PATTERNS OF NATURAL DEGRADATION OF CYPERMETHRIN IN TOMATO FRUITS, WATER AND SOIL UNDER THE DESERT ENVIRONMENT OF OGLA OASIS CYRENAICA - LIBYA

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Received – August 10, 2015; Revision – September 02, 2015; Accepted – October 16, 2015

Available Online – October 20, 2015

DOI: [http://dx.doi.org/10.18006/2015.3\(5\).458.463](http://dx.doi.org/10.18006/2015.3(5).458.463)

KEYWORDS

Cypermethrin

Degradation

Tomato

Soil

Libya

GC-ECD

Desert

ABSTRACT

Degradation line of cypermethrin were studied in different samples of tomato fruits, water, and soil from ogla oasis in the desert environment of Cyrenaica, -Libya. The targeted insecticide was applied to the tomato crop, water, and soil of the studied area with the recommended dose. Representative samples from all three subjects were taken daily which started from the first day of treatment to the 20th days of experimentation. Extraction and cleanup were conducted on the 20th days and finely detection of the residues was measured by using Gas chromatography (GC-ECD) instrument. Results of the study revealed 0.06, 1.06, and 2.44 ppm insecticide concentration on the first sampling date from tomato fruits, water, and soil respectively. However after one week 33, 56 and 65% reduction in insecticide concentration was reported in tomato fruits, water and soil respectively. After 2 weeks the reduction percentage was reported 66%, 88%, and 93% chronologically, and the degradation exert 91%, 97%, and 99.1% in the same order at the last sampling date. Results concluded that the trends of cypermethrin degradation were fluctuating and slow in tomato fruits while in water and soil it appears regular. However the degradation in soil was the fastest.

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Peer review under responsibility of Journal of Experimental Biology and Agricultural Sciences.

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1 Introduction

Pesticides were extensively used at various stage of agricultural production to control pest and diseases (Menezes et al., 2006). Concerns about the excessive use of pesticides and its residues were raised more than fifty years ago. Pesticides residues are associated with many health problems; it became more serious in case of fresh vegetables and fruits (Jergentz et al., 2005). Many efforts deeded to reduce the residues of these insecticides in the food stuff through legislation of laws at locally or internationally levels (Dogheim et al., 2001). The levels of pesticide residues are monitored at the maximum residue limits (MRLs), which are established by each country (Torres et al., 1996; Zawiyah et al., 2007).

Cypermethrin is a synthetic pyrethroid insecticide which used at large scale in commercial agricultural production. It has neurotoxic effect on the target organisms. Various studies conducted on its natural degradation, results of these studies suggested that it naturally degraded in soil and plant materials and its exposure to sunlight, water and oxygen will accelerate its decomposition. González-Rodríguez et al. (2008) calculated cypermethrin residues in vegetables and found higher concentrations of insecticide than the suggested maximum residue limit in 18 collected samples. However, Metwally et al. (1997) studied the degradation pattern of cypermethrin in tomato by using HPLC and reported 0.66 ppm insecticides concentration on the first sampling, this concentration was reduced up to 0.28 ppm after 120 hours. Furthermore, Al-Eed et al. (2006) conducted a study to evaluate the behavior of cypermethrin reduction in three types of water viz. distilled, mineral, and hard water and reported high cypermethrin residues from all three water types after one week, this concentration reduced up to 75% after three weeks of its application. In a different study, Roberts & Standen (1981) measured the degradation of cypermethrin in a soil stored under laboratory condition and reported the presence of this insecticide from the sample collected from wheat growing soil after 52 weeks. Oglá oasis represents the agriculture in desert environment of Libya. This selected area is well known for its vegetable production, where cypermethrin insecticide was often used to control tomato pests. Though this study aimed to measure and monitors the natural degradation of cypermethrin insecticide in the tomato fruits, water and soil of Oglá oasis.

2 Materials and Methods

This study was conducted in Oglá oasis located in the south east of Libya at latitude 29° N and longitude 2° E, 220 kilometers away from the Mediterranean Sea. It is characterized by the warmth winter and the higher temperature in the summer. Most of the area is cultivated by tomatoes in the winter.

