

EFFECTS OF UV-LIGHT, TEMPERATURE AND STORAGE ON THE STABILITY AND BIOLOGICAL EFFECTIVENESS OF SOME INSECTICIDES

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Abstract: The degradation and biological effectiveness of five insecticides, ES-Fenvalerate (Soumi Gold), pirimicarb (Afox), imidacloprid (Emax), buprofenzin (Abloud) and methomyl (Methiolate) in their aqueous preparations and emulsifiable concentrates, on immature stages of whitefly insect *Bemisia tabaci*. when exposed to UV-light, two different temperatures and daylight and dark storage after exposure intervals was studied. The results indicated the degradation rates of the five tested insecticides varied according to the chemical structure, time of exposure and wavelength of UV-rays used. Of all the five insecticides, methomyl was the most affected by UV-rays. Losses of ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl within this period were 11.30, 14.80, 29.03, 31.83 and 39 %, respectively after one hour to UV-ray exposure. A significant increase in LC₅₀ value was obtained when ES-Fenvalerate in aqueous preparation was exposed to UV-light for 6 hr. The LC₅₀ values and their confidence ranges in aqueous preparations and emulsifiable concentrates were 107.5 ppm (51.7–199.2) and 93.10 ppm (48.3–150.4). The residual level of Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl were 13.52, 17.54 ppm; 12.67, 15.87 ppm; 11.78, 16.47 ppm; 11.38, 14.73 ppm; and 11.36, 11.83 ppm for two days exposed to daylight and dark storage. Insecticides could be arranged according to LC₅₀ values at zero-time as follow: ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl. The corresponding values of LC₅₀ were 3.40, 15.4, 15.6, 16.2 and 23.5 ppm for daylight storage. On the other hand, the dark storage exposure for the tested insecticides could be arranged according to LC₅₀ values as follow: ES-Fenvalerate, imidacloprid, pirimicarb, buprofenzin and methomyl. The corresponding LC₅₀ were 3.20, 14.8, 14.9, 15.9 and 21.3 ppm, respectively. In general, the amount recovered after a one day, 45°C exposure were 14.63, 12.84, 12.79, 12.14 and 11.76 ppm, for ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl, respectively. While the amounts recovered after a three day 45°C exposure were 9.28, 8.34, 7.76, 7.72 and 5.83 ppm for ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl, respectively. Efficiency against whitefly insect, *B. tabaci* immature stages was affected when aqueous preparations of the five tested insecticides were stored at 45°C for one and three days, compared to those stored under normal condition of 25°C for the same periods of time. Generally it could be concluded that buprofenzin and methomyl, were more affected by UV-light, storage and temperature than ES-Fenvalerate, pirimicarb, imidacloprid.

Key words: UV-light, insecticides, biological effectiveness

INTRODUCTION

Pesticides have been widely used in agriculture to fight against insects, weeds and other agriculture pests for many years. Pesticide use was meant to increase crop productivity. The use of pesticides in agriculture increased after World War II in order to increase world food production. Since then, there has been a marked development of different types of pesticides belonging to various groups (Dipakshi Sharma *et al.* 2010). A wide range of insecticides, including organophosphorus, carbamates, pyrethroids and new groups of pesticides, have been used on vegetable crops to control insect pests. In developing countries, these chemicals are too expensive for farmers and often ineffective against sap sucking pests (Christou and Capell 2009). An important consider-

ation in the choice of insecticides for crop protection is the length of time for which the toxic residues will persist on foliage or reproductive tissue, as well as on soils. Persistent insecticides might be preferable to use against a continuous, heavy infestation of pests, while insecticides of short persistence might be preferable for the control of sporadic infestations to allow the survival or rapid reestablishment of natural enemies (Raha *et al.* 1993)

