



## Environmental Influences on the Stability of two Chlorpyrifos Formulations, with a Focus on Sulfotep Content.



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### Abstract

GLC determined the presence of sulfotep, a toxic contaminant in chlorpyrifos formulations (Tak and Chlorfos 48% EC), as well as the effect of different temperatures (25, 35, and 45), direct sunlight, and UV-rays on the stability of chlorpyrifos a.i and sulfotep content in the formed products. The levels of sulfotep in Tak and Chlorfos, measured in micrograms, were 50.01 and 63, respectively. In addition, when exposed to high temperatures, chlorpyrifos a.i. in all tested formulations became unstable (45°C). In contrast, sulfotep, is relatively stable. After 336 hours of exposure to 45°C, the loss percentage of the active ingredient (a.i) for the chlorpyrifos formulations Tak and Chlorfos was 99 and 99.3 %, respectively, while the loss percentage of sulfotep was 9.998 and 7.08 % for Tak and Chlorfos, respectively. The data showed that direct sunlight was more successful than UV-rays in degrading chlorpyrifos in their tested formulations Tak and Chlorfos with a loss percentage of 79 and 81 % after 48 hours of direct sunlight exposure, respectively. After 48 hours of exposure to direct sunlight, Tak and Chlorfos lost 9.80 and 7.41 % of their sulfotep, respectively. On the contrary, Tak and Chlorfos lost 50 and 51 % of chlorpyrifos (a.i) in their tested formulations after 24 hours of UV exposure, respectively, and lost 6.92 and 5.81 % of sulfotep after 24 hours of UV exposure, respectively.

**Key words:** GLC, sulfotep, chlorpyrifos, UV, direct sunlight and temperatures

### 1. Introduction

Chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridyl phosphorothioate) is an organophosphate insecticide, acaricide, and miticide used to control foliage and soil-borne insect pests on a variety of food and feed crops. Chlorpyrifos is an organophosphorus insecticide with broad-spectrum insecticidal activity against a variety of insect and other arthropod pests. The purity of technical chlorpyrifos is between 940 and 990 g/kg [1]. Chlorpyrifos is an organophosphorus insecticide with a broad spectrum of chlorine that is used to control agricultural and residential insect pests [2]. In Korea, chlorpyrifos has been licensed for use against mites, aphids, and lepidopteran insects on apples, grapes, pears, peaches, cucumbers, cabbage,

and mandarins as a single product or combined product with some pyrethroids [3].

Chlorpyrifos is an organophosphate insecticide used to kill a variety of pests, including insects and worms, on crops, animals, buildings, and other surfaces. It works by blocking the acetylcholinesterase enzyme in insects' nervous systems. Chlorpyrifos<sup>(3)</sup> is produced industrially by reacting 3,5,6-trichloro-2-pyridinol (TCPy)<sup>(1)</sup> with O,O-diethyl phosphorochloridothioate<sup>(2)</sup> [4].

Bayer was the first company to commercialise sulfotep in 1946. During 1951, tetraethyl dithiopyrophosphate was approved for usage in the United States for the first time. The Environmental Protection Agency set a Registration Standard for the substance in September 1988. The Environmental Protection Agency announced a plan

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in 1999 to phase down production by September 30, 2002, and make the use and distribution of products containing it illegal by September 30, 2004 [5].

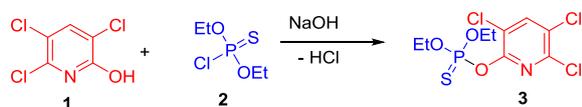


Fig. 1. Synthesis of Chlorpyrifos

Table (1): Chemical and physical properties of chlorpyrifos

Chlorpyrifos	
Common name	Chlorpyrifos
IUPAC Name:	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate
CAS No	2921-88-2
F.Wt	C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS
MWt	350.6
Structural formula:	

The interaction of tetraethyl pyrophosphate (TEPP) with sulfur produces sulfotep. Philippe de Clermont was the first to synthesise TEPP in 1854 [6]. Diethyl chlorophosphate is converted to TEPP by reacting with water to replace the chloro group with a hydroxyl group. The ester, TEPP, is formed when the product reacts with another molecule of diethylchlorophosphate. Pyridine is frequently used to neutralise the hydrochloric acid produced in this process [7].

Sulfotep is an extremely dangerous impurity that can be found in trace amounts in chlorpyrifos, which contains two interesting impurities and/or breakdown products: sulfotep and 3, 5, 6-trichloro-pyridinole, according to [8].

Some Asian regional producers can generate chlorpyrifos with sulfotep levels as high as 17% [9]. Sulfotep can also be made photochemically from phosphorothioate insecticides such as chloropyrifos [10]. Since sulfotep is a moderately stable hazardous impurity that may accumulate in the environment and cause unanticipated health and ecological concerns, the amount of sulfotep in chlorpyrifos formulations is controlled to a maximum concentration of 0.3 percent by [11].

