Effect of Post-harvest and Washing Treatments on Pesticide Residues of Fenpropathrin, λ-cyhalothrin, and Deltamethrin Applied on Tomatoes Grown in an Open Field in Sudan

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Abstract
In this study, controlled application of fenpropathrin, λ-cyhalothrin, and deltamethrin were carried out on tomato fruits grown in open field to study the reduction of their residues in harvest period and times of washing. The applied samples were collected immediately after application and after each 3 days up to 30 days, and then divided into same three groups in which the first was unwashed, the second washed once time by tap water and the last group was washed three times. Additionally, the control samples were collected before the application of tomato. The pesticide residues were analyzed by gas chromatography with electron capture detector (GC-ECD).

Apre-harvest was observed safety for fenpropathrin after 27 days; 0.926 mg/kg, λ-cyhalothrin after 18 days 0.467 mg/kg, and deltamethrin after 3 days 0.29 mg/kg less than of MRL recommended by Codex Alimentarius (FAO/WHO, 2009). The samples of tomato fruits was washed once time to reduce the residues of fenpropathrin, λ-cyhalothrin, and deltamethrin 37.36±0.44, 16.74±0.25, 26.88±0.31% respectively, and washing three times reduce the three pyrethroid residues 58.26±0.34, 39.65±0.41, 56.20±0.31 respectively.

Keywords
Fenpropathrin; λ-cyhalothrin; Deltamethrin; Tomato; GC-ECD

Introduction
Tomato (Lycopersicon esculentum) is one of the most popular and widely grown vegetables in the world ranking second in importance to potato in many countries. The fruits are eaten raw or cooked. Tomato in large quantities is used to produce soup, juice ketchup, puree, paste and powder; it supplies vitamin C and adds variety of colors and flavors to the food. Premature tomatoes are also used for pickles and preserves. Its many forms are adapted to wide range of soils and climates extending from the tropics to almost the Arctic Circle. It has many other uses; tomato seeds contain 24 percent oil used as salad oil and in the manufacture of margarine. By virtues of its many attributes, tomato is considered as a favorite crop for research in physiology and cyrogenetic, all over the world API (Agriculture Planning and Information 2011), (Basharat, et al., 2007; Adalberto, et al., 2006; Gambacorta, et al., 2005). On the other hand, the tomato crop is susceptible to pest attack throughout the season. The reason with various insects such as fruit worm (Heliothis armigera), Epilachna beetles (Epilachna vigintioctopunctata), Jassids (Empoasca devastans), Tobacco caterpillar (Spodoptera littoralis), White fly (Bemesia tabaci), and Thrips (Thrips tabaci and Frankliniella intonsa) (Adalberto, et al., 2006). So, pesticides are extensively used in this culture at various stage of cultivation to control pest and diseases that may cause yield reduction (Adalberto, et al., 2006). Therefore, residues of pesticide could affect the ultimate consumers especially when these commodities are freshly consumed. The total dietary intake of pesticide residues that remain on agricultural commodities are known as carcinogens and / or toxin, therefore, it is desirable to reduce these residues. The levels of pesticide residues are controlled by the maximum residue limits (MRLs), which are established by each country (Zawiyah., et al., 2007; Torres, et al., 1996). Washing is considered to be one of the efficient...
methods for removing pesticides residues from different vegetables. Several studies have examined the effects of washing on removing pesticide residues (Cengiz et al., 2006; Krol et al., 2000; Kumari, 2008; Soliman, 2001; Zohair, 2001, C. Mee and Kin, 2010; Chavarri et al., 2004). The removal of pesticides is related to the physiochemical properties of pesticides. The effect of washing, processing of tomatoes, pre-harvest interval on the residue organochlorines in tomatoes grown in green houses and collect from market were reported (Abou-Arab, 1999; Cengiz et al., 2007; Gambacorta et al., 2005). Many insecticides were found to be used on tomato by the responded farmers. Of these most frequently used insecticides in Sudan were pyrethroids, (namely cypermethrin), fenvalerate, fenpropathrin, λ-cyhalothrin, and deltamethrin (Shinger et al., 2012; Albadri, et al., 2012). However the effect of washing and pre-harvest interval time on fenpropathrin, λ-cyhalothrin, and deltamethrin and determination (Fig. 1) residues in tomatoes grown in an open field in Sudan was not investigated before. In this study the effects of interval time and washing cycles with tap water on the removal of above mentioned pesticides were investigated by gas chromatography with electron capture detector (GC-ECD).

