



Chemical and physical determination of prochloraz formulations and 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin as impurities

Rasha, M. A. El-Saman and Hala, M. Ibrahim

Central Agricultural Pesticides Laboratory, Agricultural Research Center, Dokki, Giza, Egypt.

ARTICLE INFO

Article History

Received: 15/7/2022

Accepted: 20/9/2022

Keywords

Active Ingredients, prochloraz, 2, 3, 7, 8-Tetrachlorodibenzodioxin (2, 3, 7, 8-TCDD), impurities, physical properties emulsifiable concentrate (EC), emulsion oil in water (EW), pH and density.

Abstract

The determination of three commercial prochloraz formulations (Leader 45% EC [Three batches EL1001202/1, (LR1001211/2 and LR3108213/R (From markets], finger 45% EW and sabamid e 15% EC) were investigated. The tested formulations were stored at 54 ± 2 °C for 14 days. During the different storage periods, samples were taken after 3, 7 and 14 days to determine the active ingredient content, physical properties (Emulsion test, pH values and density), fingerprint (GC/MS) and toxic impurities content according to FAO (2010). The active ingredient (A.I.) of prochloraz in tested formulations leader 45% EC (Batch 1,2 and 3), finger 45% EW and sabamid 15% EC were (44.7, 45.08 and 44.15%),44.89 and 14.78% before storage and decreased to (44.34, 44.72, and 43.73%),44.45and 14.4% after 14 days of storage at 54 ± 2 °C, respectively. Calculated half life ($T_{0.5}$) values for Prochloraz were 1242.86, 1119.56,1076. 1001.2 and 344.92 days for leader 45% EC (Batch 1), (Batch 2) ,(Batch 3), finger 45% EW and sabamid 15% EC, respectively. This result refers that sabamid 15% EC is less stable than leader 45%EC and finger 45% EW. During different intervals of storage, the impurities 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (TCDD) before storage 0.001111, 0.001119 and 0.001120 $\mu\text{g}/\text{kg}$ and become increased to 0.001845, 0.001895 and 0.001800 $\mu\text{g}/\text{kg}$ for leader 45% EC (Batch EL1001202/1, LR1001211/2 and LR3108213/R). Also, were 0.00469 and 0.000997 $\mu\text{g}/\text{kg}$ and increased to 0.00564 and 0.00164 $\mu\text{g}/\text{kg}$ for Finger 45% EW and sabamid 15% EC respectively after 14 days of storage at 54 ± 2 °C, respectively. These levels of 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin of the tested sample are lower matching the maximum level ($\geq 0.1 \mu\text{g}/\text{kg}$ from prochloraz) defined by FAO (2016). The emulsion test refers that no sediment was formed during different of storage times after 14 days storage for all tested formulations. The increase of storage period pH value decreased. On the other hand, the density increases during storage periods. GC/MS analysis appeared 2,4,6- Trichlorophenol in prochloraz formulations.

Introduction

Prochloraz, is an imidazole fungicide and is used in a lot of countries in agriculture to control fungi. Prochloraz is widely used on plants to avoid the plant from deterioration during storage but the final metabolites are harmful to health (Li *et al.*, 2010). Prochloraz has left the only alternative for the growers to protect their crops from the fungal disease (Fang *et al.*, 2017). Prochloraz is used on fruit and vegetables to prevent the fruit from degrading during storage. The 2, 4, 6-TCP have toxic effects and are carcinogenic, being listed by the Environmental Protection Agency (EPA). Prochloraz and its metabolites such as 2,4,6-TCP are harmful to health (Qingkui Fang *et al.*, 2017).

The imidazole fungicide which inhibition of activity the CYP51A1 enzyme, this enzyme is responsible for 14-demethylation of lanosterol who is important in the biosynthesis of ergosterol, which is essential for the fungal cell component (Stoker and Kavlock, 2010).

2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD) is a polychlorinated chemical impurity and long persistence both in the environment and the human body, because their dioxin in not hydrolysis by chemical and biological degradation and tend to accumulate in the food chain. Also, it is byproduct in some manufactures chlorinated organic compound as Prochloraz. According to Kulkarui *et al.*, 2008 and Orazio *et al.*, 1992.

Prochloraz undergoes different transformations. In plants, the primary metabolic step is a breaking of the imidazole ring with the formation of N²-formyl-N-propyl-N-[2-(2,4,6-trichlorophenoxy) ethyl] urea (BTS 44596) and N-propyl-N-[(2- (2,4,6 trichlorophenoxy) ethyl)] urea (BTS

4459), which are then degraded to 2,4,6-trichlorophenol (2,4,6-TCP), present as free and conjugated metabolites, together with traces of 2-(2,4,6-trichlorophenoxy)-acetic acid (Polese *et al.*, 2006). Emulsifiable concentrate (EC) and emulsion oil in water (EW) are physical properties; emulsion concentrate is containing an oil soluble liquid active ingredient, organic solvent and emulsifier.