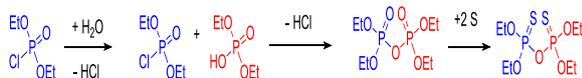


Fig. 2. Synthesis of sulfotep.

Table (2): Chemical and physical properties of sulfotep

Sulfotep as impurity	
IUPAC Name:	O, O, Ó, Ó – Tetraethyl dithiopyrophosphate
Molecular formula:	C <sub>8</sub> H <sub>20</sub> O <sub>5</sub> P <sub>2</sub> S <sub>2</sub>
Molecular mass:	322.32
CAS number	3689-24-5
Structural formula:	

Pesticides are primarily used in Egypt during the summer months, when the temperature is high due to the long, sunny days. Pesticide photolysis in the environment is caused by the ultra-violet component of sunlight, which ranges from 240 to 400 nm. The efficiency of pesticides, which is assessed by the length of their residual effect, may be affected by both heat and light [12].

Sulfotep is the primary impurity in chlorpyrifos (technical and formulations), according to FAO specifications and evaluations for Chlorpyrifos (2008). It should not exceed 3g/kg for technical chlorpyrifos and 0.3 percent of the chlorpyrifos content in all formulations of chlorpyrifos. Sulfotep is an extremely hazardous impurity in chlorpyrifos that can be found in trace amounts [9]. Since sulfotep has been demonstrated to be generated during the manufacturing process [13] and is not a hydrolysis product [14].

When aqueous preparations of the five tested pesticides were stored at 45°C for one and three days, immature stages of *B. tabaci* were impacted, compared to those maintained at 25°C for the same periods of time [15].

Temperature degrees or intensity of sunlight & UV-rays, long storage time, and the rate of degradation of active ingredient in pesticides under study all have a positive relationship, the pesticides under research had the best stability when stored at lower temperatures, however storage at high temperatures, such as 72°C, was more effective on pesticide breakdown than 54°C. Also, the pesticides would have the optimum storage stability if they were kept in a dark spot rather than a sunny place and were not exposed to UV rays [16].

Storage stability testing is used to show how a product's quality changes over time as a result of environmental conditions such temperature, humidity, and light. These investigations will provide an idea of how these factors may affect product

quality, safety, and performance. The major goal of the experiment was to see how long the product would keep the % active ingredient in its packaging and to collect data on how the product's composition changed over time. If certain ingredients breakdown at high or low temperatures and humidity, new compounds may develop, and their toxicity must be taken into account [17].

Chemical and physical changes in agricultural chemical products can occur during storage. The rate at which these changes occur is determined by the active constituent(s), formulation type, packaging, and, most importantly, storage conditions (temperature, light and humidity) [18]. According to [19], diazinon was more stable after storage at 54±2°C and at room temperature, although the rate of degradation increased following sun exposure.

The purpose of the current work to investigate how temperature, sunlight, and direct UV-rays (short waves) affect the stability of two chlorpyrifos formulations and their sulfotep content.

## 2. Experimental

### 2.1. Chlorpyrifos formulations (Tak and Chlorfos 48 % EC).

Trade Name	Common Name	Registration No.
Tak	Chlorpyrifos	1488
Chlorfos	Chlorpyrifos	1030

### 2.2. Sample preparation.

Two acetone solution (500 ml each), 1.04 ml of formulation (Tak and chlorfos 48% EC) were added in the first and second solution, respectively, were prepared in this respect, the concentration in each solution was 1000 µg/ml. One millilitre of acetone containing 1000 µg of the active ingredient from the two chlorpyrifos formulations examined (Tak and Chlorfos 48 % EC) was applied as a thin film to the surface of 5cm (i.d) uncovered Petri plates and allowed to dry and divided into three groups. The first group of uncovered petri-dishes containing deposits were exposed to different temperatures 25, 35, and 45 for different periods of exposure from 0 to 336 hours inside a dark electric oven to study the effect of temperature degree on the stability of two chlorpyrifos formulations and their content of chlorpyrifos (a.i) and sulfotep, after 1, 2, 6, 12, 24, 48, 96, 192, and 336 hours. The second batch of uncovered Petri-dishes was subjected to short-wave ultraviolet radiation of 254 nm. The deposits in the last group were exposed to direct sunlight for 1, 2, 6, 12, 24, 48, 96, 192, and 336 hours, respectively. The timing of exposure to sunlight in April 2020 as the dominant temperature ranged between 32 to 38 degrees Celsius according to [20, 21 and 12].

### 2.3. Extraction.

Using redistilled acetone as a solvent, residues of chlorpyrifos and sulfotep were transferred (i.e. extracted) from treated uncovered petri-dishes with the two tested formulation of chlorpyrifos to glass stopper test tubes without clean up. The residues were ready for GLC to determine the active ingredient of chlorpyrifos and sulfotep or GC/MS to determine the mass fragmentation of chlorpyrifos and its metabolites.

