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Study the persistence of pesticides under certain different environmental condition and evolution of their impurities

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Keywords

Propiconazole, dimethomorph , fludoxanil , cholrpyrifos ,deltamethrin and storage .

Abstract:

The present work was carried out to study the effect of storage under high temperature pesticides of naserzol (Propiconazole 25 % EC W/V), nofostar (Dimethomorph 5%WDG W/W), self (Fludioxonil 25 %WG W/W) butox (Deltamethrin 50 % W/v EC), lamba pawer (Lambda-cyhalothrain 10 % W/v Sc) and teknofos (Cholrpyrifos 45 % W/v EC).The stability of active ingredient of the tested pesticides under storage 54 ºC for 14 days and influence direct sunlight were studied . The active ingredient were propiconazole, dimethomorph and fludioxonil 25.31, 5.03 and 10.21 before storage for propiconazole, dimethomorph and fludioxonil, respectively and become after storage 54 ºC 18.65 , 4.67 and 7.68 at the end experiment .The loose percentages were 26.31, 7.15 and 24.77 % when the pesticides compound previously were stored at 54 ºC for 14 days. Also, the stability active ingredient before influence sunlight 25.07 , 5.03 and 10.21 after influence sunlight 22.01, 4.10 and 9.11 %, respectively . Stability of active ingredient were deltamethrin, lambada-cyhalothrin and cholrpyrifos 50.45 ,10.23 and 45.03 before storage become after storage 54 ºC 25.50 , 4.92 and 45.03 at the end experiment. The loose percentage were 49.45 , 51.91and 22.71%, respectively, were stored at 54 ºC for 14 days . Deltamethrin impurities' before and after influence storage 54 ºC for 14 days indictable but cholrpyrifos impurity of sulfotep (O,O,O',O'-tetraethyl dithiopyrophosphate) become storage 54 ºC for 14 days 5.098 mg/kg.

Introduction

Pesticides general became an important component of worldwide agriculture systems during the last century, allowing for a noticeable increase food production and increase in crop yields (Alexandratos and Bruinsma, 2012). Influence on pesticides and agrichemical can be through contact with the skin, inhalation or ingestion. The type of pesticide, the duration and route of exposure, and the individual health status (e.g., healthy/damaged and skin nutritional deficiencies) are determining factors he possible health

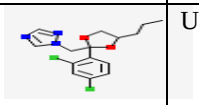
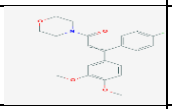
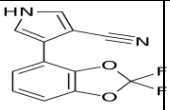
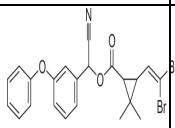
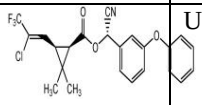
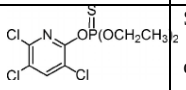
outcome. Within animal or human body, pesticides may be metabolized excreted, stored, bio accumulated in body fat or (WHO, 1990 ; Pirsaheb *et al*., 2015 and Alewu and Nosiri, 2011). The numerous negative health effects that have been associated with chemical pesticides include, among other effects, gastrointestinal, dermatological neurological, carcinogenic, respiratory, reproductive, and endocrine effects (WHO, 1990 ; Sanborn *et al.*, 2007; Mnif *et al*., 2011 and Thakur *et al*., 2014). Furthermore, high occupational, accidental, or intentional exposure to pesticides can result in hospitalization and death (WHO, 1990 and Gunnell *et al*., 2007). Pesticides and agrochemical pollution that enter waterways through agricultural runoff, industrial discharges and storm water drains may persist in the environment for long periods and be transported by water or air over long distances. They may disrupt the function of the endocrine system, result-ing in reproductive, developmental, and behavioral problems (WHO and International Programme on Chemical Safety, 2002). In Egypt, as in many other agricultural countries, pesticides are widely accustomed control harmful pests, mainly, cotton, maize and rice. Nearly of these chemicals are readily soluble in plant oils and waxes; this common property places all under suspicion as food (Fatin *et al.* , 2016).