The emulsifier allows the active ingredient in the solvent to mix with water to form an emulsion form; while emulsion in water (EW) contains the dispersion of liquid active ingredients in water, these formulations can reduce phytotoxicity, ecotoxicity, dermal toxicity, safer, low volatile and increase active ingredient effect on the leaf surface and improve the effectiveness compared to emulsion concentrate (Oil based) because water based (EW) pesticide formulation is hydrophilic according to Iqbal *et al.*, 2020 and Gasic *et al.*, 2012.

The present study aimed to comparative the commercial formulation of Prochloraz by active ingredient and content of impurities (2, 3, 7, 8-tetrachlorodibenzodioxin).

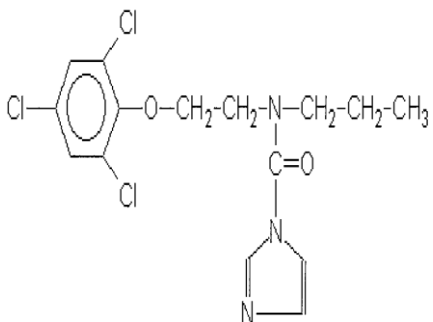
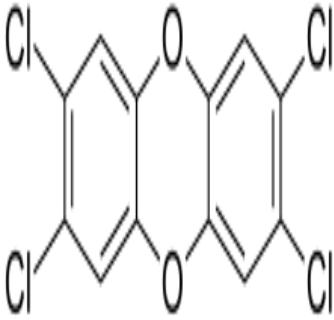
We determinate the effect of storage at 54± 2°C for 14 days on Prochloraz formulations [Leader 45% EC (Three Batches EL1001202/1,) LR1001211/2 and LR3108213/R from markets], Finger 45% EW and sabamid e 15% EC) and determine physical properties (Emulsion test, pH and density); the active ingredient of Prochloraz by HPLC, 2, 3, 7, 8-tetrachlorodibenzodioxin as impurities by (GC/MS) , and fingerprint (GC/MS).

Materials and methods

1. Pesticide used:

Table (1) indicated that the structure of tested prochloraz formulations.

Table (1): The structure of tested prochloraz formulations and its impurities.

Trade name	Structure of Prochloraz	Structure of impurities 2, 3, 7, 8-tetrachlorodibenzo-dioxin (2, 3, 7, 8-TCDD).
Leader 45% EC* Batch number 1- EL1001202/1 2- LR1001211/2 3- LR3108213/R <hr/> Finger 45% EW** Sabamid e 15% EC*		

*- EC - Emulsifiable Concentrate

**- EW- Emulsion oil in water

2. Storage at elevated temperature:

Three tested formulations from different companies, one of the companies we take three batches [Leader 45%EC (EL1001202 /1, LR1001211/2 and LR3108213/R)] two batches (LR1001211/2 and LR3108213/R) from markets were stored in an oven at 54 ± 2 °C. During the storage period, samples were taken at 1, 3, 7 and 14 days to determine the active ingredient content its impurity and some physical properties example (Emulsion concentrate and emulsion in water) for prochloraz according to FAO (2016). Also, we determine pH and density during storage.

2.1. Standard preparation of the prochloraz:

Individual standard solutions were prepared in 25 ml volumetric flask and complete with methanol, at 10 mg for prochloraz. Next, we prepare concentrations of 400, 300, 200, 100 and 50 ppm to make the standard curve.

2.2. Standard preparation of the 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin:

Individual standard solutions for 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin were produced in a 25 ml volumetric flask with methanol at 10 mg for 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin. Next, we prepare concentrations of 100, 50, 25, 10 and 1 ppb to make the standard curve (Calibration).

Calibration for the HPLC has usually carried out at the above different

concentrations for prochloraz and 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin standard. Inject all different concentration standards solution individuals into HPLC column. Ensure reproducibility of injection to obtain retention time for prochloraz and its impurity. Ensure linearity of prochloraz and 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin.

2.3. Sample preparation for tested pesticides:

Accurately weighed sufficient samples formulation equivalent to 10 mg of standard in a different 25 ml volumetric flask for each sample, and slowly mixed with methanol. All samples were measured three times for each test and take the mean average for each sample.

3. Determination of prochloraz by HPLC instrument:

The active ingredient percentage for prochloraz was determined before and after storage by using equipment HPLC (Agilent technologies 1260 Infinity II) was used UV- detector, Quat. Pump and wave length detector at 210 nm. A C18 column was used and the flow rate was 1.3 ml/min. The mobile phase was acetonitrile: methanol (70:30). Respectively. According to a modified method of (CIPAC, 2016) for prochloraz. At these conditions, the retention time (RT) of prochloraz was 2.516 min.

4. Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin by GC/MS instrument:

The active ingredient percentage for Prochloraz was determined before and after storage by using equipment GC/MS Agilent 7890 B, 5977 A MSD gas chromatography equipped with an Agilent mass spectrometric detector, with a direct capillary interface and fused silica capillary column (30 m \times 0.025 mm HP-5-0.25 micron -60 to 325/325 $^{\circ}$ C) was used. Samples were injected under the following conditions: Helium was used as carrier gas at approximately 1 ml/min, pulsed sim mode. The solvent delay was 4 min and the injection size was 1 μ L. oven temperature program, 100 $^{\circ}$ C for 1 min, then 10 $^{\circ}$ C /min ramp to 280 $^{\circ}$ C held for 3 min (Total run time: 22 min) the injector temperature was set at 280 $^{\circ}$ C. At this condition the retention time (RT) of 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin was 12.954 min respectively.

5. Fingerprint characteristics for prochloraz formulations and their impurities by GC/MS analysis:

Apparatus Agilent 7890 B, 5977 A MSD gas chromatography equipped with an Agilent mass spectrometric detector, with a direct capillary interface and fused silica capillary column (30 m \times 0.025 mm HP-5-0.25 micron -60 to 325/325 $^{\circ}$ C) was used. Samples were injected under the following conditions: 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 was 1 μ L. oven temperature program, 50 $^{\circ}$ C for 4 min, then 10 $^{\circ}$ C /min ramp to 210 $^{\circ}$ C followed by a 10 $^{\circ}$ C /min. ramp to 270 $^{\circ}$ C for 1 min followed by a 10 $^{\circ}$ C /min ramp to 300 $^{\circ}$ C and held for 2 min (Total run time: 35 min) the injector temperature was set at 280 $^{\circ}$ C. Nist14 mass spectral database

was used in the identification of the separated peaks. At this condition, the retention time (RT) of prochloraz was 25.527 min.

6. Determination of the main physical criteria corresponding to each of investigated formulations:

6.1. Preparation and determination of physical properties of standard water used:

CIPAC (1995a), MT 18.3 Non-CIPAC Standard Waters, 18.3.1 WHO Standard Hard Water, (342 ppm hardness) were used in all tests of physical properties. Calcium chloride CaCl₂ (0.304 g) and magnesium chloride MgCl₂ \cdot 6 H₂O (0.139 g) were dissolved in distilled water and made up to 1000 ml.

6.2. Emulsion stability evaluation for prochloraz formulations (EC) and (EW):

The test was carried out according to CIPAC (2003). 5 ml of the formulation was added to 95 ml of standard water (In cylinder 100 ml), the cylinder was inverted 30 times in one min, and then placed in the water bath at 30 $^{\circ}$ C \pm 2 $^{\circ}$ C for 30 min. At the end of this time, the separated materials, if any, were measured. The volume of free oil, froth, cream, or any sediment present, was recorded at the end of the 30 min period.

6.3. Effect of storage at 54 \pm 2 $^{\circ}$ C on pH values of prochloraz in tested formulations:

According to CIPAC (1995b), the pH value of an aqueous liquid is defined as the common logarithm of the reciprocal of the hydrogen ion concentration expressed in g l⁻¹. The pH meter (Hanna instruments pH electrode) was operated according to the manufacturer's instructions. The pH meter was standardized to (pH7). One gm of the sample was transferred to a measuring cylinder containing about 50 ml water, the volume was completed to 100 ml with water, and agitated

vigorously for 1 min. The suspension, if any, was allowed to be settled for 1 min and then the pH of the supernatant was measured.

6.4. Effect of storage at 54±2°C on density of prochloraz in tested formulations:

Density of prochloraz in tested formulations was determinate according to CIPAC (1995a).

7. Kinetic study:

The rate of degradation of the tested active ingredient and half life periods ($T_{0.5}$) for the tested pesticides were calculated according to equation Moye *et al.* (1987).

$$T_{0.5} = \ln 2 / K = 0.6932/K \text{ and } K = \frac{1}{TX} \ln \frac{a}{bx}$$

Were K = rate of decomposition

a = initial residue

tx = Time in days or hours

bx = residue at x time

Results and discussion

1. Influence of storage at 54±2 °C on active ingredient (A.I.) of prochloraz in tested formulations:

Data in Table (2) showed that the active ingredient (A.I.) of prochloraz in tested formulations leader 45%EC (Batch 1,2 and 3), finger 45% EW and sabamid 15% EC were (44.7, 45.08 and 44.15%),44.89 and 14.78% before storage and decreased to(44.34, 44.72, and 43.73%),44.45 and 14.4% after 14

days of storage at 54± 2°C, respectively.