Sunlight photo degradation is one of the most destructive pathways for pesticides after their release into the environment. Plant surfaces, especially leaf surfaces, are the first reaction environment for a pesticide molecule after application, and spray drift would indirectly present a similar situation. Light plays an important role in the behaviour of pesticides in the environment. The mol-

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ecule absorbing a photon becomes unstable, and undergoes a variety of primary processes, such as chemical reaction, isomerization etc. to return to a stable state (Zepp and Chine 1973). Photolysis on soil surfaces becomes important when a pesticide is directly applied to soil or not significantly intercepted by plants. This is true, providing that leaf cover does not shade the ground from sunlight (Linders *et al.* 2000). The fate of synthetic chemicals after application is a major problem.

The present investigation was carried out to evaluate the effects of indoor dark and daylight storage, UV-light and temperature on the biological effectiveness of aqueous preparations and emulsifiable concentrates of certain insecticides applied to immature stages of the whitefly insect, *Bemisia tabaci* under laboratory conditions.

MATERIALS AND METHODS

Insecticides used

The tested insecticides are presented as follow:

Common name	Trade name	Rate/100 l water	Stock solution [ppm]
ES-Fenvalerate	Soumi Gold EC 20%	75 ml	100
Pirimicarb	Afox DG 50%	150 ml	100
Imidacloprid	Emax SC 35%	50 g	100
Buprofenzin	Ablloud 25% SC	300 ml	100
Methomyl	Methiolate 20% SL	600 ml	100

Insect

Whitefly, *Bemisia tabaci* (Homoptera: Aleyrodidae). Infested squash leaves with *B. tabaci* (immature stages) were collected from the field and transferred to the laboratory.

Bioassay

Laboratory bioassay experiments were carried out to evaluate the effects of indoor dark and daylight storage, UV-light and temperature on the biological effectiveness of aqueous preparations and emulsifiable concentrates of certain insecticides applied to immature stages of the whitefly insect, *B. tabaci* by using the leaf-dipping method (Park *et al.* 2002). Mortality counts were recorded 24 h after treatment. The percentage of mortality was calculated after 24 h. Next, mortality counts were corrected according to formula (Abbott 1925). Then, the corrected counts were submitted to probit analysis (Finney 1971).

Two sets of experiments were carried out to evaluate the effect of UV light on the biological effectiveness of the tested compounds. The first was to evaluate the effect of UV light on the tested insecticides in their aqueous preparations. Stock solutions (100 ppm/ml) of each insecticide were prepared in water. Ten milliliter of the stock solution of each insecticide was placed inside a Petri-dish [12 cm internal diameter (i.d.)]. Uncovered Petri-dishes containing the insecticide deposits were exposed to UV-rays from an Ultraviolet lamp (254 A) at a distance of 10 cm for 1, 2, 3, 4 and 6 hours. In the second set of experiments, the same aliquots of insecticides in their EC form, placed inside the Petri-dishes, were exposed to UV-light for 2, 4 and 6 hours. At the end of the exposure

period, 5 ml of acetone were added to each Petri-dish to allow for the making of water emulsions. Dilutions were then made and tested on immature stages of the whitefly, *B. tabaci*. Mortality counts were recorded 24 h after treatment.

Evaluation of the effect of indoor dark and daylight storage of aqueous preparations on the efficiency of the tested insecticides was studied. Stock solutions (100 ppm/ml) of each insecticide were prepared in water and placed in ca. 1000 ml glass bottles. Stock solutions of each insecticide were divided into two halves, one-half was stored in complete darkness and the other half was stored under room conditions. Storage temperature averaged 27°C. Serial dilutions of these solutions were prepared at 0-time, and after storage periods of 2, 3, 4 and 8 days. They were tested against the immature stage of *B. tabaci* as described before. The insecticide residues were extracted from the remaining water emulsions and EC form using chloroform; the solvent was evaporated to dryness, transferred to a stoppered test tube and finally determined by Gas Chromatography. Chromatography was used for quantitative analysis using the method adopted by Gupta *et al.* (2005).