1000 ng of chlorpyrifos (a.i) and 50 and 63 ng of sulfotep were prepared to calculate the recovery rate, and put 1 ml in a Petri - dish and left until completely dry, then transferred to a test tube and it was determined by the GLC, it was found that the recovery rate reached 100%.

### 2.4. Determination of chlorpyrifos and sulfotep.

The residues of chlorpyrifos and sulfotep were analysed according to the method of [22-23] with some modification using (GLC), an hour before and after treatments.

At 250 °C, Agilent 7890B gas chromatograph with autosampler 7693 equipped with Flame Ionization Detector (FID), capillary column HP-50+ (30 m x 0.53 mm I.D., 1 µm film thickness), 8 ml/min continuous flow of nitrogen was used as a carrier gas. The oven temperature programme was set at 200 °C for 1 minute, and then ramped up to 260°C at a rate of 20°C per minute for 2 minutes. With splitless mode, the injector temperature was 250°C. One µl of injection was used. Chlorpyrifos had a typical retention time of 3.978 minutes while sulfotep had a retention time of 2.594 minutes under similar conditions. Under identical GLC conditions, the results of chlorpyrifos and sulfotep were quantitatively quantified by comparison with known purity standards, under the previous conditions, chlorpyrifos and sulfotep showed retention times 3.978 and 2.594 min and a good chromatographic separation in figs 3 and 4.

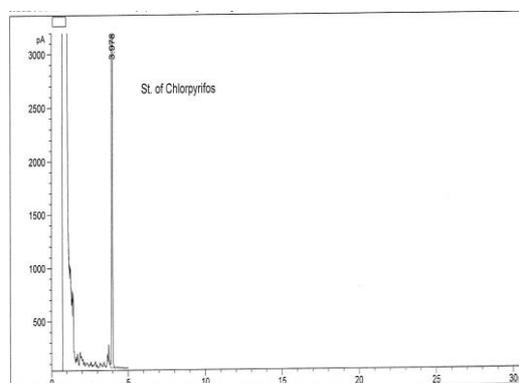


Fig. 3. Standard of chlorpyrifos.

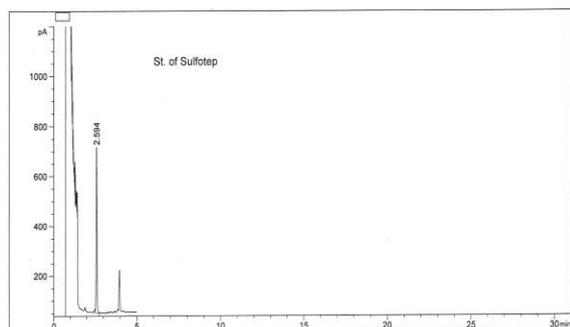


Fig. 4. Standard of sulfotep.

### 2.5. Kinetic study:

The half-life period ( $t_{0.5}$ ) was estimated using an equation to analyse the degradation rate of the tested chlorpyrifos formulations [24-25].

$$t_{0.5} = \ln 2/k = 0.693/k$$

$$k = 1/T_x \cdot \ln A/B_x$$

Where

K= Rate of decomposition.  $T_x$ =Time in days.

A=Initial residue.  $B_x$ =Residue at time(x).

### 2.6. Analysis using gas chromatography and mass spectrometry (GC/MS).

An Aglient 6890 gas chromatograph with an Aglient mass spectrometric detector, a direct capillary interface, and an HP-5MS fused silica capillary column (30 m x 320  $\mu$ m x 0.25  $\mu$ m film thickness) was used for the GC-MS analysis. Helium was used as a gas carrier in a pulsed splitless mode at 1.0 ml/min. The injection volume was 1  $\mu$ l and the solvent delay was 3 minutes. With an ionization energy of 70 e.v., the mass spectrometric detector was operated in electron impact ionizing mode, scanning from  $m/z$  50 to 500. The temperature of the ion source was 230 $^{\circ}$ C, while the temperature of the quadrupole was 150 $^{\circ}$ C. The electron multiplier voltage (EM voltage) was kept above auto tuning at 1050 volts. Perfluorotributyl amine was used to manually tune the instrument (PFTBA). The GC temperature programme was set at 80 $^{\circ}$ C for 3 minutes, then increased to 260 $^{\circ}$ C at a rate of 8 $^{\circ}$ C /min, with the detector and injector temperatures set to 280 $^{\circ}$ C and 250 $^{\circ}$ C, respectively [26].

## 3. RESULTES AND DISSCUSSION

### 3.1. Effect of exposure to direct sunlight

As shown in Table (3), the residues of chlorpyrifos in the tested formulations Tak and Chlorfos were significantly deteriorated when exposed to direct sunlight for longer periods of time (336 hours). The loss percentages of chlorpyrifos

were 11.9 and 20% after one hour of exposure in Tak and Chlorfos, respectively. These values gradually increased by the prolongation of the exposure period, reaching 79 and 81 % after 48 hours and 100 % after 192 hours of exposure.