Also, the results in Table (2) illustrated the percentage loss which reached 0.81, 0.79 and 0.95% for leader 45%EC (Batch 1, batch 2 and batch 3, respectively and % loss of 0.95 and 2.57 % for finger 45% EW and sabamid 15% EC after 14 days of storage at 54± 2°C, respectively. This result for prochloraz is in agreement with Mortada *et al.* (2018) and FAO (2016) according to FAO specifications, the tolerance level of active ingredient content is ± 5% of the declared content for the formulation ranging from 45% equal to 5%. The limited tolerance of leader 45%EC and finger 45% EW content (5×45/100) equal ± 2.25 (42.85-47.25%) this conforms to the FAO specifications in all results and the limited tolerance of sabamid 15% EC content (6×15/100) equal ± 0.9 (14.1-15.9%) this conforms to the FAO specifications in all results.

Also in Table (2) show that calculated half life ($T_{0.5}$) values for prochloraz were 1242.86, 1119.56,1076. 1001.2 and 344.92 days for leader 45%EC (Batch 1), (Batch 2), (Batch 3), finger 45% EW and sabamid 15% EC, respectively. This result refers that sabamid 15% EC is less stable than leader 45%EC and finger 45% EW. This is due to the difference in it batch, concentration and types of prochloraz formulations.

Table (2): Influence of storage at 54±2 °C on active ingredient of prochloraz in tested formulations.

Storage Periods (Days)	Leader 45% EC						Finger 45% EW		Sabamid 15% EC	
	Batch number EL1001202/1		Batch number LR1001211/2		Batch number LR3108213/R		% A.I.	% loss	% A.I.	% loss
	% A. I.	% loss	% A.I.	% loss	% A.I.	% loss				
0	44.7	0.00	45.08	0.00	44.15	0.00	44.89	0.00	14.78	0.00
3	44.63	0.16	44.98	0.22	44.07	0.18	44.79	0.22	14.68	0.68
7	44.52	0.41	44.9	0.39	43.95	0.45	44.69	0.45	14.58	1.35
14	44.34	0.81	44.72	0.79	43.73	0.95	44.45	0.98	14.4	2.57
$T_{0.5}$ (days)	1242.86		1119.56		1076.57		1001.2		344.92	

Zero: One hour before storage.

A.I.: Active ingredient of Prochloraz

$T_{0.5}$ =half life

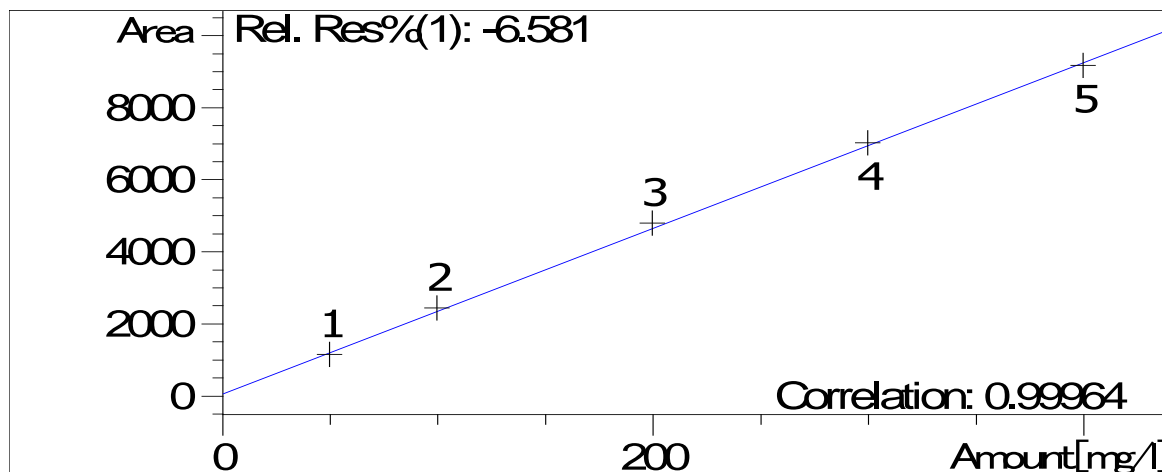


Figure (1): Calibration curve for prochloraz (Concentration from 50-400 mg/L).

2. Influence of storage at 54±2 °C on 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (Impurity) of prochloraz formulations:

The result in Table (3) showed that 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (TCDD) before storage 0.001111, 0.001119 and 0.001120 µg/kg and become increased to 0.001845, 0.001895 and 0.001800 µg/kg for leader 45% EC (Batch EL1001202/1, LR1001211/2 and LR3108213/R) respectively after 14 days of storage at 54±2°C.

Also, the result in Table (3) showed the amount of (TCDD) before storage were 0.00469 and 0.000997 µg/kg and increased to 0.00564 and 0.00164 µg/kg for finger 45% EW and

sabamid 15% EC, respectively after 14 days of storage at 54±2°C. From above results, it is found that, these levels of 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin of the tested sample are lower matching the maximum level (≥ 0.1µg/kg from prochloraz) defined by FAO (2016).