**Experimental**

**Apparatus**

A Shimadzu (GC-2010) gas chromatograph apparatus (Japan), supplied with a DB-5 (5% phenylmethylpolysiloxane,) J&W scientific, Serial No. US6564667H capillary column 30 m x 0.25 mm id, 0.25 µm film thickness under the following operating conditions: injection port temperature 280 °C; ECD temperature, 300 °C; Column temperature 240 °C, 1.5 mL/min nitrogen as carrier gas, N₂/Air make-up gas, 30 mL/min, splitless injection opening splitter 1 min after injection, purge flow, 9 ml/min.

The following equipment was used for sample preparation: Homogenizer, Rotary evaporator (Heidolph, laborota 4000 efficient, German), Filtration unit (Vacuum pump, filter paper 12 cm, Buchner funnel 12cm).

**Chemicals**

Sodium sulfate anhydrous and sodium chloride, acetone, acetonitrile, ethyl ether and n-hexane were obtained from Scharlau (Gota Perez, Spain), and glass wool from Loba Chemie (Mumbai, India).

- Eluting solvent: 6% ethyl ether in hexane
- Saturated Acetonitrile: 30 ml of acetonitrile and 100 mL of n-hexane were added to 500 ml separatory funnel and shaken 5min then acetonitrile layer drained in a storage bottle (Pang et.al., 1999).

* Deactivation of Florisil: Florisil was activated at 650 °C 4h, left to stand for 5h at 130 °C, stored in glass stoppered bottle and cooled overnight. Then deactivated by adding 5% (w/w) deionized water and shaken for 1h then left over night (Pang et al., 1999).

**Preparation of Chromatographic Column**

5 ml of deactivated florisil was added to column containing 50 ml hexane and the sides of the column were taped for an even packing, then the solvent drained until just above florisil packing (Pang et al., 1999).

**Optimized GC Condition**

Optimized GC conditions were carried out by standard solutions of fenpropathrin, λ-cyhalothrin, and deltamethrin. The best resolution was found with injection port temperature 280°C; ECD temperature, 300°C; Column temperature 240 °C, 1.5 mL/min Nitrogen as carrier gas, N₂/Air make-up gas,
30ml/min, splitless injection opening splitter 1 min after injection, purge flow, 9 ml/min.

**Calibration Curves**

(0.001–0.01 mg/mL) each of fenpropathrin, λ-cyhalothrin, and deltamethrin standards were prepared and injected into the GC system under optimized condition. A Calibration curves obtained by plotting concentrations of various standards corresponding peak areas with a regression coefficient (R²) 0.9950, 0.9947, 0.9895, limit of detection (LOD) 0.00122, 0.00125, 0.00260 mg/ml and limit of quantification (LOQ) 0.00406, 0.00418, 0.00868 mg/mL for fenpropathrin, λ-cyhalothrin, and deltamethrin respectively.

**Recovery Study**

Recovery studies were carried out by spiking fresh samples which did not contain any pesticides, with three levels of standards solutions (0.2, 1.0 and 2.0 mg/kg) of fenpropathrin, λ-cyhalothrin and deltamethrin. These standard solutions added to chopped tomato sample in the blender jar before homogenization. The same extraction procedures and GC condition as applied for sample analyses were used for recovery studies. In this way, recoveries were obtained in range 85.77 ± 1.52%, 95.61±3.65%, 91.77±4.34%, 98.59±2.46%, and 92.61±2.46% for fenpropathrin, λ-cyhalothrin, and deltamethrin in tomatoes respectively.

**Field Experiment**

The site of this study lies in Elelfone area at the southern part of Khartoum, North Sudan. The area cultivated with tomato was 12 basins of 6 meter in length and 4 meter in wide the total area is 288 m², every basin contains 50 plants. Tomato open field was sprayed with mixture of fenpropathrin, λ-cyhalothrin and deltamethrin commercial formulations in level of local farmers, when tomatoes were close to ripeness, by means of backpack-spraying pump at 10 hours on sunny day, with temperature 32 ºC.