Concerning the toxic contaminate of chlorpyrifos sulfotep formulations, it was found that can be noticed in Table 3 sulfotep (50.01 and 63  $\mu$ g were detected in Tak and Chlorfos formulation, respectively an hour before treatment) was more photo stable than chlorpyrifos under exposure to sunlight. Sulfotep loss percentages ranged from 3.17 to 15.88% in the tested chlorpyrifos formulations.

The half-life ( $t_{0.5}$ ) of chlorpyrifos (a.i) in Tak and Chlorfos were 14.7 and 9.9 hours, respectively. Sulfotep, a chlorpyrifos impurity, was shown to be more photo stable than chlorpyrifos. In Tak and Chlorfos, the loss percentages of sulfotep were 3.58 and 3.17 after one hour of exposure to direct sunlight, respectively, and reached 9.80 and 7.41 % after 48 hours of exposure to direct sunlight, half-life ( $t_{0.5}$ ) for sulfotep in Tak and Chlorfos formulations were 109.9 and 126.5 hours after exposure to direct sunlight.

After pesticides are released into the environment, photodegradation by sunlight is one of the most damaging mechanisms. The intensity of sunlight, the qualities of the application site, the application method, and the properties of the pesticide are important factors that influence pesticide photodegradation [27].

The effects of heat, UV rays, and sunlight on chlorpyrifos and profenofos degradation were investigated. The persistence of chlorpyrifos pesticide residues was found to be greater than that of profenofos insecticide residues, and both showed increasing degradation as temperature and exposure time rose. This means that at high temperatures, the time between successive sprays should be shorter, and vice versa. UV photodegradation was shown to be positively associated with exposure time and pesticide chemical structure, with profenofos degrading faster than chlorpyrifos. The photodecomposition of chlorpyrifos and profenofos residues was accelerated more by sunlight than by UV radiation. [12].

Barcelo et al investigated the photodegradation of chlorpyrifos in water/methanol under simulated sunlight and discovered that 3,5,6-trichloro-2-pyridinol was the only degradation product. During photodecomposition, a method was developed to evaluate the rate of interaction of chlorpyrifos with HO radicals in the gas phase at high temperatures [29]. The effects of humic materials and metal ions on the photochemical breakdown of several organophosphorus pesticides (including chlorpyrifos) were investigated by [30] and [31].

**Table (3): Effect of exposure to sunlight on the degradation of chlorpyrifos and sulfotep content in Tak and Chlorfos formulations.**

Time exposure in hours	Tak 48% EC				Chlorfos 48% EC			
	Chlorpyrifos		Sulfotep		Chlorpyrifos		Sulfotep	
	ug*	Loss %	ug	Loss %	ug	Loss %	ug	Loss %
Initial	1000±1	0	50.01±0.01	0	1000±1	0	63±0.23	0
1	881±3	11.9	48.22±0.04	3.58	800±7	20	61±0.19	3.17
6	700±2	30	48±0.14	4.02	600±5.09	40	60.77±0.48	3.54
12	590±4	41	46.65±0.34	6.72	470±2	53	59.55±0.11	5.48
24	400±1.5	60	46.08±0.01	7.86	350±2.63	65	59.02±0.35	6.32
48	210±3.67	79	45.11±0.05	9.80	190±1.56	81	58.33±0.16	7.41
96	55±1.12	94.5	45±1.11	10.02	30±0.54	97	57.22±0.3	9.17
192	N.F	100	43.65±0.43	12.72	N.F	100	56.18±0.1	10.83
336	N.F	100	42.07±0.57	15.88	N.F	100	55.01±0.01	12.68
<i>t</i> <sub>0.5</sub>	14.7		109.9		9.9		126.5	

Initial: one hour before treatment. ug\*: mean or average and STDEV.

Photodegradation is an abiotic process in pesticide dissipation in which molecular excitation by light energy results in various organic processes, or reactive oxygen species such as OH\*, O<sub>3</sub>, and O<sub>2</sub> oxidise the function groups of a pesticide molecule particularly or none specifically [32].

The degradation of pesticides by light, particularly sunlight, is known as photochemical degradation. Photochemical pesticide breakdown can aid in the purification of natural water and contaminated soils [33].

### 3.2. The effect of Heat

The effect of different temperature degrees on the stability of chlorpyrifos the active ingredient in Tak and Chlorfos formulations and their content of sulfotep are presented in Tables (4 and 5).

As shown in Table (4), chlorpyrifos a.i. losses in Tak formulation were 9, 21 and 25% after six hours of exposure to 25, 35, and 45°C, respectively, and reached 32, 98, and 99% after 336 hours of exposure to these temperatures, respectively, with the calculated half-life (*t*<sub>0.5</sub>) for chlorpyrifos 57.9, 23 and 19.53 hours after exposure to these temperatures, respectively. In addition, the results in Table (4) show that the level of sulfotep in Tak formulation was 50.01 micrograms before exposure to various temperatures, and the loss percentages of sulfotep were 1.78, 1.98, and 3.88 percent after six hours of exposure to 25, 35, and 45 °C, respectively, and become 7.96, 8.62 and 9.998% after 336 hours of exposure to these temperatures, half-life (*t*<sub>0.5</sub>) for

sulfotep in Tak formulations were 328.5, 266.6 and 142.1 hours after exposure to 25, 35 and 45 °C, respectively.