According to Kulkarui *et al.* (2008), tetrachlorodibenzo-P-dioxin (TCDD) is a poly chlorinated chemical compound having toxicity and long persistence in the environment and in the human body, because dioxin is resistant to chemical or biological degradation and tend to accumulate in food chain Orazio *et al.*1992.

Table (3): Influence of storage at 54 ±2 °C on 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (Impurity) of prochloraz formulations.

Storage Periods (Days)	Leader 45% EC			Finger 45% EW	Sabamid 15% EC
	Batch number EL1001202/1	Batch number LR1001211/2	Batch number LR3108213/R		
	2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (µg/kg)				
0	0.001111	0.001119	0.001120	0.00469	0.000997
3	0.001218	0.001208	0.001228	0.00553	0.00111
7	0.001262	0.001298	0.001298	0.00554	0.001153
14	0.001845	0.001895	0.001899	0.00564	0.00164

Zero: One hour before storage.

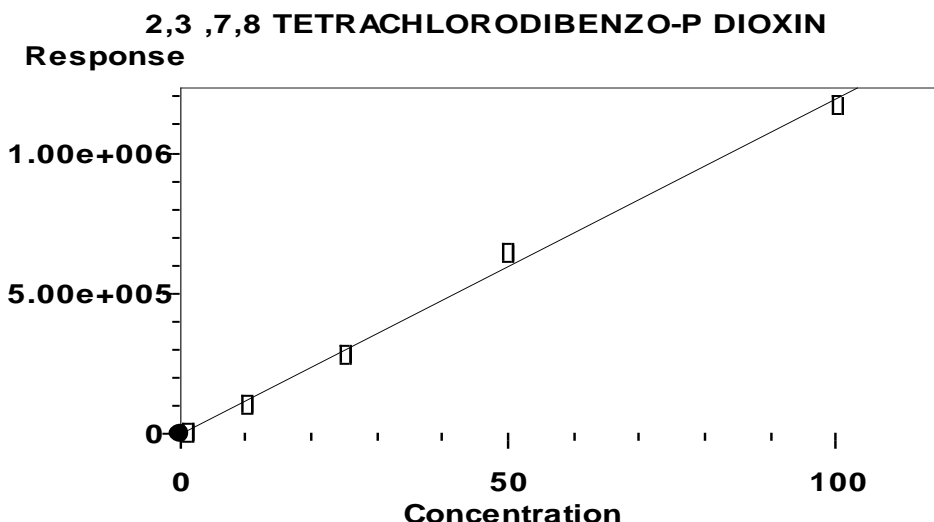


Figure (2) : Calibration curve for 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (Concentration from 1-100 ppb) (Correlation 0.996442).

3. Effect of storage at 54 ±2 °C on emulsion test for prochloraz formulations:

The data presented in Table (4) showed the emulsion test for prochloraz emulsifiable concentrate (EC) and emulsion oil in water (EW) formulations stored at 54 ± 2°C. Data

revealed that no sediment was formed during the storage period in the initial, 3 and 7 and 14 days from storage. According to FAO (2016) specifications data showed that the samples conform to these specifications.

Table (4): Effect of storage at 54 ±2 °C on emulsion test for prochloraz formulations.

Storage Periods (Days)	Leader 45% EC			Finger 45% EW	Sabamid 15% EC
	Batch number EL1001202/1	Batch number LR1001211/2	Batch number LR3108213/R		
0	-	-	-	-	-
3	-	-	-	-	-
7	-	-	-	-	-
14	-	-	-	-	-

Zero: One hour before storage. (-) Referred to no sediment appeared.

4. Effect of storage at 54±2°C on pH values of prochloraz in tested formulations:

The data presented in Table (5) show that the recorded pH values of prochloraz in tested formulations were 7.3, 7.32 and 7.35 for Leader 45% EC

in batch (1, 2 and 3), 6.9 and 6.4 for finger 45% EW and sabamid 15% EC at initial of the experiment. The pH values decreased after 14 days were 6.8, 6.78 and 6.83 for leader 45% EC in batch (1, 2 and 3), 6.3 and 5.85 for finger 45% EW and sabamid 15% EC.

Table (5): Effect of storage at 54±2°C on pH values of prochloraz in tested formulations.

Storage Periods (Days)	Leader 45% EC			Finger 45% EW	Sabamid 15% EC
	Batch number EL1001202/1	Batch number LR1001211/2	Batch number LR3108213/R		
0	7.3	7.32	7.35	6.9	6.4
3	7.18	7.21	7.22	6.77	6.35
7	7.05	7.08	7.1	6.64	6.13
14	6.8	6.78	6.83	6.3	5.85

Zero: One hour before storage.