The rates of degradation of the tested insecticides as influenced by UV-light, and indoor dark and daylight storage was referred to zero-time samples.

The effect of temperature on the tested insecticides in their aqueous solutions was also studied. A stock concentration (100 ppm/ml) of each insecticide was prepared, then the concentrations were placed in ca. 100 ml volumetric flasks and exposed to 25°C and 45°C in a dark electric oven for 1 and 3 days. At the end of exposure periods various dilutions of insecticides were prepared and tested against the immature stage of *B. tabaci*.

RESULTS AND DISCUSSION

In tables 1–6 data concerning the following were tabulated: the degradation and biological effectiveness of five insecticides, ES-fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl in their aqueous preparations and emulsifiable concentrates, applied to immature stages of the whitefly insect, *B. tabaci* when exposed to UV-light, two degrees of temperature and daylight and dark storage after various intervals of exposure. In order to facilitate the presentation of data, each factor is discussed separately.

Effect of exposure to UV-light on the degradation and effectiveness of insecticides against the whitefly insect, *B. tabaci*

Data presented in table 1 and 2 clearly showed that the rate of degradation and effectiveness of five tested insecticides varied according to their chemical structure as well as time of exposure to UV-rays. Methomyl suffered more loss than the other four insecticides in this respect and this was pronounced by lapse of time exposure. The rapid and considerable degradation in the amount of insecticide residues in their aqueous preparations within a short period of exposure to UV-rays, *i.e.* one hour, is worth noting. The percent rates of loss within

Table 1. Effect of UV-light on the degradation of aqueous preparation and emulsifiable concentrates of the tested insecticides

Time exposure [hr]	ES-Fenvalerate		Pirimicarb		Imidacloprid		Buprofenzin		Methomyl	
	amount recovered [ppm]	loss [%]	amount recovered [ppm]	loss [%]	amount recovered [ppm]	loss [%]	amount recovered [ppm]	loss [%]	amount recovered [ppm]	loss [%]
Aqueous preparations										
0	11.86	0.00	11.28	0.00	11.92	0.00	11.06	0.00	11.34	0.00
1	10.52	11.30	9.61	14.80	8.46	29.03	7.54	31.83	6.92	39.00
2	8.63	27.23	7.32	35.11	6.29	47.23	5.18	53.16	3.61	68.17
3	6.45	45.62	5.83	48.32	4.31	63.84	3.42	69.08	2.14	81.13
4	3.87	67.37	3.54	68.62	2.67	77.60	2.28	79.40	1.78	84.30
6	2.34	80.27	2.14	81.03	1.87	84.31	1.54	86.08	0.84	92.60
Emulsifiable concentrates										
0	13.67	0.00	13.61	0.00	13.21	0.00	12.83	0.00	12.76	0.00
2	12.17	10.97	11.83	13.08	10.52	20.36	9.17	28.53	8.43	33.93
4	7.64	44.12	7.12	47.69	5.63	57.38	5.54	56.82	3.28	76.29
6	4.87	64.37	3.82	71.93	2.27	82.90	2.14	83.32	1.39	89.11

Table 2. Effect of UV-light on the biological activity of aqueous preparations and emulsifiable concentrates of the tested insecticides