Concerning the results in table (5); the loss rates of chlorpyrifos a.i. in Chlorfos formulation were 9.5, 20.5 and 26 % after six hours of exposure to 25, 35, and 45°C, respectively. With regard to the results displayed in Table (5), the loss rates of chlorpyrifos a.i. in Chlorfos formulation were 9.5, 20.5 and 26 % after six hours of exposure to 25, 35, and 45°C, respectively.

After 336 hours of exposure at these temperatures, the losses increased to 33%, 95%, and 99.3%, respectively. Also, following exposure to 25, 35, and 45°C, the half-life (*t*<sub>0.5</sub>) for chlorpyrifos in Chlorfos formulation were 56.5, 23.8 and 18.6 hours, respectively. Furthermore, the determined quantity of sulfotep in Chlorfos formulation was 63 micrograms, and sulfotep losses were 2.30, 2.63, and 2.86 % after six hours of exposure to 25, 35, and 45°C, respectively, and reached to 6.30, 6.71, and 7.08 % after 336 hours, half-life (*t*<sub>0.5</sub>) for sulfotep in Chlorfos formulations were 234.8, 218.7 and 201.5 hours after exposure to 25, 35 and 45 °C, respectively.

Thermodynamic and photodecomposition were investigated by [34] who demonstrated that with the increase in the temperature and exposure duration, the proportion of the chemical lost increased.

**Table (4): Effect of different temperature degrees on the stability of chlorpyrifos and sulfotep in Tak formulation 48% EC.**

Time exposure in hours	25°C				35°C				45°C			
	Chlorpyrifos		Sulfotep		Chlorpyrifos		Sulfotep		Chlorpyrifos		Sulfotep	
	ug*	Loss %	ug	Loss %	ug	Loss %	ug	Loss %	ug	Loss %	ug	Loss %
Initial	1000±1	0	50.01±0.01	0.00	1000±1	0	50.01±0.01	0.00	1000±1	0	50.01±0.01	0.00
1	940±1.01	6	49.5±0.2	1.02	895±1	10.5	49.33±0.02	1.36	880±5	12	48.64±0.03	2.74
6	910±1.14	9	49.12±0.13	1.78	790±0.9	21	49.02±0.01	1.98	750±2.02	25	48.07±0.05	3.88
12	860±4.63	14	48.66±0.52	2.70	688±0.5	31.2	48.44±0.08	3.14	650±5.34	35	47.73±0.04	4.56
24	835±0.06	16.5	48.33±0.33	3.36	490±8.3	51	48.13±0.14	3.76	420±2.74	58	47.08±0.03	5.86
48	800±5.61	20	48.05±0.22	3.92	390±2.45	61	48.01±0.15	3.999	330±0.9	67	46.55±0.03	6.92
96	788±6.42	21.2	47.13±0.03	5.76	200±2.18	80	47.03±0.01	5.96	150±3.2	85	46.12±0.04	7.78
192	720±0.29	28	47.05±0.04	5.92	97±0.91	90.3	46.88±0.06	6.26	50±2	95	45.88±1.16	8.26
336	680±0.9	32	46.03±0.36	7.96	20±0.1	98	45.7±0.6	8.62	10±0.01	99	45.01±0.01	9.998
t <sub>0.5</sub>	57.9		328.5		23		266.6		19.53		142.1	

Initial: one hour before treatment. ug\*: mean or average and STDEV.

Organophosphates are typically stable at room temperature; however their isomers can be formed at higher temperatures. The P=S (thiono) connection could be isomerized to P-S (thiolo), making the product far more poisonous to mammals [35]. Temperature plays an important role in the degradation of pesticides, with the chemical reaction rate doubling for each 10°C increase in temperature and is halved for every 10°C decrease in temperature. [36].

Our findings (Tables 4 & 5) are consistent with those of [37], who found that the kind and concentration of catalysts, temperature, stirring rate, and reaction duration all influence the generation of sulfotep (the primary byproduct and yield) during the synthesis of chlorpyrifos. In addition, the findings in the same tables demonstrate that exposure to various temperatures, sunlight, and UV-rays had no effect on the synthesis of sulfotep in all chlorpyrifos formulations examined. The findings are in agreement with those of [26], who found that storage at 54°C and 72°C had no effect on the synthesis of sulfotep in two produced sources of chlorpyrifos. Also, according to [8], the sulfotep concentration of commercial items has no relationship to the storage period.

The stability of chlorpyrifos and sulfotep in the studied formulations depends on temperature and exposure time. In addition, temperature is one of the

most critical parameters determining pesticide stability, persistence, and degradation [17].