It could be concluded that with the increase in storage period pH value decreased. Data also showed that the trend of decrease in pH values didn't differ from one formulation to another. This result agrees with Eto *et al.* (1968) EC and in aqueous solution, our tested pesticides are most stable between pH 5-7 based on theories (Muhlman and Schrader, 1957) and matching with El-Sayed and Mohammad (2014) they mentioned that pH values decreased with storage periods.

5. Effect of storage at 54±2°C on density g/cm³ of prochloraz in tested formulations:

Table (6): Determination of density of prochloraz in tested formulations (EC) and (EW).

Storage Periods (Days)	Leader 45% EC g/cm ³			Finger 45% EW g/cm ³	Sabamid 15% EC g/cm ³
	Batch number EL1001202/1	Batch number LR1001211/2	Batch number LR3108213/R		
0	0.99983	0.99975	0.99991	1.10534	0.93789
3	0.99851	0.99832	1.0005	1.10721	0.93653
7	1.03521	1.03501	1.03862	1.11736	0.94211
14	1.06294	1.06283	1.06401	1.12897	0.95792

Zero: One hour before storage.

6. Identification of prochloraz by GC mass spectroscopy (GC/MS).

6.1. The primary metabolic step of prochloraz is breaking or opening imidazole (Ring) to form N-propyl (2-2,4,6-Trichlorophenoxy) ethyl carbamoyl form amide (BTS 44596) and next to N-propyl-n-(2-2,4,6-Trichlorophenoxy ethyl urea (BTS 4459).
6.2. Cleavage formylurea and urea to form 2,4,6-Trichlorophenoxy acetaldehyde and covert to 2,4,6-Trichlorophenoxyacetic acid (BTS 9608) by oxidation and then it is degraded to 2,4,6-Trichloro phenol (BTS 45186) and final metabolite of Prochloraz by

Table (7): Metabolite of prochloraz.

Code of compounds	IUPAC name	Molecular formula
Prochloraz	N-propyl-N-[2-(2,4,6-Trichlorophenoxy) ethyl] imidazole-1-carboxamide	C ₁₅ H ₁₆ Cl ₃ N ₃ O ₂
BTS 44596 (1)	N-(propyl -[2-(2,4,6-Trichlorophenoxy) ethyl carbamoyl formamide	C ₁₃ H ₁₄ Cl ₃ N ₂ O ₃
BTS 44595 (2)	N-propyl-N-[2,4,6-Trichlorophenoxy) ethyl urea	C ₁₂ H ₁₅ Cl ₃ N ₂ O ₂
BTS 44770	(N-[2-(2,4,6-Trichlorophenoxy) ethyl urea	C ₉ H ₉ Cl ₃ N ₂ O ₂
BTS 40348 (3)	(N-2-(2,4,6-Trichlorophenoxy ethyl) propan-1 amino	C ₁₁ H ₁₄ Cl ₃ NO
BTS 3037	2-(2,4,6-Trichlorophenoxy ethanol	C ₈ H ₇ Cl ₃ O ₂
BTS 9608 (4)	2,4,6-Trichlorophenoxy acetic acid	C ₈ H ₅ Cl ₃ O ₃
BTS 45186 (5)	2,4,6-Trichlorophenol	C ₈ H ₃ Cl ₃ O

Data in Table (6) indicated that the density g/cm³ of prochloraz in tested formulations were 0.99983, 0.99975 and 0.99991 for leader 45% EC in batches (1, 2 and 3), 1.10534 and 0.93789 g/cm³ for finger 45% EW and sabamid 15% EC at initial of the experiment. The density g/cm³ increased after 14 days were 1.06294, 1.06283 and 1.06401 for leader 45% EC in batch (1, 2 and 3), 1.12897 and 0.95792 for finger 45% EW and sabamid 15% EC, respectively.

hydrolysis as shown in Figure (3), Figure (4) and Table (7).

The Retention time of Prochloraz and 2,4,6-Trichlorophenol was 25.527 and 11.811 min before storage and slightly to 25.537 and 11.823 after 14 days of storage at 54 ±2 °C, the retention time (RT) of 2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin was 12.954 min. According to Qingkui Fang *et al.* (2017), it is found that continuous increase of 2,4,6 trichlorophenol (TCP) residue in plants and its presence in the environment becomes harmful to health because TCP increased gradually with the degradation of prochloraz.

