Effect of Heat, Direct Sunlight and UV-Rays on the Stability of some Chlropyrifos Formulations with Emphasis to their Content of Sulfotep.

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Abstract: Sulfotep is a toxic impurity in formulations of chlorpyrifos (Teragard, Bestban and Dursban) was determined by GLC in their tested formulations, also the effect of exposure to different temperatures (30, 35, 45 and 50°C), direct sunlight and UV-rays on the stability of chlorpyrifos a.i and sulfotep content of the formulated products was studied. The results showed that Teragard formulation was the lowest in its content of sulfotep than both Dursban and Bestban formulations where the level of sulfotep as micrograms was 53.71, 164.96 and 323.92 for Teragard, Dursban and Bestban, respectively. Also results show that chlorpyrifos a.i. in all tested formulations was unstable when exposure to high degrees of temperature (45and50°C), while Sulfotep is relatively stable. The loss of the active ingredient (a.i) in chlorpyrifos formulations Teragard, Bestban and Dursban was 89.07, 87.96 and 88.63%, respectively after 144 hours of exposure to 5o°C; while the percentage loss of sulfotep was 33.22, 23.56 and 13.41 % for Teragard, Dursban and Bestban, respectively after 144 hours of exposure to this temperature.

The data showed that exposure to direct sunlight was more effective in chlorpyrifos degradation in its formulations than exposure to UV-rays where, the percentage loss of chlorpyrifos (a.i) in its tested formulation were 92.72, 90.69 and 91.08% after 48 hours of exposure to direct sunlight for Teragard, Dursban and Bestban, respectively and the percentage loss of sulfotep was 37.61, 25.77 and 15.76% after 48 hours of exposure to direct sunlight for Teragard, Dursban and Bestban, respectively. On the other hand, the percentage loss of chlorpyrifos (a.i) in its tested formulation was 42.19, 44.44 and 44.64% after 24 hours of exposure to UV-rays for Teragard, Dursban and Bestban, respectively and the percentage loss of sulfotep was 19.66, 7.0 and 3.18% after 24 hours of exposure to UV-rays for Teragard, Dursban and Bestban, respectively.

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1. Introduction:

Chlorpyrifos is an organophosphorus insecticide which is one of the most widely-used active ingredients in agricultural insect control in the world because of their acute toxicity to insect pests and short persistence after application. Chlorpyrifos is formulated into various products such as Dursban, Bestban and Teragard, etc.

Sulfotep is a highly toxic impurity that may be present in trace quantities in chlorpyrifos which contain two interesting impurities and /or breakdown products; sulfotep and 3, 5, 6-trichloro-pyridinole Allender and James (1991). Some regional manufacturers from Asia may be producing chlorpyrifos with sulfotep concentrations as high as 17% (Ambrus et al., 2003). Also sulfotep may be formed photochemicaly from a number of phosphorothioate insecticides including chloropyrifos (Abdel Bagi and Gaston, 1998)

Sulfotep is relatively a stable toxic impurity that may concentrate in the environment and causing unanticipated health and ecological problems, so that the level of sulfotep is limited to be 0.3% maximum concentration in chloropyrifos formulations FAO (2004).

Organophosphates are normally stable at ambient temperature, but at elevated temperatures its isomers may be obtained. The P=S (thiono) linkage may be isomerized to P= S (thiolo) form and the product may be substantially more toxic to mammals (Jack 2001).

Photodegradation is an abiotic process in the dissipation of pesticides where molecular excitation by absorption of light energy results in various organic reactions, or reactive oxygen species such as OH*, O3 and 1O2 specifically or none specifically oxidize the function groups in a pesticide molecule. (Katagi., 2004).

Ultraviolet (UV) light is a very high source of energy, and it promotes the breakdown of many chemicals. Most of the pesticides we use today are somewhat subject to photodecomposition. Some pesticide formulations contain UV light blockers that lessen the amount of photodecomposition of the pesticide active ingredient. (K. State 1990).