In general, we can deduce from mentioned statistics that Chlorpyrifos a.i. was unstable in all tested formulations (Tak and Chlorfos) and showed a high degradation rate when exposed to high temperatures of 45 °C during the course of the study, with no differences in the loss rates of the two formulations.

Since sulfotep has been demonstrated to be generated during the manufacturing process [13] and is not a hydrolysis product [14], starting material of Tak and Chlorfos contain 50.01 and 63 ug sulfotep respectively which equal to (5.001% and 6.3%) sulfotep, so at all stages of experiments Tak and Chlorfos contain sulfotep higher than Fao Max. 0.3%.

As a result, chlorpyrifos may not be utilised for pest management at high temperatures. These findings corroborated those of [38], who discovered that temperature had a substantial impact on the rate of chlorpyrifos breakdown, which elevated with increasing temperature and peaked at 35 degrees. According to [39], chlorpyrifos is thermally sensitive to temperatures above 50°C and degrades quickly in the environment. The role of temperature in increasing the degradation of insecticide residues were studied and confirmed by several investigators i.e. [40] and [12].

**Table (5): Effect of different temperature degrees on the stability of chlorpyrifos and sulfotep in Chlorfos formulation 48% EC.**

Time exposure in hours	25°C				35°C				45°C			
	Chlorpyrifos		Sulfotep		Chlorpyrifos		Sulfotep		Chlorpyrifos		Sulfotep	
	ug*	Loss%	ug	Loss%	ug	Loss%	ug	Loss%	ug	Loss%	ug	Loss%
Initial	1000±1	0	63±0.1	0	1000±1	0	63±0.1	0	1000±1	0	63±0.1	0
1	940±2	6	62.05±0.02	1.51	900±2	10	62±0.7	1.59	870±3.71	13	61.88±0.88	1.78
6	905±4	9.5	61.55±0.11	2.30	795±1	20.5	61.34±0.44	2.63	740±1.24	26	61.2±0.2	2.86
12	850±2.64	15	60.44±0.27	4.06	685±4.32	31.5	60.22±0.22	4.41	653±3	34.7	60.12±0.12	4.57
24	830±2.45	17	60.22±0.22	4.41	495±2.09	50.5	60.03±0.02	4.71	415±4.67	58.5	59.88±1.74	4.95
48	790±0.7	21	60.07±0.08	4.65	397±2.11	60.3	59.79±0.02	5.095	320±2.41	68	59.66±1.01	5.30
96	775±4	22.5	59.77±0.1	5.13	190±1.63	81	59.44±0.23	5.65	170±2.69	83	59.29±1.09	5.89
192	715±4.2	28.5	59.12±0.06	6.16	100±0.3	90	59.03±0.24	6.30	40±0.1	96	58.88±0.19	6.54
336	670±3.01	33	59.03±0.02	6.30	50±0.89	95	58.77±1.6	6.71	7±0.2	99.3	58.54±0.26	7.08
t <sub>0.5</sub>	56.5		234.8		23.8		218.7		18.6		201.5	

Initial: one hour before treatment ug\*: mean or average and STDEV.

As a result, chlorpyrifos may not be utilised for pest management at high temperatures. These findings corroborated those of [38], who discovered that temperature had a substantial impact on the rate of chlorpyrifos breakdown, which elevated with increasing temperature and peaked at 35 degrees. According to [39], chlorpyrifos is thermally sensitive to temperatures above 50°C and degrades quickly in the environment. The role of temperature in increasing the degradation of insecticide residues were studied and confirmed by several investigators i.e. [40] and [12].

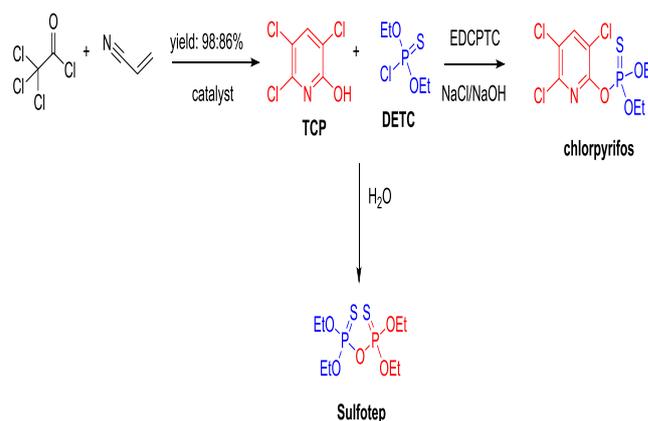
Sulfotep concentrations were more stable at different temperatures than chlorpyrifos a.i. in all examined formulations (Tak and Chlorfos); these findings are consistent with [36], who indicated that sulfotep is a relatively stable toxic impurity.

Organophosphates are normally stable at ambient temperature, but at elevated temperatures their isomers can be obtained. The P=S (thiono) linkage may be isomerized to P-S (thio) form and the product may be substantially more toxic to mammals [35].