2.1 Optimizing GC Condition

Gas Chromatography instrument (GC) with Electron Capture Detector provided with column (Thermo TR- 5MS 30 mx 0.25mm ID x 0.50 µm film) was used in this study. Optimization GC conditions were carried out by standard solutions of cypermethrin. (Port temperature 280°C; ECD temperature 300°C; Column temperature 240 °C; Carrier gas Nitrogen; Flow rate 2.5 mL/min)

2.2 Calibration Curve

Standards solution of cypermethrin were prepared on concentrations (0.001 - 0.01 mg/mL) and injected into the GC system under optimized condition. A calibration curves was obtained by regression of concentrations on standard peak areas with a regression coefficient 0.9895, limit of detection (LOD) 0.00260 mg/ml and limit of quantification (LOQ) 0.00868 mg/ml.

2.3 The Recovery

The recovery rate of cypermethrin were accounted by adding three standard solutions (0.2, 1.0 and 2.0 mg/kg) to tomato samples as chops in blender to homogenization. The same extraction procedures and GC condition was used for recovery studies as used for standard sample. The recovery rate reached to 85% by this method.

2.4 The Degradation in tomato fruits

Tomato variety Red Boll (PETO 111) produced by Peto seed Company was grown in one hector study area plot in the mid of August. The planting was in lines under drip irrigation system, and the distance between lines was 1 meter while the distance between each plant was 50 cm. Cyperkill 25^R insecticide produced by Chemical Agripharm was used at its Emulsifiable Concentrate (EC) contains 250 g/L cypermethrin at 20°C. This insecticide was applied after tomato fruits ripening and then fruit samples were collected.

2.4.1 Samples Collection

The cultivated area was divided into 4 regions, and three representative samples of 2kg were collected from each region. All these collected samples were mixed together and divided into sub-samples each weight 100 gm to serve as 3 replicates. The sampling process was started from the first day of insecticide application, and continued daily until reach 20 day of application.

2.4.2 Extraction

Extraction process was carried out according to the method described by Luke (1981), using acetonitrile solvent 100g\100ml, with 7g anhydrous Sodium sulfate. 100 ml of this filtrate was transferred in to a separating funnel, this was followed by addition of 100 ml of petroleum ether and 10 ml sodium chloride solution. This mixture shaken for two

minutes. This process was repeated several times using petroleum ether. Evaporation was done using rotary evaporator at 32°C, and then re-melted in 5ml of petroleum ether.

2.4.3 Cleanup and detection

The extracted samples were purified as the method described by Bolles et al. (1999), using florisil activated column at 130°C temperature for 24 hours with anhydrous sodium sulfate and series of Petroleum ether solutions (with elution volume of 75 ml). The extraction was then evaporated in a rotary evaporator and 1 micro liter was injected in Gas.

2.5 The Degradation in water

Water basin of 2×1×0.5 m was settled in the same area where tomato cultivated and the basin was filled with 200L water. Recommended concentration of cypermethrin insecticides (20mg/1000L) was applied in to the adjusted basin and coincides with its application in tomato field.

2.5.1 Samples collection

200ml water sample was collected from the treated basin; this collected sample was transferred to 250 ml bottle, covered with aluminum foil and kept in 20°C freezer. Same procedure was repeated daily starting from the first day of application to the 20th days.

2.5.2 Extraction

Extraction was carried out by the method described by Al-Sarar (1996). Collected samples were extracted by using 50ml acetonitrile, this mixture shaken for 3 minutes. These samples were transferred to a separatory funnel and 50 ml petroleum ether was added and shaken. This was done twice to separate the organic layer, which finally concentrated it by using a rotary evaporator.

2.5.3 Cleanup and detection

The extracted samples were getting through cleanup step according to the method described by Abo-El-Saad (2001). Initially, column chromatography was prepared for cleanup by adding 10gm of activated florisil (30°C temperature for 16 hours). Then the column was filled with the florisil 30cm long and 25 ml in diameter, and a layer of anhydrous sodium sulphate was added over the florisil layer. 20-25 ml of petroleum ether was used to initiate the column and mixer of 40ml benzene/ petroleum ether was used for elution. Then the sample was injected in the same GC for detection.

2.6 The Degradation in soil

Four different land pieces with 16m² in diameter were selected in the study area where tomato crop was grown. Cypermethrin

insecticide was applied to the selected areas with the same dose and in the same time where tomato field was treated.

2.6.1 Sample collection

Twenty soil samples were taken daily from 20cm depth in each selected land pieces. These collected samples were mixed together and a representative sample (20kg) was collected in a poly ethylene bag, this bag was stored at 20°C till the completion of study.