In this paper, we studied the effect of storage and influence direct sunlight of pesticides (Propiconazole, dimethomorph, fludioxonil deltamethrin , lambada-cyhalothrin and cholrpyrifos) and determination of impurities pesticides .

Materials and methods

Source of sample pesticides: Center Agric. Pesticides Laboratory (Table 1)

Table (1): Showed the formulation of pesticides .

Treed name for fungicides	Active ingredient	Types of pesticides	Formu-lation types	Structure	Impurities
Naserzol 25 %	Propiconazole	Fungicides	EC		UND
Nofostar 5%	Dimethomorph	Fungicides	WDG		UND
Self 25 %	Fludioxonil	Fungicides	WG		UND
Butox 50 %	Deltamethrin	Insecticides	EC		Bromovinyl) becisthemic acid chloride [(1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane carboxoyl chloride]
Lamba - pawer 10 %	Lambada-cyhalothrin	Insecticides	SC		UND
Teknofos 45 %	Cholrpyrifos	Insecticides	EC		Sulfotep (O,O,O',O'-tetraethyl dithiopyrophosphate,)

1. Sample preparation for tested pesticides:

Accurately weighed enough samples formulation equivalent to 10 mg of standard in a different 25 ml volumetric flask for each sample, and slowly mixed with methanol and the volume was completed with methanol.

2. Storage stability tests:

The Previously fungicides (Propiconazole , fludioxonil and dimethomorph deltamethrin , lambada-cyhaothrin and cholrpyrifos) formulation were stored in oven at 54 **ºC** for 14 days according to the (FAO, 1999, 2004, 2010 , 2016 and 2018), respectively 14 days storage. During the storage period the samples were taken at 0, 1, 3 ,7 and 14 , days from storage to determine the active ingredient for formulation under testes if is present .

3. Influence of direct sunlight:

The pesticides (Propiconazole , fludioxonil ,dimethomorph , deltamethrin , lambada-cyhaothrin and cholrpyrifos) formulation were influence of direct sunlight for 14 ,The samples were taken at 0, 1, 3 ,7 and 14 days from influence direct sunlight to determine the active ingredient and impurities content for formulation under testes if is present .

4. Chromatographic High-performance liquid chromatography:

The type of Chromatographic High-performance liquid chromatography (HPLC) system model (Agilent Technologies 1260 Infinity) with quaternary pump, UV-detector was employed. The chromatographic C18 stainless steal column (25 cm length, 4.6 mm inner diameter, and 4.0 µm particles) .

5. Determination of active ingredient Gas Liquid Chromatography (GLC):

Determination of cholrpyrifos residues by GLC analysis compared with the standard used cholrpyrifos was carried out GLC model Agilent Technologies, column with flame ionization detector (FID).

Conditions

Injection temperature: 225 °C
Detector temperature: 300 °C
Oven temperature: 130 °C for 5 min., 4 °C/min., 184 °C

6. Determination of fungicides by GC/Ms:

Apparatus Agilent B, 5977 AMSD gas chromatography equipped with an agilent mass spectrometric detector , with a direct capillary interface and fused silica capacity colum (30 m x 0.025 mm HP -5 0.25 microm 60 to 325/325 ºC). Samples were injected under the following condition ; Helium was used as carrier gas at approximately 1 ml /min , pulsed split mode , split ratio (10:1) split flow 10 ml /min . The solvent delay was 4 min and the injection size were 1 UL . Oven temperature program , %0 ºC for O<5 min , the 10 /min ramp to 190 ºC followed by a 10 ºC /min ramp to 210 ºC for 1 min followed by a 10 ºC /min ramp to 300 ºC and held for 2 min (total run time followed by a injection temperature was set at 280 ºC. Wiley mass spectral data was used in the identification of the separated peaks .

Results and discussion

1. The effect of storage 54 ºC and influence sunlight on propiconazole, dimethomorph and fludioxonil:

Date in Table (2) show that the active ingredient in tested propiconazole dimethomorph and fludioxonil formulation were affected by storage 54ºC of exposure. Stability of propiconazole , dimethomorph and fludioxonil (a.i) 25.31, 5.03 and 10.21 before storage for propiconazole, dimethomorph and fludioxonil, respectively and become after storage 54 ºC 18.65 , 4.67 and 7.68 at the end experiment .The loose percentages were 26.31, 7.15 and 24.77 % when the

pesticides compound previously were stored at 54 ºC for 14 days.