Exposure time [hr]	ES-Fenvalerate			Pirimicarb			Imidacloprid			Buprofenzin			Methomyl		
	LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀	
		lower	upper		lower	upper		lower	upper		lower	upper		lower	upper
Aqueous preparations															
0	12.50	9.90	15.60	12.80	10.0	15.5	18.1	16.0	20.3	23.90	18.80	34.60	62.30	55.2	69.8
1	12.70	9.30	16.80	14.00	11.8	16.4	23.5	21.1	26.4	31.50	25.70	42.70	147.4	102.1	332.4
2	20.30	14.80	34.00	15.60	13.3	18.0	31.0	25.8	39.9	47.70	30.10	199.0	183.0	134.7	328.4
3	32.20	22.30	74.80	19.50	16.0	23.5	37.1	22.8	57.4	48.80	23.50	106.6	185.3	135.6	340.2
4	60.50	34.40	306.1	43.70	30.8	85.0	64.7	45.0	147.4	138.70	56.60	314.4	323.7	197.9	702.6
6	107.50	51.70	199.2	194.8	83.2	344.0	132.2	62.4	214.8	293.40	142.3	323.7	601.4	294.8	703.1
Emulsifiable concentrates															
0	11.80	9.0	16.60	8.90	4.20	13.2	7.70	5.50	13.4	12.80	9.0	16.60	55.9	47.9	64.2
2	13.60	12.60	19.70	13.8	11.3	16.5	11.4	6.6	50.60	15.60	12.70	19.10	58.8	49.5	69.1
4	47.70	26.80	116.5	20.4	15.5	28.0	11.80	0.60	2.80	15.70	12.60	19.30	81.7	67.5	101.9
6	93.10	48.30	150.4	95.6	57.4	142.4	102.90	42.10	190.0	146.60	67.20	267.2	258.8	177.6	402.2

this period were 11.30, 14.80, 29.03, 31.83 and 39% loss with ES-fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl, respectively (Table 2). The residue limit of methomyl in EC form recorded after one hour of exposure was 8.33 ppm, and dropped to 1.39 ppm after 6 hours of exposure. The percent rates of loss within this period were 33.93 and 89.11% loss. Generally, it is found that photodegradation is positively correlated with the exposure period. These results are in accordance, to a great extent, with those obtained by several investigators, El-sayed *et al.* (1980), Abdel-Razik *et al.* (1982), Abu-Zahw *et al.* (1988), Barakat *et al.* (1994), and Shokr (1997).

Exposure of aqueous preparations and emulsifiable concentrates of five tested insecticides, to UV-light for different periods, caused various effects depending on the time of exposure. Significant increase of LC₅₀ value (no overlapping in the confidence ranges of irradiated and non-irradiated control groups) was obtained when ES-Fenvalerate in aqueous preparation, was exposed to UV-light for 6 hr. The LC₅₀ values and their confidence ranges in aqueous preparations and emulsifiable concentrates were 107.5 ppm (51.7–199.2) and 93.10 ppm (48.3–150.4), respectively. The increased LC₅₀ is an indication of decreased potency against immature stages of the whitefly

insect, *B. tabaci*. Results, represent the biological stability of the tested insecticides: ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl as affected by UV-light in aqueous preparation and emulsifiable concentrates. ES-Fenvalerate and pirimicarb were the most persistent insecticides under UV-light exposure aqueous preparations and imidacloprid and pirimicarb in emulsifiable concentrate, while methomyl was the least persistent (Table 2).

The insecticides could be arranged according LC₅₀ values at zero-time as follow: ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl. The corresponding LC₅₀ were 12.50, 12.80, 18.10, 23.90 and 62.30 ppm, respectively. On the other hand, the emulsifiable concentrates of tested insecticides could be arranged according LC₅₀ values as follow: imidacloprid, pirimicarb, ES-Fenvalerate, buprofenzin and methomyl. The corresponding LC₅₀ were 7.70, 8.90, 11.80, 12.80 and 55.90 ppm, respectively. Katagi (2004) reported that sunlight photo degradation is an important factor influencing the fate of pesticides in the field, and one of the most destructive pathways for organic compound decomposition. Pena *et al.* (2011) reported that the UV spectrum of thiamethoxam shows a high intensity absorption band at 250–255 nm, extending > 290 nm, which means that insecticide is

absorbed in tropospheric range of sunlight, being thus susceptible to direct photolysis. Thiacloprid, however, does not show any absorption above 290 nm, therefore no direct photolysis is expected to occur.