In Egypt, pesticides are mainly applied during the summer season where, the temperature is high because of the long sunny unclouded days. The ultra-violet component of sunlight which varies from 240-400 nm is responsible for pesticide photolysis in the environment. Both heat and light might affect the efficiency of pesticides which are measured by the length of their residual effect (Ruzo and Casida 1982and James et al 1984).

The present study was undertaken to investigate the effect of temperature, sunlight and direct UV-rays (short waves) on the stability of some chlorpyrifos formulations and their content of sulfotep.

2. Materials and Methods

Pesticides used: Chlorpyrifos (Dursban, Teragard and Bestban 48% EC)

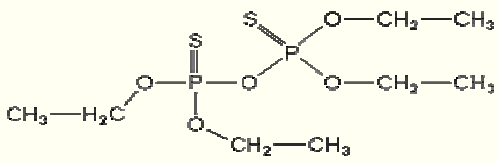
IUPAC Name:	O,O-diethylO-3,5,6-trichloro-2-pyridyl phosphorothioate
Structural formula:	

Common name: sulfotep

IUPACName:

O,O,O′,O′-tetraethyl dithiopyrophosphate

Structural formula:



2-preperation of deposits:-

One milliliter acetone containing 72000µg active ingredient of the three tested chlorpyrifos formulations (Dursban, Bestban and Teragard 48% EC) was spread as a thin film on the surface of 5cm (i.d) uncovered Petri dishes and the acetone solvent was left to dry. Three groups of these preparations were prepared.

In order to study the effect of temperature degree on the stability of three chlorpyrifos formulations and their content of

sulfotep , one group of three uncovered petri-dishes containing deposits were exposed to different temperature 30,35,45 and 50°C for different periods of exposure from 0 to 144 hours inside dark electric oven.

Other group of three uncovered Petri-dishes containing the insecticide deposits was exposed to the short wave of the ultraviolet rays 254 nm at 1,3,6,12 and 24 hours. The last group of deposits was exposed to direct sunlight for 1, 4, 8, 12, 24 and 48 hours.

3-Extraction: Insecticides residues were transferred to glass stopper test tubes using redistilled acetone as a solvent.

4-Determination of chlorpyrifos and sulfotep:

The residual of chlorpyrifos and sulfotep were analyzed according to the method of DAS (2004) with some modification by using (GLC).

A Hewlett-Packard G.C. Model 6890 instrument, equipped with flam ionization detector (FID), capillary column 15m x 0.53 mm. Nitrogen was used as carrier gas at flow rate 7 ml/min Oven temperature 160°C, injector temperature 200°C and detector temperature 250°C. Under these conditions the retention time of chlorpyrifos and sulfotep were 7.51and 3.62 min, respectively. The results of chlorpyrifos and sulfotep were quantitatively determined by comparison with the standards of known purity under the identical GLC conditions.

5-Kinetic study:

In order to study the rate of degradation of tested chlorpyrifos formulations and the half lives period (t0.5) were calculated according to equation (Weerasinghee et al., 1992).

$t0.5 = \ln 2/k = 0.693/k$

$k = 1/Tx.\ln a/bx$

Where

K= Rate of decomposition. Tx=Time in days.

A=Initial residue. Bx=Residue at time(x).

3. Results and Discussion:

Obtained data from this investigation revealed that Teragard formulation was the lowest in its content of sulfotep, while Dursban and Bestban formulation were the moderate and the highest in its content of sulfotep, respectively. This indicate that the amount of sulfotep present in the commercial formulations vary from one sample to another ,and that depend on the manufacturing practice, the storage condition and the inert ingredients used for formulating pesticide such as carriers, solvents, surfactants. These result are in harmony with those obtained by Fakhraian et al (2004) who stated that the formation of sulfotep (the major byproduct and yield) during the synthesis of chlorpyrifos are influenced by the nature and concentration of the catalysts, temperature, stirring rate ,and time of reaction. Also data show that formation of sulfotep did not affect by exposure to different temperature degrees, sunlight and UV-rays in all tested chloropyrifos formulations. The obtained results are in line with Ahmed el al (2010) who found that formation of sulfotep did not affect by storage at 54°C and 72°C for three manufactured source of chlorpyrifos. Also Allender and James (1991) demonstrated that sulfotep content of commercial products did not show any correlation with storage time.