**Sampling**

Tomato fruits were collected at firm red maturity stage every 3 days up to 30 days from the final application of pyrethroids. In addition, a sample of tomatoes was taken 1 h after pesticide spraying to determine the initial deposits of the pesticide residues. Each sample was divided into three subsamples. The first one was unwashed whereas the other two were washed one time and three times with distilled water. All samples were then analyzed by GC-ECD.

Samples of 500–700 g were chopped and then homogenized, then analyzed as described in procedures below. Fenpropathrin, λ-cyhalothrin and deltamethrin peak areas were recorded, and concentrations were calculated using calibration curves.

**Extraction and Cleanup Procedures**

Fifty grams of chopped samples was homogenized in blender with 120 mL acetone for 3 min at 18 000 rpm, the homogenized sample was filtered through 12 cm Buchner funnel with filter paper into 500 mL suction flask, the solid residues in blender jar were rinsed with two 25 mL portions of acetone, and rinses were used to wash residues in Buchner funnel. The combined filtrate was then transferred to 500 mL separatory funnel for liquid/liquid partition, and suction flask was washed with two 10 mL portions of acetone and was added to separatory funnel. Next, 60 ml hexane was added to the separatory funnel containing the extract, which was vigorously shaken with frequent venting (5 min). Then 200 ml 4% NaCl (w/v) was added and vigorously mixed for approximately 30 s, and then the aqueous layer was discarded. The hexane layer was filtered through the glass funnel containing glass wool plug and around 15 g anhydrous sodium sulphate to eliminate residues water. Extract was collected in 250-mL round-bottom flask, and the separatory funnel was rinsed with two 20-mL portions of hexane. Next, then rinses were passed through funnel content to the round bottom flask. Content of round bottom flask was evaporated to dryness on rotary evaporator at 40 ºC. The residues in round bottom flask were dissolved with10 mL, and two 5 mL hexane, and then transferred to 100 mL separatory funnel for liquid/liquid partitioning with 30 mL saturated acetonitrile with n-hexane for 5 min; the acetonitrile layer was drained into 250 mL round bottom flask. The liquid/liquid partitioning with 30 mL acetonitrile saturated with n-hexane step was repeated again two times, and the acetonitrile was collected and evaporated.
flask to dryness, at 60°C. The residue in round bottom flask was dissolved with 5ml, and two 10 mL hexane, and was transferred to a florisil column. Pyrethroid residues eluted by 150 mL of 6% elution solvent described above. Elution was collected at 3ml/min, then elution was evaporated to less than 50ml at 40 ºC, then was transferred in to 50 mL volumetric flask and was diluted to volume with n-hexane, finally 1μL of the solution was injected in GC-ECD (Pang et al., 1999).

Results and Discussion

Residue Analysis

It has been reported that gas chromatography with electron captured detector (GC-ECD) is highly sensitive to pyrethroids pesticides (Jayakrishnan et al., 2005; Shinger et al., 2012; Albadri, et al., 2012). The chromatogram of three pyrethroids after 10 days of treatment is shown in Fig. 2.

The residues of the pesticides after the field treatment are shown in Table 1. The table shows the residue values detected on first day with concentrations of 27.355, 3.047 and 1.103 mg/kg for fenpropathrin, λ-cyhalothrin, and deltamethrin respectively. These values are higher than the maximum residual levels (1.0 mg/kg) established by Codex Alimentarius (FAO/WHO, 2009), 0.5 mg/kg established by Japan Food Chemical Research, and 0.3 mg/kg established by Codex Alimentarius (FAO/WHO, 2009) for fenpropathrin, λ-cyhalothrin, and deltamethrin respectively. The data show that the three pesticides dissipated very slow and only deltamethrin reached below detectable level after 21 days from application. As the time elapsed after the treatment, the residues were continuously decreased to different levels. The pesticides reached level lower than MRL after 27, 18, and 3 days for fenpropathrin, λ-cyhalothrin and deltamethrin, respectively.

