, 12, 24, 48, 96, and 192 hours of exposure at 50 °C, respectively. These values were 5.34, 14.62, 27.34, 30.06, 47.12, 86.27 and 97.53% and 3.33, 11.46, 16.83, 20.61, 23.88, 30.00 and 58.45 % when pirimiphos-methyl was exposed to 40 and 30 °C for the same periods of exposure, respectively. The data also showed that there was no loss of pirimiphos-methyl until 48 hours of exposure at 20°C, while the percent loss reached 4.21 and 11.58% after 96 and192 hours from exposure at 20 °C, respectively.

The calculated half-life values of this insecticide were >192, 158.44, 57.76 and 31.94.51 hours at 20, 30, 40, and 50°C, respectively.

The results clearly showed that the rates of persistence of the two insecticides were influenced by many factors, including chemical structure, vapor pressure, concentration of insecticide applied, temperature degrees and period of exposure. In general, increasing temperature enhanced the rate of residues degradation. It is clear that the percent loss of insecticide residues gradually increased with prolongation of the exposure period.

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.

Pirimiphos-methyl showed a high degradation rate when exposed to high degrees of temperature (40 and 50 °C) within the period of experiments, it is recommended for use in areas of dominant low temperatures 20-30 °C during the winter season.

Several investigators had studied and confirmed the role of temperature in degradation of insecticides, Tantawy and Hussein (1978) Abu-zahw *et al.* (1988) and Ab-

Table 1. Presistance of diazinon and pirimiphos-methyl insecticides under different temperature degrees.

Time of exposure in hour	20 ° C				30 ° C				40 ° C				50 ° C			
	µg Diazinon	Loss %	µg Pirimiphos-m	Loss %	µg Diazinon	Loss %	µg Pirimiphos-m	Loss %	µg Diazinon	Loss %	µg Pirimiphos-m	Loss %	µg Diazinon	Loss %	µg Pirimiphos-m	Loss %
0	1000	0	1000	0	1000	0	1000	0	1000	O	1000	0	1000	0	1000	0
1	942.85	5.71	1000	0	920.35	7.96	966.68	3.33	887.38	11.26	946.57	5.34	788.01	21.19	914.43	8.55
4	892.85	10.71	1000	0	880.54	11.94	885.4	11.46	756.36	24.36	853.76	14.62	551.61	44.83	847.86	15.21
12	876.59	13.34	1000	0	856.3	14.37	831.63	16.83	551	44.9	726.6	27.34	81.98	91.8	681.83	31.21
24	835.65	16.43	1000	0	753.84	24.61	793.81	20.61	247.37	75.26	699.35	30.06	0.39	g9.96	541.74	31.21
48	800	20	1000	0	575.21	42.47	761.61	23.88	30.97	96.9	528.71	47.12	0.12	99.98	88.27	45.82
96	735.51	26.44	957.82	4.21	239.67	76.03	700	30	0.19	99.98	137.29	86.27	0.03	99.9	35.25	91.17
192	609.67	39.03	884.15	11.58	0.27	99.97	415.15	58.48	0.07	9.99	24.68	97.53	0	100	0.98	96.47
$t_{1/2}$ in hrs	>192		>192		70.79		158.44		17.46		57.76		7.78		31.94	

Table 2. Effect of UV rays and sunlight on the degradation of diazinon and pirimiphos-methyl.

Time of exposure in hours	Effect of UV rays on				Effect of sunlight on			
	Diazinon		Pirimiphos-methyl		Diazinon		Pirimiphos-methyl	
	μ g insecticide	Loss %	μ g insecticide	Loss %	μ g insecticide	Loss %	μ g insecticide	Loss %
0	1000.000	0.000	1000.000	0.000	1000.000	0.000	1000.000	0.000
1	794.040	20.590	867.870	13.210	506.180	49.380	314.280	68.570
3	701.930	29.800	796.740	20.320	23.230	97.670	13.500	98.650
6	641.180	35.880	537.580	46.240	0.330	99.960	0.890	99.910
12	541.600	45.840	375.480	62.450	0.160	99.980	0.230	99.970
24	383.820	61.610	194.630	80.530	0.000	100.000	0.000	100.000
$t_{1/2}$ in hrs	13.580		8.770		1.020		0.600	

del-Baki *et al.* (1999)

2. Effect of UV-rays on the two insecticides

Data in Table 2 show that the decomposition percentages of diazinon and pirimiphosmethyl on glass surfaces increased gradually after exposure to UV-rays. The percent of loss for diazinon and pirimiphos-methyl were 20.59 and 13.21 % after one-hour exposure to UV-rays. The decomposition percentages of diazinon increased to 29.80, 35.88, 45.84 and 61.61% and pirimiphos-methyl 20.32, 46.24, 62.45 and 80.53 % after 3, 6, 12 and 24 hours of exposure to UV-rays, respectively. This showed a high degradation rate with respect to diazinon. The residue half-life values were 13.59 and 8.77 hours for diazinon and pirimiphos-methyl, respectively.