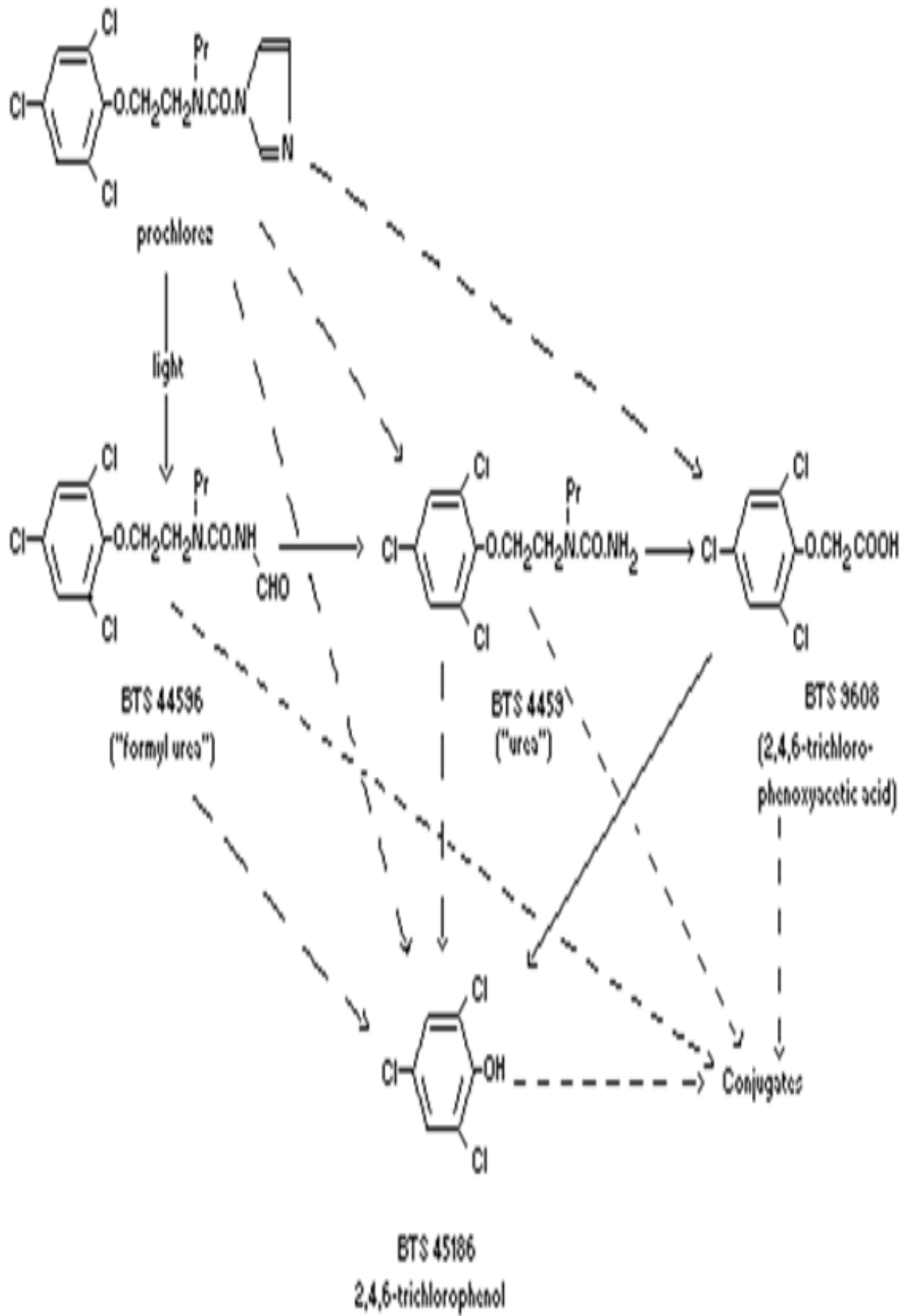


Figure (3): Metabolism of prochloraz in plant.

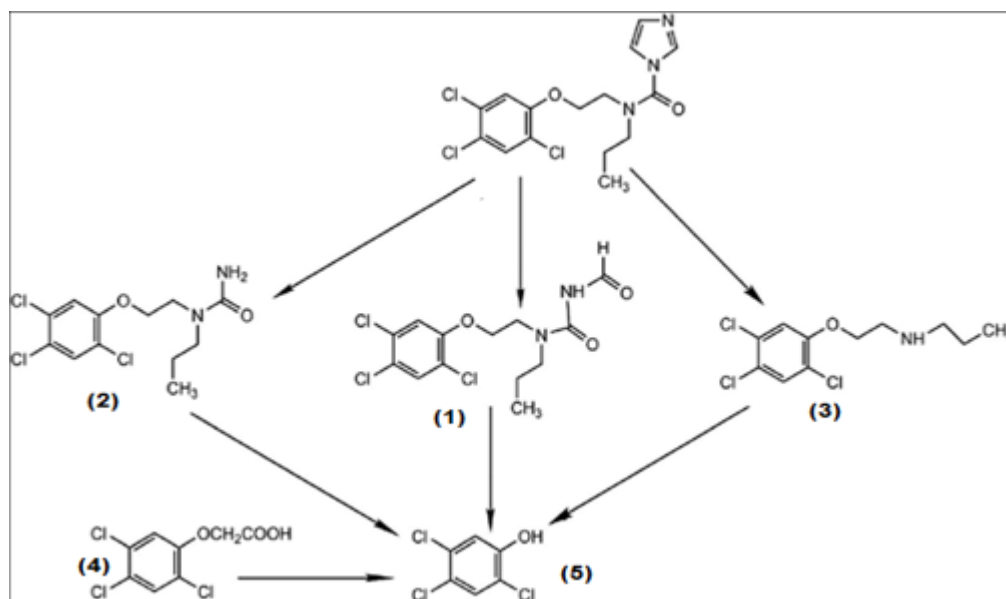


Figure (4): Degradation of prochloraz in the environment.