Sulfotep concentration in all tested formulation (Tak and Chlorfos) was more stable at different degrees of temperature, than chlorpyrifos

### 3.3. The effect of exposure to UV-rays.

a.i, These result are in line with [40] who stated that sulfotep is a relatively stable toxic impurity. This is due to the production technique described by [41], which states that sulfotep can be created as a by-product from the hydrolysis of diethyl thionylphosphoryl chloride (DETC) [37] using the equation:



Furthermore, these findings were consistent with those of [8], who found that the sulfotep concentration of commercial items had no relationship to the storage period.

**Table (6): Effect of exposure to UV-rays on the degradation of chlorpyrifos and sulfotep content in Tak and Chlorfos formulations.**

Time exposure in hours	Tak 48% EC				Chlorfos 48% EC			
	Chlorpyrifos		Sulfotep		Chlorpyrifos		Sulfotep	
	ug*	Loss %	ug	Loss %	ug	Loss %	ug	Loss %
Initial	1000±1	0	50.01±0.01	0	1000±1	0	63±0.1	0
1	900±12	10	49.12±0.12	1.78	895±1.9	10.5	61.76±0.76	1.97
6	800±5.64	20	48.15±0.15	3.72	790±0.6	21	61.09±0.08	3.03
12	700±1	30	47.09±0.09	5.84	688±4	31.2	60.08±0.05	4.63
24	500±2.07	50	46.55±0.55	6.92	490±1.42	51	59.34±0.04	5.81
48	400±1.86	60	46±0.5	8.02	390±3.65	61	59.01±0.01	6.33
96	210±0.2	79	45.19±0.27	9.64	200±1.01	80	58.06±0.04	7.84
192	101±1	89.9	44.08±0.31	11.86	97±1	90.3	57.12±0.02	9.33
336	17±0.5	98.3	43.22±0.12	13.58	20±0.45	98	56.1±0.33	10.95
$t_{0.5}$	23.94		49.5		23.03		181	

Initial: one hour before treatment. ug\*: mean or average and STDEV.

When a molecule has the ability to absorb photons in the UV spectrum, photodegradation occurs. UV irradiation has wavelengths from 100 to 400 nm, and is further separated into UVA (315 to 400 nm), UVB (280 to 315 nm), and UVC (100 to 280 nm) [42].

Table (6) shows that when exposed to UV rays for longer periods, the residues of chlorpyrifos the two tested formulations were less affected than when exposed to direct sunlight; however, the effect of UV rays was primarily due to the effect of light only, whereas the effect of direct sunlight was due to both light and heat.

The loss percentages of chlorpyrifos (a.i.) in Tak and Chlorfos were 10 and 10.5 % after one hour of UV-ray exposure, respectively, and 50 and 51 % after 24 hours of UV-ray exposure. According to the data, in Tak and Chlorfos calculated half-life ( $t_{0.5}$ ) for chlorpyrifos were 23.94 and 23.03 hours respectively.

These findings are consistent with those of [39], who found that chlorpyrifos is non-volatile in air and UV-resistant. [38] found that photochemical degradation of chlorpyrifos in water followed a first-order mechanism, with a half-life of 19.74 hours upon exposure to UV light. The rates of pesticide degradation varied depending on the chemical structure, exposure time, and UV-ray wavelength utilized [15].

UV radiation is a powerful source of energy that accelerates the degradation of many compounds. The majority of pesticides on the market today are photodegradable in some way. UV light blockers are used in some pesticide formulations to reduce the quantity of photodecomposition of the pesticide active component. [36].

Also, chlorpyrifos was converted to chlorpyrifos oxon by UV oxidation as in the following equation [43].

Chlorpyrifos was also found to be more degradable in the presence of UV irradiation with sea sand than UV irradiation with  $TiO_2$  powder, according to [44]. [45] reported that there are two techniques to photodegrade chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate]. The synthesis of [O-ethyl-O-(3,5,6-trichloro-2-pyridil)-hydrogenephosphorothioate and [O,O-diethyl-O-(3,5-dichloro-2-pyridil) phosphorothioate] may be the outcome of the cleavage of an ethyl or chloro group.

In contrast, the data in Table (6) show that sulfotep was more stable to UV- rays than chlorpyrifos where, the percentage losses of sulfotep was 1.78 and 1.97% after one hour of exposure to UV rays and reached to 6.92 and 5.81% after 24 hours of exposure to UV- rays for Tak and Chlorfos, respectively, half-life ( $t_{0.5}$ ) for sulfotep in Tak and Chlorfos formulations were 49.5 and 181 hours after exposure to UV- rays.

Table (6) shows the influence of UV radiation on chlorpyrifos residue. The results showed that the rate of degradation of chlorpyrifos insecticides varied depending on their chemical composition and time of UV exposure. In general, photodegradation with UV rays was positively correlated with exposure time. These results are in accordance with those obtained by [46], [47], and [16].

The above mentioned results showed that, Sunlight was more effective than UV-rays in accelerating the photodecomposition of chlorpyrifos. These findings may be due to thermal, evaporation and light intensity considerations and are consistent with results of [46].