The results clearly showed that the rate of degradation of the two tested insecticides varied according to their chemical structure, time of exposure and wavelength of UV-rays. Residues were considerably degraded at different rates due to the chemical nature of each compound and the prolongation of exposure time.

In general, photodegradation was positively correlated with the exposure period. These results are in accordance with those Riskalla (1975), Murai and Igawa (1977), El-sayed *et al.* (1980), Abdel-Razik *et al.* (1982), Hegazy *et al.* (1982), Abu-Zahw *et al.* (1988), Chukuwudebe *et al.* (1989) and Abdel-Baki *et al.* (1999).

3. Effect of sunlight on the decomposition of the insecticides

Data presented in Table 2 showed that the percentage of loss for diazinon and pirimiphos-methyl were 49.38 and 68.57% after one hour of exposure to direct sunlight. The decomposition percentages of pirimiphos-methyl rapidly increased to 97.67, and 98.65% after four hours of exposure. For diazinon, the percentage loss was 99.96, 99.98 and 100% at the time of exposures of 12, 24 and 48 hours, while at the same time of exposures, pirimiphos-methyl showed f 99.91, 99.97 and 100%, respectively. The residue half-life values were 1.02 and 0.6 hours for diazinon and pirimiphos-methyl, respectively. It was concluded that the residues of the tested insecticides greatly deteriorated when exposed to direct sunlight especially for longer periods.

The results obtained agreed with the findings of Marei *et al.* (1979), El- Sayed *et al.* (1980), Abdel-Razik *et al.* (1982), Hegazy *et al.* (1982), Abu-Zahw *et al.* (1988), Chukuwudebe *et al.* (1989) and Abdel-Baki *et al.* (1999).

Considering the time of exposure to sunlight, it was obvious that 24 hours exposure seemed to be nearly decompose completely the two insecticide. Also, sunlight was more effective than UV-rays in accelerating the photodecomposition of diazinon and pirimiphos-methyl. This could be due to thermal, evaporation and light intensity considerations.

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التحطم الحرارى والضوئى لاثنين من المبيدات الفسفورية العضوية

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يهدف هذا البحث إلى دراسة تأثير درجات الحرارة المختلفة والأشعة فوق البنفسجية وأشعة الشمس المباشرة على تحطم مبيدى الدايازينون والبيريموفوس-ميثيل المستخدمان على نطاق واسع فى مكافحة الآفات الحشرية على محاصيل الخضر فى مصر.

أوضحت النتائج أنه عند تعريض متبقيات الدايازينون والبيريموفوس-ميثيل لدرجات حرارة مختلفة كانت النسبة المئوية للفاقد بعد ١٩٢ ساعة هى ٣٩,٠٣٪ و١١,٥٨٪ عند ٢٠م ، ٩٩,٩٧٪ و ٥٨,٤٨٪ عند ٣٠ م ، ٩٩,٩٩٪ و٩٧,٥٣٪ عند ٤٠ م ، ١٠٠٪ و ٩٩,٩٠ ٪ عند ٥٠ م على التوالى وكانت فترات نصف العمر هى < ١٩٢ و < ١٩٢ ساعة عند ٢٠ م ، ٧٠,٧٩ و ١٥٨,٤٤ ساعة عند ٣٠ م ، ١٧,٤٦ و ٥٧,٧٦ ساعة عند ٤٠ م . وأيضاً ٧,٧٨ و ٣١,٩٤ ساعة عند ٥٠ م . على التوالى.

وأوضحت النتائج أنه عند تعريض متبقيات الدايازينون والبيريموفوس-ميثيل للأشعة فوق البنفسجية كانت النسبة المئوية للفاقد بعد ١٢ ساعة هى ٤٥,٨٤٪ و٦٢,٤٥٪ على التوالى وكانت فترات نصف العمر هى ١٣,٥٩ و٨,٧٧ ساعة على التوالى.

كما أوضحت النتائج أنه عند تعريض متبقيات الدايازينون والبيريموفوس-ميثيل لضوء الشمس المباشر كانت النسبة المئوية للفاقد بعد ٤٨ ساعة ١٠٠ ٪ و ١٠٠ ٪ على التوالى وكانت فترات نصف العمر هى ١,٠٢ و ٠,٦٠ ساعة على التوالى.