<table>
<thead>
<tr>
<th>Sampling days</th>
<th>Fenpropathrin Residues mg/kg</th>
<th>%Dissipation</th>
<th>λ-Cyhalothrin Residues mg/kg</th>
<th>%Dissipation</th>
<th>Deltamethrin Residues mg/kg</th>
<th>%Dissipation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>27.355</td>
<td>-</td>
<td>3.047</td>
<td>-</td>
<td>1.103</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>20.651</td>
<td>24.5</td>
<td>1.686</td>
<td>44.7</td>
<td>0.290</td>
<td>73.8</td>
</tr>
<tr>
<td>6</td>
<td>16.206</td>
<td>40.8</td>
<td>1.381</td>
<td>54.7</td>
<td>0.276</td>
<td>75.0</td>
</tr>
<tr>
<td>9</td>
<td>14.523</td>
<td>46.9</td>
<td>1.300</td>
<td>57.3</td>
<td>0.222</td>
<td>79.9</td>
</tr>
<tr>
<td>12</td>
<td>13.419</td>
<td>50.9</td>
<td>0.930</td>
<td>69.5</td>
<td>0.163</td>
<td>85.2</td>
</tr>
<tr>
<td>15</td>
<td>11.445</td>
<td>58.2</td>
<td>0.805</td>
<td>73.6</td>
<td>0.081</td>
<td>92.7</td>
</tr>
<tr>
<td>18</td>
<td>6.380</td>
<td>76.8</td>
<td>0.467</td>
<td>84.7</td>
<td>0.053</td>
<td>95.2</td>
</tr>
<tr>
<td>21</td>
<td>5.945</td>
<td>78.3</td>
<td>0.112</td>
<td>96.3</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>24</td>
<td>1.727</td>
<td>93.7</td>
<td>0.063</td>
<td>97.9</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>27</td>
<td>0.926</td>
<td>96.6</td>
<td>0.019</td>
<td>99.4</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>30</td>
<td>0.708</td>
<td>97.4</td>
<td>0.004</td>
<td>99.9</td>
<td>ND</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND: not detected
Effects of Washing on Removal of Pesticides Residue in Tomatoes

1) Effects of Washing on Removal of Fenpropathrin Residue in Tomatoes

The effect of washing time on the removal fenpropathrin residue is shown in table 2. The fenpropathrin residue in unwashed tomatoes ranged from 27.355 to 0.708 mg/Kg after field treatment for 1 h to 30 days, respectively. The fenpropathrin residue in washed is ranged from 17.094 to 0.465 mg/Kg (washed once) and from 13.273 to 0.080 mg/Kg (washed 3-times) after field treatment for 1 h to 30 days, respectively. In general, it is clear that the washing treatments were effective in reducing the fenpropathrin residue. Washing three times it seems to be more effective compare to single wash.

**TABLE 2 CONCENTRATION OF FENPROPATHRIN RESIDUES IN UNWASHED, WASHED ONE TIME, AND WASHED THREE TIMES SAMPLES AFTER 1 H, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30 DAYS FROM THE TREATMENT FIELD AREA, (n=3).**

<table>
<thead>
<tr>
<th>Days (after application)</th>
<th>Residue after washing, mg/kg ± (RSD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unwashed</td>
</tr>
<tr>
<td>Initial</td>
<td>27.355 (0.082)</td>
</tr>
<tr>
<td>3</td>
<td>20.651 (0.051)</td>
</tr>
<tr>
<td>6</td>
<td>16.206 (0.173)</td>
</tr>
<tr>
<td>9</td>
<td>14.523 (0.086)</td>
</tr>
<tr>
<td>12</td>
<td>13.419 (0.106)</td>
</tr>
<tr>
<td>15</td>
<td>11.445 (0.049)</td>
</tr>
<tr>
<td>18</td>
<td>6.380 (0.013)</td>
</tr>
<tr>
<td>21</td>
<td>5.945 (0.016)</td>
</tr>
<tr>
<td>24</td>
<td>1.727 (0.025)</td>
</tr>
<tr>
<td>27</td>
<td>0.926 (0.011)</td>
</tr>
<tr>
<td>30</td>
<td>0.708 (0.034)</td>
</tr>
</tbody>
</table>