Since sulfotep has been demonstrated to be generated during the manufacturing process [13] and is not a hydrolysis product [14], starting material of Tak and Chlorfos contain 50.01 and 63 ug sulfotep

respectively which equal to (5.001% and 6.3%) sulfotep, so at all stages of experiments Tak and Chlorfos contain sulfotep higher than Fao Max. 0.3%.

### 3.4. Identification of photodegradation compounds of chlorpyrifos by GC/MS

The photodecomposition of chlorpyrifos residues was accelerated more quickly by sunlight than by UV radiation [12]. The photodegradation of chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate] (Fig. 5, No. 1) may occur via two reaction patterns (Fig. 5). It may 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-pyridyl)-hydrogene-phosphorothioate] (Fig. 5, No. 2) and [O,O-diethyl-O-(3,5-dichloro-2-pyridyl) phosphorothioate] (Fig. 5, No. 3). The following step of the decomposition is the scission of chloro and ethyl groups ([O-ethyl-O-(3,5-dichloro-2-pyridyl)-hydrogene-phosphorothioate]) (Fig. 5, No. 4). Dissociation of another chloro-group leads to the formation of [O-ethyl-O-(5-chloro-2-pyridyl)-hydrogene-phosphorothioate] (Fig. 5, No. 5). Loss of the other ethyl group transforms the previous compound into the end product [O-(5-chloro-2-pyridyl)-dihydrogene-phosphorothioate] (Fig. 5, No. 6).

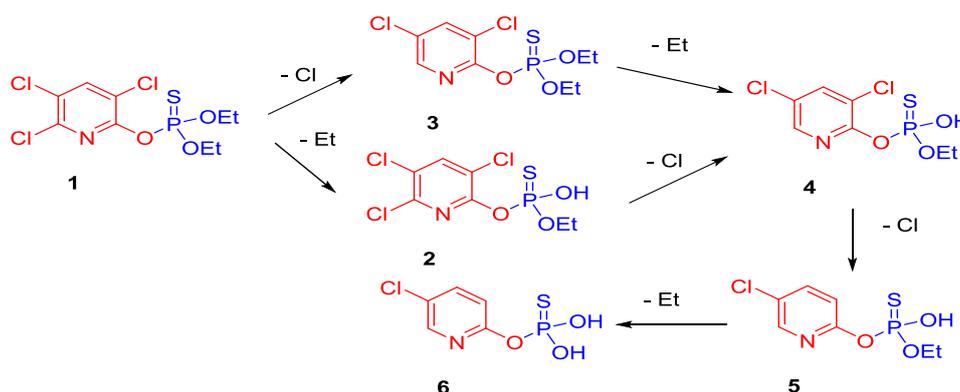
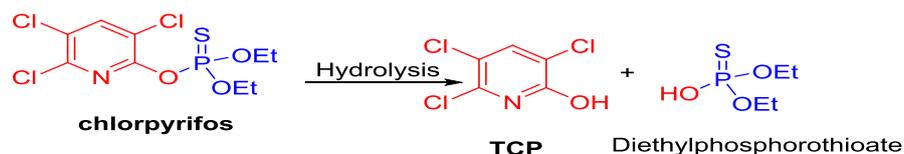


Fig. 5. Proposed photodegradation pathway for chlorpyrifos.

Our samples were analysed by GC-MS after exposure to direct sunlight, which revealed that chlorpyrifos can be hydrolyzed to 3, 5, 6-trichloro-2-pyridinol (TCP), as well as by electron impact, which revealed components 1,2 in agreement with the

hydrolysis. TCP and diethyl phosphorothioate were produced by cleaving the phosphorus oxygen link; these results are consistent with [48]. This can be demonstrated according to the following equation:



MS spectrum of chlorpyrifos as follows

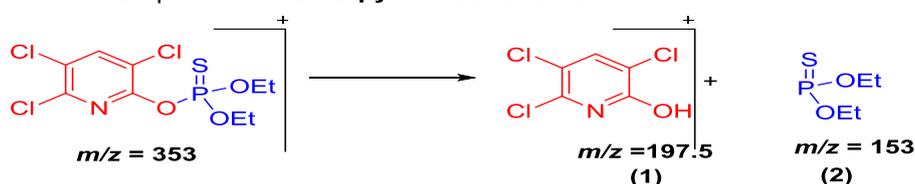


Fig. 6. Mass fragmentation pattern of chlorpyrifos after exposure to direct sunlight

## 4. Conclusion

Sulfotep, a toxic contaminant was found in chlorpyrifos formulations. The stability of chlorpyrifos was affected by the temperatures (45°C) followed by sunlight and UV rays. The photodegradation of chlorpyrifos may occur via two

reaction patterns it might be initiated by the cleavage of an ethyl group or a chloro group.

## 5. Conflicts of interest

“There are no conflicts to declare”.

## 6. Acknowledgment

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