2.6.2 Extraction

The extraction process was conducted according to the method described in the Pesticide Analytical Manual (1999). A sample of 50gm soil was weighted from the collected soil, mixed it with 100gm anhydrous sodium sulphate and transferred to a chromatographic column (40cm long and 2.2 in diameter), which then eluted with 250ml of acetone-hexane mixture in 3-5 minutes elution time. The supernatant was concentrated by a rotary evaporator to a volume of 100ml, and transferred to 1L separation funnel. A volume of 300ml distilled water and 25ml of saturated solution of sodium chloride were added and shaken for 2 minutes to separate the organic layer. This step was done two times, but with 20ml of methylene chloride-hexane mixture. Then the two extracted layers washed twice with 100ml distilled water and desiccated using anhydrous sodium sulphate to be added to the florisil column.

2.6.3 Cleanup and detection

Cleanup step was done according to the method mentioned in the Pesticide Analytical Manual (1999). The method used Activated florisil column with 40cm length, 2.2 diameter and 10cm florisil height. A Layer of anhydrous sodium sulphate was added to the column, which was then initiated using 40-50 ml of petroleum ether, and eluted with 50ml of diethyl ether/ petroleum ether mixture. Finally this elutes were concentrated in a rotary evaporator and injected in the GC instrument.

3 Results and Discussion

3.1 Degradation in tomato fruits

Results presented in Figure (1) showed the degradation pattern of cypermethrin in tomato fruits. It was characterized by a fluctuation in the degradation behavior at first and last 5th days, mediated by a fixed period of about 10 days at which no degradation was observed. These results are in agreement with the findings of Metwally et al. (1997). These researchers reported a fluctuation between 0.66, 0.7 and 0.55 ppm. Results of the same figure also represented that the initial concentration in tomato fruits (0.06 ppm) was less than the Maximum Residue Limit (MRL) recommended by Codex (1996). This was agreed with the result reported by Zawiyah et al. (2007); those were calculated the cypermethrin residues in vegetables samples especially in tomato and reported its concentration less than 0.47ppm and it was less than the MRL.

Figure 1 Concentration of cypermethrin and its reduction percentages in tomato fruits.

Figure 2 Concentration of cypermethrin and its reduction percentages in water.

3.2 Degradation in water

Results presented by figure 2, revealed the degradation pattern of cypermethrin in water. It occurred in descending manner which started from the first day depicted 0.99ppm with 5.9% losses and degrade up to 0.24ppm on the last sampling date, with losses of approximately 97.8%. These results are superior to the results obtained by Al-Eed et al. (2006), degradation percentage in hard water was calculated as 85% after two weeks from cypermethrin application, while in the present study it was 88.1% after the same period of time.

3.3 Degradation in soil

Results presented in Figure 3 revealed the general trend of cypermethrin degradation in soil of the study area. Regular and fast rate degradation was reported in the cypermethrin and the degradation percentage reached 30.3% after the second day of application (1.7 ppm).

Moreover this reduction reached to 55.2% (1.09ppm) and 99.1% (0.02ppm) on third and last day of sampling. These results agreed with the report of WHO (1989) where study pointed out the rapid degradation of cypermethrin under natural conditions at under balanced pH.

3.4 Comparison of cypermethrin degradation in the three materials

Results of this study concluded that the initial concentrations of cypermethrin residues measured in the three studied materials were in a descending manner starting from soil (2.44ppm), water (1.06ppm), and tomato fruits (0.06ppm). The general degradation behavior in soil and water could be described as regular, which could be attributed to the presence of organic matter combined with soil microorganisms. While in tomato the pattern appeared as an irregular and slower than both counterparts. Results also demonstrated that the degradation percentage on the last sampling date reached up to 99.1%, 97% and 91.6% in soil, water, and tomato fruits respectively. This confirmed with the initial degradation behavior in the three materials. Fortunately the levels of cypermethrin residues in the three tested materials were reported below than the recommended MRL. However, that not allow to consumption the products without detect the cypermethrin levels in this products. Moreover, the degradation of this chemical in the desert environment like Oglia oasis maybe don't repeat at the same pattern in the different environments, if we concern the hard conditions in desert (high temperature; dryness; concentrate of sunlight) that may help to increase the degradation of cypermethrin more than other soft environments.

Figure 3 Concentration of cypermethrin and its reduction percentages in soil

Conflict of interest

Authors would hereby like to declare that there is no conflict of interests that could possibly arise.

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