Residues and Half-lives of Abamectin, Diniconazole and Methomyl on and in Strawberry under the Normal Field Conditions.

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Abstract: The residual behavior of abamectin (Vertemic 1.8% EC), diniconazole (Sumi-eight 5%EC) and methomyl (Lannate 90%SP) in strawberry fruits under the environmental condition of Egypt was studied. The tested pesticides were sprayed at recommended dose of 60, 25 cm³ in 100 liter water and 300g per feddan for abamectin, diniconazole and methomyl, respectively on strawberry plants. The treated strawberry fruits were randomly sampled in triplicates after one hour, 1, 3, 5, 7, 10, 12, 15 and 21 days period after pesticides application. Samples were extracted, clean up and analyzed using HPLC and GC/ECD. The half–life values were calculated to be 1.02, 4.25 and 3.97 days for abamectin, diniconazole and methomyl respectively. The pre-harvest interval (PHI) was determined to be 7, 15 and 15 days for strawberry treated with abamectin, diniconazole and methomyl under prevailed local field conditions, respectively.

Key words: Abamectin, Diniconazole, Methomyl, Pesticide residues, Strawberry.

INTRODUCTION

Strawberry (Fragaria x ananassa) is one of the most widely grown vegetable crops in the world. If the fruits are not commercialized on the fresh market or used in jam production, the fruits juice. In Egypt the planted area of strawberry are estimated by 4000 feddan, 1800 feddan planted in Kalubia Governorate. To cultivate strawberries with reasonable yields and in line with real marked conditions, it is necessary to apply pesticides. They are effective against a number of fungal diseases and pests. In this respect, the protection of strawberry crop from the attacking of pests is considered as a key factor for the mass production of fruits. However there are a wide range of pests including insects, fungi, bacteria, virus and acaros. Such pests are affecting significantly the quantity and quality of strawberry production. To protect strawberry crop from target pests it was followed different techniques of pest control, i.e. agricultural, legal, mechanical and chemical among others. As chemical control technique, pesticides have been used in a wide variation of agricultural application in strawberry crops to control insects. Pesticides are, however still used in a large scale through the world, especially in the developing countries as a major mean for pest management [1]. Abamectin used for controlling motile stage of mites and leaf miners in many vegetables and fruits crops. While the triazole fungicide Diniconazole is recommended for controlling powdery mildew, and Methomyl recommended to control many pests of strawberry, these pests include Egyptian cotton leaf worm[2]. This study aimed to:

1. The behavior of abamectin, diniconazole and methomyl residue on and in strawberry fruits grown in open field.
2. Determine the dissipation rate, half-life values (RL50) and pre-harvest interval (PHI) for the tested pesticide.

MATERIALS AND METHODS

1. Pesticides Used:
   - Abamectin (Vertemic 1.8%EC) obtained from Syngenta Agro. Egypt.
   - Diniconazole (Sumi-eight 5%EC) obtained from Sumitomo Corporation, Egypt.
   - Methomyl (Lannate 90% SP) obtained from DuPont, Egypt.

2. Field Experiments: Strawberry was planted at Nawa, Kalubia Governorate, Egypt, in December 15, 2007 in plots of 0.05 feddan. Strawberry was sprayed in February 28, 2008 under prevailed field, temperature (approximately, 27°C). Untreated plots were left as control check.
Abamectin (Vertemic 1.8% EC) and diniconazole (sum-eight 5%EC) were sprayed at the rate of 60 and 25 Cm³ in 100 liters water, respectively. While methomyl (Lannate 90%SP) was 300g per feddan. A knapsack hand sprayer fitted with one nozzle boom was used.

3. Sampling: Treated and untreated samples of strawberry fruits were randomly packed up one hour after treatments and then 1, 3, 5, 7, 10, 12, 15 and 21 days after pesticides spraying. Samples were transported to the laboratory immediately after collected (kept in an ice box). Sub-sampling was carried out in the laboratory and three replicates sub-samples were taken from fruits, which weighed (50 g). Samples were kept in polyethylene pages in a deep freezer at -20ºC till residue analysis.