Effect of temperature:

Temperature is very significant factor in the breakdown of pesticides where for every 10°C rise in temperature, the chemical reaction rate doubles and for every 10°C drop in temperature, the chemical reaction rate is cut in half. (K. State 1990).

The effect of different temperature degrees on the stability of chlorpyrifos active ingredient in Dursban, Teragard and Bestban formulations and their content of sulfotep are presented in Tables from (1 to3).

Data show that the stability of chlorpyrifos and sulfotep in tested formulations was dependent on the temperature and period of exposure. Temperature is known to be one of the most important factors influencing the stability, persistence and degradation of pesticides (Suett, 1979).

As shown in table (1) losses of chlorpyrifos a.i. in Dursban formulation was 10.79, 12.03, 42.23 and 52.91% after six hours of exposure to 30, 35, 45, and 50°C, respectively and reached to 51.96, 55.82, 77.09 and 88.63% after 144 hours of exposure to these temperatures, respectively and the calculated half lives (t0.5) was 138.57, 128.98, 43.4 and 5.67 hours after exposure to 30, 35, 45 and 50°C, respectively.

In addition, the results presented in Table (1) show that the level of sulfotep as micrograms was 164.96 in Dursban formulation before exposure to different temperature degrees and was affected by the temperatures and period of exposure where the percentage of losses of sulfotep was 2.87, 3.11, 4.97 and 6.72% after six hours of exposure to 30, 35, 45 and 50°C and become 15.77, 17.56, 20.66 and 23.54% after 144 hours of exposure to these temperatures.

Also the calculated half lives (t0.5) were 456.56, 410.03, 348.49 and 305.6 hours after exposure to 30, 35, 45 and 50°C, respectively.

As shown in table (2); the rate loss of chlorpyrifos a.i. in Teragard formulation was 7.55, 15.72, 44.13 and 54.49% after six hours of exposure to 30, 35, 45 and 50°C, respectively.

Losses were increased to 52.94, 60.36, 84.29, and 89.07% after 144 hours of exposure to these temperatures, respectively. Also results show that the half lives (t0.5) for chlorpyrifos in Teragard formulation were 136.0, 103.96, 23.08 and 5.51 hours after exposure to 30, 35, 45 and 50°C, respectively. In addition; the determined level of sulfotep was 53.71 micrograms in Teragard formulation and the losses of sulfotep was 4.61, 6.66, 7.56 and 8.82% after six hours of exposure to 30, 35, 45 and 50°C and reached to 25.11, 25.76, 29.28 and 33.22% after 144 hours of exposure to these temperatures and the calculated half lives (t0.5) were 286.73, 279.50, 245.90 and 216.73 hours after exposure to 30, 35, 45 and 50°C, respectively.

Data in Table (3) illustrate that the percentage loss of chlorpyrifos a.i in Bestban formulation was 5.77, 14.95, 31.95 and 44.62 after six hours of exposure to temperature at 30, 35, 45 and 50 °C, respectively and reached to 56.58, 61.86, 71.29 and 87.96% after144 hours' exposure to these temperature, also the data show that the level of sulfotep in Bestban formulation was 323.92 micrograms and influenced by temperature and period of exposure where the losses of sulfotep was 0.83,1.25, 2.78 and 3.75% after six hours of exposure to 30,35,45 and 50 °C, respectively and increased to 9.93, 10.29, 10.89 and 13.41 % after 144 hours of exposure to these temperatures. Results also show that the half lives (t0.5) for chlorpyrifos a.i. in Bestban formulation was 127.25, 87.39, 47.52 and 6.72 hours and the half lives (t0.5) for sulfotep in Bestban formulation was 725.07, 699.71, 661.16 and 536.91 hours after exposure to 30,35,45 and 50°C, respectively.