Table (2): The effect of storage 54 ºC Active ingredient (a. i) on propiconazole , dimethomorph and fludioxonil formulation .

Storage period (days)	Storage 54 ºC					
	Propiconazole 25 %		Dimethomorph 5 %		Fludioxonil 10 %	
	(a.i)	Loss	(a.i)	Loss	(a.i)	Loss
0*	25.31	00	5.03	00	10.21	00
1	25.31	00	5.03	00	10.02	1.86
3	25.07	0.23	4.95	1.59	9.02	11.65
7	21.41	15.40	4.80	1.51	8.87	13.12
14	18.65	26.31	4.67	7.15	7.68	24.77

0*One hour before exposure to storage.

2. Effect of storage at 54 ºC on active ingredient (a.i) of deltamethrin ,lambada-cyhalothrin and cholrpyrifos formulation :

Date in Table (3) showed that the stability of active ingredient was deltamethrin, lambada-cyhalothrin and cholrpyrifos before storage were 50.45 ,10.23 and 45.03 %, respectively and become after storage for 14 days 25.50 , 4.92 and 34.8 % , respectively at the end experiment. In general, increasing temperature and period of exposure of increasing the rate of degradation insecticides El-Deeb *et al.* (1991) and Emara and Mohssen (2009). Deltamethrin impurity before and after influence storage 54 ºC for 14 days indictable but cholrpyrifos impurity of sulfotep (O,O,O',O'-tetraethyl dithiopyrophosphate) become storage 54 ºC for 14 days 5.098 mg/kg, this results with disagreement FAO maximum impurity 3mg/kg in cholrpyrifos.

Table (3): Effect of Storage at 54 ºC on active ingredient (a.i) of deltamethrin ,lambada-cyhalothrin and cholrpyrifos formulation.

Storage period (Days)	Deltamethrin 50%			Lambada-cyhalothrin 10 %		Cholrpyrifos 45 %			
	Active Ingredi-ent (a.i)	Loss	Dibro-movinyl	(a.i)	Loss	Active Ingredient (a.i)	Loss %	Sulf-otep	Sulfotep %g/kg Cholrpyrifos
0	50.45	00	UND	10.23	00	45.03	00	0.043	0.852
1	50.40	0.08	UND	10.20	0.03	45.00	0.06	0.043	0.853
3	40.66	19.40	UND	8.18	16.60	44.51	1.1	0.091	2.238
7	31.12	38.31	UND	6.22	39.19	42.08	6.55	0.130	4.177
14	25.50	49.45	UND	4.92	51.91	34.8	22.71	0.13	5.098

0* One hour before exposure to storage. UND Indictable.

3. Effect of influence sunlight on active ingredient (a.i) of propiconazole ,dimethomorph and fludoxanil formulation:

Date in Table (4) indicated that the stability of active ingredient propiconazole, dimethomorph and fludoxanil were 25.07, 5.03 and 10.21 before storage and become 22.01, 4.10 and 9.11 after 14 days of influence sunlight respectively.

Table (4): Effect of influence sunlight on Active ingredient (a.i) of propiconazole ,dimethomorph and fludoxanil formulation.

Storage period (Days)	Sunlight					
	Propiconazole 25 %		Dimethomorph 5 %		Fludioxonil 10%	
	(a.i)	Loss	(a.i)	Loss	(a.i)	Loss
0	25.07	00	5.03	00	10.21	00
1	25.00	2.79	5.00	0.59	10.00	2.20
4	24.00	4.26	4.85	3.57	9.94	2.60
3	22.27	11.16	4.17	17.09	9.59	6.07
7	22.01	1.03	4.10	18.48	9.11	10.77
14	22.01	1.03	4.10	18.48	9.11	10.77

0* One hour before exposure to storage.