4. Analytical Procedure:
4.1 Extraction and Cleaning Up:
4.1.1. Abamectin: The extraction and cleaning up of abamectin residue from strawberry fruits were carried out according to JohnVuik [3]. Exactly 50g of chopped fruits was weighed into a 250 ml flask. And 100 ml of ethyl acetate was added. The mixture was macerated in shaker for 10 min. The extract was centrifuged at 2000r.p.m for 1min. Then filtrate and exactly 50 ml of the supernatant was transferred to round-bottomed flask and evaporated to dryness on rotary evaporator at 30ºC. The residue was dissolved in 2 ml ethyl acetate. Next, 3ml of hexane was added. The contents of round-bottomed flask were mixed and applied to Sep-Pak silica gel cartridge. The round bottomed flask was washed two times with 40%ethyl acetate in hexane, and the contents of the flasks were applied to the cartridge. The cartridge was washed first with 8 ml of 40%ethyl acetate in hexane and then eluted with 5 ml of 50% ethyl acetate in methanol. This elute was evaporated to dryness on rotary evaporator at 30ºC. The residue was dissolved in 2 ml ethyl acetate. Next, 3ml of hexane was added. The contents of round-bottomed flask were mixed and applied to Sep-Pak silica gel cartridge. The round bottomed flask was washed two times with 40%ethyl acetate in hexane, and the contents of the flasks were applied to the cartridge. The cartridge was washed first with 8 ml of 40%ethyl acetate in hexane and then eluted with 5 ml of 50% ethyl acetate in methanol. This elute was evaporated to dryness on rotary evaporator at 30ºC and the residue dissolved in 1ml methanol. Of this solution 20 µl was injected into the high pressure liquid chromatography for determination.

4.1.2. Diniconazole: The extraction technique mentioned by Möllhof[4] was adopted to use methanol instead of acetone as a solvent for extraction. Strawberry fruits (50 g) were placed in the blender cup. A constant volume of distilled methanol (200ml) was used for extraction of the sample which was blended for three minute at high speed and filtered through dry cotton into graduated cylinder. A known volume of the extracts (100ml) was taken and shaken successfully with 100, 50 and 50ml of methylene chloride phases were dried by filtration through 30g anhydrous sodium sulfate. Then it was evaporated just to dryness using rotary evaporator at 40ºC. Then the residue was dissolved in 5ml methanol and cleaned up using the coagulating solution [5]. The coagulating solution was prepared as followed (0.5 g of ammonium chloride was dissolved in 400 ml of distilled water and 1 ml of orthophosphoric acid 85% was added and shacked well). The solution was cooled in a refrigerator till used. The extracts were dissolved in 5 ml of methanol and thoroughly mixed with 10 ml of freshly prepared coagulation solution. The content was filtered under vacuum through a 5 mm layer of hyflo-super cell, prepared in a 2.5 cm i.d. glass column on a plug of glass wool. Then the content rinsed four times with 5 ml methanol followed by adding 10 ml of coagulating solution. The aqueous filtrate was collected and partitioned three times in a 125 ml separating funnel using 20, 15, and 10 ml of methylene chloride which was received on a layer of anhydrous sodium sulfate and collected in a 100 ml flask, then taken to evaporation using a rotary evaporator at 40 ºC.

4.1.3. Methomyl: Extraction and clean up of methomyl residue on Strawberry were applied in one step according to the well established technique[6] in which Strawberry samples was homogenized with methylene chloride (200ml) and eluted through anhydrous sodium sulphate (15g) and charcoal (0.3-0.5g). The methylene chloride extract were combined and evaporated to near dryness at rotary evaporator at (40ºC).

4.2. Chromatographic Analysis:
4.2.1. Abamectin and Methomyl: Table 1 indicated (HPLC) conditions for abamectin and methomyl.

4.2.2. Diniconazole: A Hewlett Packard (HP) 6890 series gas chromatography (GC) system equipped with electron capture detector (ECD) was used for the determination of diniconazole residues at following condition:
Capillary column: DB-17 (3.0m×0.32mm (i.d)×0.25um film thickness), Column temperature: 270ºC, Detector temperature: 320ºC and Nitrogen Carrier gas 4 ml/min. under these conditions the retention time was 6.92 min.