Generally, from the above mentioned data, we can conclude that. Chlorpyrifos a.i. in all tested formulations (Dursban, Teragard and Bestban) was unstable and show a high degradation rate when exposure to high degrees of temperature 45 and 50 °C with the period of experiment and there are no differences in the losses rate of the three tested formulations. Accordingly, chloropyrifos might not be used at high temperature for pest control. These data confirmed the findings of Wux et al (2006) who found that temperature had a significant effect on the degradation rate of chloropyrifos, which was increased with increasing temperature and reached the maximum at 35 degrees. Also NRA (2000) stated that chloropyrifos is thermally sensitive to temperatures over 50°C and breaks down relatively quickly in the environment.

Sulfotep concentration in all tested formulation (Dursban, Teragard and Bestban) was more stable at different degrees of temperature, than chloropyrifos a.i.; these result are in line with Meier et al (1979) who stated that sulfotep is relatively stable toxic impurity, also the rate of sulfotep degradation was more in Teragard formulation than both Dursban and Bestban formulations.

Effect of sunlight:

Sunlight photodegradation is one of the most destructive

pathways for pesticides after their release into the environment. Factors that influence pesticide photodegradation include the intensity of the sunlight, properties of the application site, the application method and the properties of the pesticide (Fred 1997).

As shown in table (4) residues of the three tested chlorpyrifos formulations greatly deteriorated when exposed to direct sunlight for longer periods, where the percentage losses of chlorpyrifos were 51.62, 59.47 and 68.07% after one hour of exposure to direct sunlight in Dursban, Teragard and Bestban, respectively and reached to 91.08, 92.72 and 90.69%, respectively after 48 hours of exposure to direct sunlight, also the calculated half lives (t0.5) were 0.97,0.84 and 0.73 hours for Dursban, Teragard and Bestban, respectively . The photodegradation of chlorpyrifos by simulated sunlight in water/methanol has been studied by Barcelo et al. (1993), and 3, 5, 6-trichloro-2-pyridinol was identified as the only degradation product.

On the contrary, Sulfotep is an impurity of chlorpyrifos was more photo stable than chlorpyrifos. Where, the percentage losses of sulfotep were 2.87, 4.5 and 1.59 after one hours of exposed to direct sunlight and reached to 25.77, 37.61 and 15.76% after 48 hours of exposure to direct sunlight in Dursban, Teragard and Bestban, respectively. The half-life periods of sulfotep were 93.13, 71.62 and 152.28 hours in Dursban, Teragard and Bestban, respectively.

Effect of ultraviolet rays:

Ultraviolet light is an extremely destructive source of energy and plays a very important role in terms of the persistence of pesticides which are exposed to it. (K. State., 1990).

Data in Table (5) show that the residues of chlorpyrifos in the three tested formulations were less affected when exposure to UV rays for longer periods as compared with exposure to direct sunlight, however the effect of UV rays was mainly due to the effect of light while the effect of direct sunlight was due to both light and heat.

Data also show that the percentage losses of chlorpyrifos a.i. in Dursban, Teragard and Bestban were 15.99, 17.98 and 17.14 % after one hour of exposure to UV- rays and reached to 44.64, 42.19 and 44.44% after 24 hours of exposure to UV- rays, respectively. Also the calculated half life (t0.5) was 26.88, 28.44 and 27.0 hours for Dursban, Teragard and Bestban, respectively; these results are in line with NRA (2000) who demonstrated that chlorpyrifos is stable in air (non-volatile) and is not sensitive to UV-rays. Also Wux et al (2006) found that photochemical degradation of chlorpyrifos in water followed the first order reaction, and its half-life was 19.74 hours under UV-rays. Also Jong and Byoung (1998) found that chlorpyrifos was more degradable in the presence of UV irradiation with sea sand than UV irradiation and UV irradiation with Tio2 powder. Kiss and Virag (2007) found that the photodegradation of chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate] may occur via two reaction patterns. It might be initiated by the cleavage of an ethyl group or a chloro group, resulting in the formation of [O-ethyl-O-(3,5,6-trichloro-2-pyridil)-hydrogene-phosphorothioate and [O,O-diethyl-O-(3,5-dichloro-2-pyridil) phosphorothioate].