Effects of daylight and indoor dark storage, on the degradation and effectiveness of insecticides against the whitefly insect, *B. tabaci*

Data presented (Tables 3, 4) showed that the residues of five tested insecticides greatly deteriorated when exposed to daylight and dark storage especially for longer periods. Methomyl showed a significant degradation occurred in comparison with the other four pesticides. On the contrary, ES-Fenvalerate showed more persistence when exposed to dark storage than daylight followed by pirimicarb. Accordingly, the type of insecticide played an important role in the nonenzymatic process due to sunlight exposure (Abdel-Razik *et al.* 1982). The residual levels of Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl were 13.52, 17.54 ppm and 12.67, 15.87 ppm and 11.78, 16.47 ppm and 11.38, 14.73 ppm and

11.36, 11.83 ppm for two days exposed to daylight and dark storage, respectively (Table 3).

Consideration the time of exposure to daylight and dark storage, it's obvious that the percent loss after 8 days to daylight and dark storage exposure were 85.28, 84.94%, 84.85, 89.92%, 87.30, 90.44%, 82.23, 92.13% and 91.73, 95.56% for Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl, respectively.

Exposure of aqueous preparations for five tested insecticides, to daylight and dark storage for different periods, caused various effects depending on the time of exposure. Insecticides could be arranged according to LC₅₀ values at 0-time as follow: ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl (Table 4). The corresponding LC₅₀ were 3.40, 15.4, 15.6, 16.2 and 23.5 ppm for daylight storage, respectively. On the other hand, the dark storage exposure for the tested insecticides could be arranged according to LC₅₀ values as follow: ES-Fenvalerate, imidacloprid, pirimicarb, buprofenzin and methomyl. The corresponding LC₅₀ were 3.20, 14.8, 14.9, 15.9 and 21.3 ppm, respectively.

Table 3. Effect of daylight and dark storage on the degradation of aqueous preparation of the tested insecticides

Time exposure [day]	ES-Fenvalerate		Pirimicarb		Imidacloprid		Buprofenzin		Methomyl	
	amount recovered [ppm]	loss [%]	amount recovered [ppm]	loss [%]	amount recovered [ppm]	loss [%]	amount recovered [ppm]	loss [%]	amount recovered [ppm]	loss [%]
	Daylight storage									
0	18.61	0.00	18.53	0.00	18.39	0.00	17.84	0.00	18.62	0.00
2	13.52	27.35	12.67	31.62	11.78	35.94	11.38	36.21	11.36	39.00
4	6.78	63.57	6.18	65.59	5.76	68.70	5.47	69.34	4.75	74.50
8	2.74	85.28	2.81	84.85	2.34	87.30	3.17	82.23	1.54	91.73
Dark storage										
0	21.72	0.00	21.63	0.00	22.39	0.00	22.36	0.00	21.87	0.00
2	17.54	19.24	15.87	26.63	16.47	26.44	14.73	34.12	11.83	45.91
4	8.64	60.22	6.93	67.96	5.83	73.96	4.83	78.40	3.27	85.05
8	3.27	84.94	2.18	89.92	2.14	90.44	1.76	92.13	0.97	95.56

Table 4. Effect of indoor, dark and daylight storage on the biological activity of aqueous preparations of the tested insecticides