References

- CIPAC (1995a): Handbook**, MT 18.3 Non-CIPAC Standard Waters, 18.3.1 WHO Standard Hard Water.
- CIPAC (1995b): Handbook MT 75**, determination of pH values, Vol., F, p.205-206.
- CIPAC (2003): Handbook**, emulsion stability test MT 36.3 CIPC K, p.137).
- CIPAC (2016): Handbook**, **determination** of prochloraz (407/EC/M/3, CIPC M, p.165, 2009).
- El-Sayed, W. and Mohammad, T. G. M. (2014)**: Preparation and characterization of alternative oil –in- water emulsion formulation of deltamethrin. *American Journal of Experimental Agriculture*, 4(4): 405-414.
- Eto, M.; Tan, L. C.; Oshima, Y. and Takehara, K. (1968)**: The isomerization of alkyl phosphorothionates induced by carboxylic acid amides. *Agric. Biol. Chem. (Tokyo)*, 32(5):656-660.
- Fang, Q; Ding, C.; Cao, H ;Yao, G. ;Shi, Y. ;Wang,Y.;Wu,X. and Hua, R. (2017)**: Residue dynamic and risk assessment of prochloraz its metabolite 2, 4, 6 trichlorophenol in Apple *Molecules*, 22: 1780.
- FAO (2010)**: Specifications and evaluations for agricultural pesticides. Manual on development and use of FAO and WHO specifications for pesticides. Second Revision of the First Edition. Available only on the Internet.
- FAO (2016)**: FAO (Food and Agriculture Organization of the United Nations) specifications and evaluations for prochloraz.
- Gasic, S.; Brkic, P. D.; Radivo J. L.; Evic, T. A. (2012)**: Development of water-based system. *Pesticide fitomedicina pesticide and phytomedicine* , 27 (1): 77-81.
- Iqbal, N.; Kumer, N.; Saini, M. K.; Dubey, S.; Agrawal, A. and Kumar, J. (2020)**: Role of high shear mixing improving stability and bio efficacy of botanical oil in water formulation for early stage mosquito eradication. *Heliyan* , 6 (2): 1-8.

- Kulkarui, P. S.; Crespo, J.G. and Afonso, C. A. M. (2008):** Dioxins sources and current remediation Technologies. A review. *Environment International*, 34: 139-153.
- Li, H; Li, J.; Hou, C.; Du,S; Ren,Y; Yang, Z; Xu,Q. and Hu, X.A.(2010):** Sub-nanomole level electrochemical method for determination of prochloraz and its metabolites based on medical stone doped disposable electrode. *Talanta*, 83: 591-595.
- Mortada, W.E.M.; Ibrahim, H.M. and El-Saman, R.M.A. (2018):** Determination stability of some fungicide formulations and impurities during storage. *J. Biol. Chem. Environ. Sci.*, 13 (1).
- Moye, H.A.; Malagodi, Y.; Leibe, G. L. and Wislocki, P.G. (1987):** Residues of avermectin B1a potato crop and soils following soil treatment with (C14) Avermectin B1a. *J. Agric. Food Chem.*, 35: 859-864.
- Muhlman, R. and Schrader, G.Z. (1957):** Hydrolysis desinsektiziden phosphors saurester. *Z. Naturforsch*, 126:196-199.
- Orazio, C.E.; Kapilo, S.; Puri, R.K. and Yanders, A.F. (1992):** Persistence of chlorinated dioxins and furans in the soil environment. *Chemosphere*, 25:1269-1274.
- Polese, L.; Jardim1, E. F. G.; Navickiene, S.; Brito, N. M. and Ribeiro, M. L. (2006):** Prochloraz residue levels in ginger submitted to Sportak 450 CE“postharvest treatment. *Ecl. Quim.*, Sao Paulo, 31(2): 59-62.
- Qingkui Fang; Gengyou Yao; Yanhong Shi; Chenchun Ding; Yi Wang; Xiangwei Wu; Rimaohua and Haiqun Cao. (2017):** Residue dynamics and risk assessment of prochloraz and its metabolite 2, 4, 6-Trichlorophenol in Apple. *Molecules*, 22: 1780.
- Stoker, T. E. and Kavlock, R.J. (2010):** Pesticides as endocrine-disrupting chemicals. *Hayes' Handbook of Pesticide Toxicology (Third Edition)*, pp. 551-569.