On, the other hand the data in Table (5) show that sulfotep was more stable to UV- rays than chlorpyrifos where, the percentage losses of sulfotep was 1.54, 4.62 and 1.0% after one hour of exposure to UV rays and reached to 7.0, 19.66 and 3.18% after 24 hours of exposure to UV- rays for Dursban, Teragard, and Bestban, respectively. Also the estimated half-life (t0.5) was 171.4, 61.03 and 377.35 hours, respectively.

Finally, we can conclude that chlorpyrifos a.i. in tested formulations is a degradable compound, and the major pathway of transformation involves cleavage of the phosphate ester bond to form 3, 5, 6- trichloro-2-pyridinol (Rack 1993).

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Table (1): Effect of different temperature degrees on the stability of chlorpyrifos and their content of sulfotep in Dursban formulation.

Exposure time (in hours)	30 °C				35°C				45°				50°C			
	chlorpyrifos		sulfotep		chlorpyrifos		sulfotep		chlorpyrifos		sulfotep		chlorpyrifos		sulfotep	
	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss
Initial*	72000	--	164.96	--	72000	--	164.96	--	72000	--	164.96	--	72000	--	164.96	--
6	64228.0	10.79	160.21	2.87	63334.3	12.03	159.82	3.11	41596.5	42.23	156.76	4.97	33907.4	52.91	153.87	6.72
24	59458.36	17.41	155.00	6.04	55604.1	22.77	152.26	7.69	39365.7	45.32	149.32	9.48	25133.2	65.09	144.65	12.31
48	50338.1	30.08	148.21	10.15	46027.7	36.07	145.13	12.02	32186.5	55.29	141.89	13.98	20025.5	72.19	137.34	16.74
96	42364.1	41.16	144.21	12.57	39102.5	45.69	139.93	15.17	25574.8	64.48	134.44	18.50	17943.9	75.07	130.21	21.07
144	34587.3	51.96	138.94	15.77	31806.2	55.82	135.99	17.56	16494.0	77.09	130.87	20.66	8188.2	88.63	126.09	23.56
t 0.5 (hours)	138.57		456.56		128.98		410.032		43.40		348.49		5.67		305.6	

- Initial: one hour before treatment.

Table (2): Effect of different temperature degrees on the stability of chlorpyrifos and their content of sulfotep in Teragard formulation.

Exposure time (in hours)	30 °C				35°C				45°				50°C			
	chlorpyrifos		sulfotep		chlorpyrifos		sulfotep		chlorpyrifos		sulfotep		chlorpyrifos		sulfotep	
	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss
Initial*	72000	--	53.71	--	72000	--	53.71	--	72000	--	53.71	--	72000	--	53.71	--
6	66561.2	7.55	51.23	4.61	60678.8	15.72	50.13	6.66	40229.1	44.13	49.65	7.56	32765.4	54.49	48.97	8.82
24	59233.8	17.73	49.87	7.15	55203.9	23.32	48.98	8.81	34561.3	51.99	47.87	10.87	24556.1	65.89	46.31	13.77
48	45126.4	37.32	47.31	11.92	42458.8	41.03	46.55	13.33	29875.1	58.50	44.34	17.44	19406.6	73.04	42.11	21.59
96	39722.6	44.83	45.66	14.98	38752.4	46.17	43.21	19.54	19211.8	73.32	40.66	24.29	13987.4	80.57	39.78	25.93
144	33880.2	52.94	40.22	25.11	28539.7	60.36	39.87	25.76	11309.9	84.29	37.98	29.28	7865.4	89.07	35.87	33.22
t 0.5 (hours)	136.0		286.73		103.96		279.50		23.08		245.90		5.51		216.73	

- Initial: one hour before treatment.

Table (3): Effect of different temperature degrees on the stability of chlorpyrifos and their content of sulfotep in Bestban formulation.