Exposure time [day]	ES-Fenvalerate			Pirimicarb			Imidacloprid			Buprofenzin			Methomyl		
	LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀	
		lower	upper		lower	upper		lower	upper		lower	upper		lower	upper
Daylight storage															
0	3.40	2.80	4.10	15.4	13.5	17.5	15.6	14.0	17.5	16.2	13.7	19.1	21.5	19.1	23.8
2	4.20	3.30	5.40	27.5	24.1	32.3	22.5	18.6	28.7	21.0	17.8	25.4	25.3	22.4	25.8
4	29.0	15.90	112.9	34.3	28.4	44.0	25.4	20.5	34.7	97.4	56.1	641.4	37.7	34.2	42.1
8	64.5	25.1	32.1	76.8	52.6	161.2	81.1	45.2	173.8	121.7	69.4	208.5	134.6	73.1	257.5
Dark storage															
0	3.20	2.7	3.8	14.9	13.1	16.8	14.8	13.4	16.4	15.9	13.5	18.5	21.3	19.0	23.6
2	3.50	2.9	4.2	27.0	23.8	31.5	19.9	17.1	23.7	20.8	17.7	24.8	25.1	22.2	28.2
4	19.8	12.9	42.9	31.9	26.9	39.8	20.6	17.7	24.7	74.5	52.1	154.8	37.1	24.5	70.6
8	56.6	22.6	151.6	70.8	52.8	162.5	69.8	41.9	182.3	81.8	51.6	128.8	91.1	74.3	188.9

Effects of temperature on the degradation and effectiveness of insecticides against the whitefly insect, *B. tabaci*

Examination of the data (Tables 5, 6) clearly showed that rate of persistence of the five tested insecticides was influenced by three factors, *i.e.* the type of insecticides, temperature, and period of exposure. In general, the amounts recovered after a one day 45°C exposure were 14.63, 12.84, 12.79, 12.14 and 11.76 ppm, for ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl, respectively. While the amounts recovered after a three day 45C exposure were 9.28, 8.34, 7.76, 7.72 and 5.83 ppm for ES-Fenvalerate, pirimicarb, imidacloprid, buprofenzin and methomyl, respectively (Table 5). The role of temperature in increasing the degradation of in-

secticide residues were studied and confirmed by several workers, *i.e.* El-Sayed and Abdallah (1979), El-Tantawy and Hussien (1978) and Barakat *et al.* (1994).

Efficiency against the immature stages of the whitefly insect *B. tabaci* was affected when aqueous preparations of the five tested insecticides were stored at 45°C for one and three days compared to those stored under normal condition of 25°C for the same periods of time (Table 6).

Generally it may be concluded, that buprofenzin and methomyl, were more affected by UV-light, storage and temperature than ES-Fenvalerate, pirimicarb, imidacloprid, although the five compounds resist, to a reasonable extent, the effect of such factors.

Table 5. Effect of high temperature storage of aqueous preparations on the tested insecticides' biological activity

Insecticides	One day		Three days	
	amount recovered [ppm]		amount recovered [ppm]	
	at 25°C	at 45°C	at 25°C	at 45°C
ES-Fenvalerate	24.63	14.63	18.71	9.28
Pirimicarb	25.17	12.84	17.36	8.34
Imidacloprid	24.87	12.79	19.58	7.76
Buprofenzin	23.65	12.14	18.36	7.72
Methomyl	26.34	11.76	17.94	5.83

Table 6. Effect of high temperature storage of aqueous preparations on the tested insecticides' biological activity

Insecticides	One day						Three days					
	at 25°C			at 45°C			at 25°C			at 45°C		
	LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀		LC ₅₀ [ppm]	confidence limit at LC ₅₀	
		lower	upper		lower	upper		lower	upper		lower	upper
ES-Fenvalerate	12.8	10.0	15.5	31.50	25.70	42.7	15.6	13.3	18.0	43.7	30.8	85.0
Pirimicarb	15.2	9.90	35.0	31.90	26.90	39.8	19.6	12.9	42.9	60.5	34.4	360.8
Imidacloprid	20.3	14.80	34.0	32.20	22.30	74.8	30.0	25.1	38.5	64.7	45.0	147.4
Buprofenzin	23.9	18.80	34.60	37.10	28.80	57.4	37.1	24.5	70.6	74.5	52.1	154.8
Methomyl	55.9	47.90	64.20	58.80	0.495	69.1	48.8	33.5	106.6	183.5	135.6	340.2

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