4. Effect of direct sunlight on active ingredient (a.i) of deltamethrin ,lambada-cyhalothrain and cholrpyrifos formulation:

Date in Table (5) showed that the stability of active ingredient was deltamethrin, lambada-cyhalothrin and cholrpyrifos before storage were 50.45 ,10.23 and 45.03 respectively and become after storage for 14 days 42.95 , 5.56 and 41.91 % respectively at the end experiment**.** Domout (1989) who reported that pyrethroid (Lambada-Cyhalothrin and deltamethrin) are a class of lipophilic insecticides very easily degradation in natural environmental and the two main cause of degradation , photo and biodegradation often operate together , the pyrethroid are sensitive to sunlight , which triggers much alternation such as isomerisation ore cleavage of the original molecule. Also, determination of deltamethrin impurity before and after influence storage 54 ºC for 14 days indictable but cholrpyrifos impurity of sulfotep (O,O,O',O'-tetraethyl dithiopyrophosphate) become storage 54 ºC for 14 days 2.17 mg/kg, this results with agreement FAO maximum impurity 3mg/kg in cholrpyrifos.

Table (5): Effect of direct sunlight on active ingredient (a.i) of deltamethrin , lambada- cyhalothrain and cholrpyrifos formulation.

Storage period (Days)	Deltamethrin 50%			Lambada-cyhalothrin 10 %		Cholrpyrifos 45 %			
	Active Ingredient (a.i)	Loss	Dibrom-ovinyl	Active Ingredi-ent (a.i)	Loss	Active Ingredient (a.i)	Loss %	Sulfotep	Sulfotep %g/kg Cholrpy-rifos
0	50.45	00	UND	0.23	00	45.03	00	0.023	0.51
1	50.35	1.98	UND	10.22	0.09	45.03	00	0.033	0.73
3	49.30	2.27	UND	8.45	17.39	44.00	2.28	0.071	1.61
7	45.50	10.87	UND	6.99	31.67	43.08	4.33	0.083	1.91
14	42.95	17.46	UND	5.56	45.65	41.91	6.9	0.091	2.17

0* One hour before exposure to storage.

5. The degradation product and possible pathway of pesticides by GC.MS .

The data in present in Table (6) show that Propiconazole degradation after 14 days 54 ºC and influence sunlight products 2,4-dichlorophenyl 1,2,4-triazole-1-ylmethylketone,1-[2-(2,4-dichlorophenyl)-4-(hydroxypropyl)-1,3-dioxolan-2-ylmethyl] and Propiconazole , Deltamethrin degradation after 14 days storage product Benzene ,1,3dimethylchloro-3,3,3-trifluoropropenyl)-2,2dimethylcyclopropanecarboxylate Also the degradation cholrpyrifos product benzene ,1,2,3,4, teramethyl , (O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) and 3,5,6 trichlor-2 pyridinol (Jayanthi, 2016) who report that biodegradation of cholrpyrifos and its hydrolysis.

Table (6): The degradation product on pesticides By GC/Ms .

Pesticides	R.T.	Compound product
Propiconazole	28.022 26.79 26.66	Propiconazole 2,4-dichlorophenyl 1,2,4-triazole-1-ylmethyl ketone 1-[2-(2,4-dichlorophenyl)-4-(hydroxypropyl)-1,3-dioxolan-2-ylmethyl]-
Fludioxonil	25.27	Fludoxanil
Dimethomorph	38.71	4-[3-(4-chlorophenyl)-3-(3,4-dimethoxy-phenyl)-1-oxo-2-propenyl]-
Deltamethrin	8.01 8.22 28.02	Benzene propeyl Benzene 1- ethyl -2 methyl . O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate
Lambda-cyhalothrin	6.33 28.49 38.50	Benzene ,1,3dimethyl . chloro-3,3,3-trifluoropropenyl)- 2,2-dimethylcyclopropanecarboxylate (1,1-bispheny) -2 carboxamide , N 1,1 dimethylethyl
Cholrpyrifos	11.74 23.685	Benzene ,1,2,3,4, teramethyl O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate **3**,5,6 trichlor-2 pyridinol

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