Exposure time (in hours)	30 °C				35°C				45°				50°C			
	chlorpyrifos		sulfotep		chlorpyrifos		sulfotep		chlorpyrifos		sulfotep		chlorpyrifos		sulfotep	
	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss
Initial*	72000	--	323.92	--	72000	--	323.92	--	72000	--	323.92	--	72000	--	323.92	--
6	67842.1	5.77	321.23	0.83	61234.5	14.95	319.87	1.25	48992.3	31.95	314.89	2.78	39876.5	44.62	311.76	3.75
24	60143.1	16.46	314.67	2.85	56432.1	21.62	311.98	3.68	40652.4	43.53	305.87	5.57	25879.6	64.06	302.15	6.72
48	46789.2	35.01	309.25	4.53	41564.5	42.27	307.61	5.03	35632.1	50.51	300.13	7.34	18554.3	74.23	296.77	8.38
96	38678.9	46.27	299.81	6.83	32456.7	54.92	297.66	8.11	28876.3	59.89	295.66	8.72	11743.2	83.69	289.54	10.61
144	31256.8	56.58	291.77	9.93	27454.3	61.86	290.56	10.29	20664.5	71.29	288.62	10.89	8667.5	87.96	280.47	13.41
t 0.5 (hours)	127.25		725.07		87.39		699.71		47.52		661.16		6.72		536.91	

- Initial: one hour before treatment.

Table (4) Effect of exposure to direct sunlight on the degradation of chloropyrifos and sulfotep content in Dursban, Teragard and Bestban formulations.

Exposure time (in hours)	Dursban				Teragard				Bestban			
	Chloroprifos		sulfotep		Chloroprifos		sulfotep		Chloroprifos		sulfotep	
	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss
Initial*	72000	--	164.96	--	72000	--	53.71	--	72000	--	323.92	--
1	34780.8	51.65	160.21	2.87	29176.3	59.47	51.24	4.59	22986.5	68.07	318.76	1.59
4	30780.4	57.25	153.26	7.96	26096.97	63.75	49.71	7.45	20266.9	71.85	311.22	3.92
8	23147.5	767.85	146.78	11.02	19766.57	72.55	45.33	15.60	13988.8	80.57	302.43	6.63
12	16637.71	76.89	139.08	15.68	13463.13	81.3	41.76	22.25	11262.5	84.35	291.55	9.99
24	11099.2	84.58	130.76	20.73	10176.8	85.86	38.99	27.41	10229.9	85.79	283.95	12.34
48	6421.5	91.08	122.44	25.77	5243.2	92.72	33.51	37.61	6701.9	90.69	272.86	15.76
t 0.5 (hours)	0.97		93.13		0.84		71.62		0.73		152.28	

Initial: one hour before treatment

Table (5) Effect of exposure to UV-rays on the degradation of chloropyrifos and sulfotep content in Dursban, Teragard and Bestban formulations.

Exposure time (in hours)	Dursban				Teragard				Bestban			
	Chloroprifos		sulfotep		Chloroprifos		sulfotep		Chloroprifos		sulfotep	
	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss	µg	% Loss
Initial*	72000	--	164.96	--	72000	--	53.71	--	72000	--	323.92	--
1	60485.0	15.99	162.41	1.54	59052.8	17.98	51.23	4.62	59656.9	17.14	320.67	1.0
3	57734.6	19.81	160.23	2.86	56050.1	22.15	49.91	7.07	56961.1	20.88	319.55	1.35
6	55401.9	23.05	158.99	3.62	54241.8	24.66	47.52	11.52	52141.6	27.58	317.43	2.0
12	47594.1	33.89	156.51	5.12	49241.8	31.61	45.81	14.70	46514.2	35.39	315.821	2.50
24	39855.8	44.64	153.41	7.00	41616.4	42.19	43.15	19.66	40013.6	44.44	313.61	3.18
t 0.5 (hours)	26.88		171.4		28.44		61.03		27.0		377.35	

Initial: one hour before treatment

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