**TABLE 3 CONCENTRATION OF Λ- CYHALOTHрин RESIDUES IN UNWASHED, WASHED ONE TIME, AND WASHED THREE TIMES SAMPLES AFTER 1 H, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30 DAYS FROM THE TREATMENT FIELD AREA (n=3).**

<table>
<thead>
<tr>
<th>Days (after application)</th>
<th>Residue after washing, mg/kg ± (RSD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unwashed</td>
</tr>
<tr>
<td>Initial</td>
<td>3.047 (0.082)</td>
</tr>
<tr>
<td>3</td>
<td>1.686 (0.044)</td>
</tr>
<tr>
<td>6</td>
<td>1.381 (0.041)</td>
</tr>
<tr>
<td>9</td>
<td>1.300 (0.021)</td>
</tr>
<tr>
<td>12</td>
<td>0.930 (0.027)</td>
</tr>
<tr>
<td>15</td>
<td>0.805 (0.029)</td>
</tr>
<tr>
<td>18</td>
<td>0.467 (0.013)</td>
</tr>
<tr>
<td>21</td>
<td>0.112 (0.016)</td>
</tr>
<tr>
<td>24</td>
<td>0.063 (0.010)</td>
</tr>
<tr>
<td>27</td>
<td>0.019 (0.002)</td>
</tr>
<tr>
<td>30</td>
<td>0.004 (0.000)</td>
</tr>
</tbody>
</table>

ND: not detected
2) Effect of Washing on Removal of λ-cyhalothrin Residue in Tomatoes

The λ-cyhalothrin residue in fresh unwashed tomatoes after 1 h from the filed treatment was 3.047 mg/kg (Table 3). These results were higher than those obtained by (Jayakrishnan et al., 2005; Chauhan and Kumari, 2012). The effect of washing one and three times on the removal λ-cyhalothrin residue is shown in table 3, in general it clear that the washing treatments was effective in reducing the λ-cyhalothrin residue. Washing three times it seems to be more effective compare to single wash. The concentration λ-cyhalothrin declined with washing and reached non-detectable on day 24 from application.

3) Effect of Washing on Removal of Deltamethrin Residue in Tomatoes

The deltamethrin residue in fresh unwashed tomatoes ranged from 1.103 to 0.0525 mg/kg after filed treatment for 1.0 h to 18 days, respectively (Table 4). These results were higher than those obtained by (Chavarri et al. 2004; El-Mouden et al. 2009). This could be due to the differences in the number of applications and initial concentration of deltamethrin used. In general it clears that the washing treatments was effective in reducing the deltamethrin residue in period from 1 h to 18 days from the application. After day 18 from filed treatment deltamethrin residue was not detected.

<p>| TABLE 4 CONCENTRATION OF DELTAMETHRIN RESIDUES IN UNWASHED, WASHED ONE TIME, AND WASHED THREE TIMES AFTER 1 H, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30 DAYS FROM THE TREATMENT FIELD AREA (n=3). |</p>
<table>
<thead>
<tr>
<th>Days (after application)</th>
<th>Residue after washing, mg/kg ± (RSD)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unwashed</td>
</tr>
<tr>
<td>Initial</td>
<td>1.103(0.082)</td>
</tr>
<tr>
<td>3</td>
<td>0.290 (0.018)</td>
</tr>
<tr>
<td>6</td>
<td>0.276(0.022)</td>
</tr>
<tr>
<td>9</td>
<td>0.222(0.012)</td>
</tr>
<tr>
<td>12</td>
<td>0.163(0.039)</td>
</tr>
<tr>
<td>15</td>
<td>0.081(0.015)</td>
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<tr>
<td>18</td>
<td>0.0525(0.016)</td>
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<td>21</td>
<td>ND</td>
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<td>ND</td>
</tr>
<tr>
<td>27</td>
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</tr>
</tbody>
</table>

ND: not detected

Conclusions

In conclusion, the residues of the investigated pesticides after pesticide treatments were generally higher than the MRL but the washing once time ore several times showed significant efficiency in removing the residues to be below the recommended MRL in most cases.

REFERENCES


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