5. Calculation of the Residues: The residues were calculated by applying the following equation[4].

\[
\frac{Ps.BV}{Pst.G.C} \times F
\]
Where
F=100/R (recovery factor)
Pst = standard peak area.
R =average of recovery.
V = final volume of sample solution. (ml).
Ps = sample peak area.
B = amount of standard injected (ng).
G = sample weight
C = amount of sample solution injected (μl).

6. Recovery Efficiency Studies: The reliability of the analytical methods was tested by fortifying the untreated samples with known quantities of the investigated pesticides, abamectin, diniconazole and methomyl at 0.1 ppm levels, followed by the same procedures of extraction, clean up and quantitation. Recovery values of abamectin, diniconazole and methomyl were 80, 85 and 90% respectively.

RESULTS AND DISCUSSION

1. Residue of Abamectin: Results in Table (2) showed that the concentration of initial deposits of abamactin in strawberry fruits were 0.51 ppm, then gradually decreased to 0.26 ppm one day of application revealing 49.01% loss. This value decline to 0.10, 0.03 and 0.01 ppm recording the rate loss 18.69, 94.11 and 98.03% at 3, 5 and 7 days after treatment respectively the calculated half-life values(RL50) of abamactin were 1.02 days. The data show that strawberry fruits could be consumed safely after 7.0 days of application according to the recommended maximum residue limit (MRL) for Abamectin in strawberry (0.02ppm)[7]. These results are in agreement with those of [8,9].

2-Residue of Diniconazole: The results given also in table (2) indicated the residues of diniconazole in strawberry fruits. The initial deposits found after one hour was 2.47 ppm. The residue levels were decreased to 2.01, 1.60, 0.46, 0.29, 0.16, 0.07 and 0.02 ppm showing the percentage loss 18.69, 35.22, 81.37, 88.25, 93.52, 97.16 and 99.19% after 1, 3, 5, 7, 10, 12and 15 days respectively. The estimated half-life value (RL50) for diniconazole on strawberry was 4.25 day. Maximum residue limits (MRL) for diniconazole on strawberry according to European Union [10] was 0.05ppm. Data indicated that strawberry fruits could be consumed safely after 15 days. These results were generally in agreement with a number of researchers[11-13].

3-Residues of Methomyl: The data in Table (2) also showed the residues of methomyl in strawberry. The initial deposit of methomyl was 3.26 ppm one hour after application then decreased to 2.21, 2.05, 1.21, 0.78, 0.47, 0.17and 0.03 ppm indicated the rate loss were 32.20, 37.11, 62.88, 76.67, 85.58, 94.78 and 99.07% after 1,3,5,7,10,12 and 15 days respectively. The half life value of Methomyl was 3.97 days. The data indicated that strawberry fruits could be consumed safely after 15 days after application, where (MRL) of methomyl residue in strawberry was 0.05ppm according to EU [10]. Such results are in agreement with those reported by several investigators[6,14,15].

The present results indicated that: Diniconazole was found to be more persistent on strawberry fruits compared with the other two tested pesticides; data also reported that the lowest residue level 0.02ppm in strawberry fruits was detected after 15 days of diniconazole application. While the lowest residue of abamectin was 0.01 ppm within 7 days.

Table 1: High pressure liquid chromatography (HPLC) conditions for abamectin and methomyl.

<table>
<thead>
<tr>
<th>Analytical parameter</th>
<th>Abamectin</th>
<th>Methomyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Models</td>
<td>Agilent 1100series</td>
<td>Agilent 1100series</td>
</tr>
<tr>
<td>Column</td>
<td>ODS C18 Hypersil</td>
<td>ODS C18 Hypersil</td>
</tr>
<tr>
<td>Dimensions</td>
<td>4mm (i.d)×150mm length</td>
<td>4mm (i.d)×150mm length</td>
</tr>
<tr>
<td>Detection wavelength</td>
<td>Diodearray 254nm</td>
<td>Diodearray 254nm</td>
</tr>
<tr>
<td>Mobile phase</td>
<td>45% acetonitrile+ 40%methanol+15%water</td>
<td>80%methanol +20% water</td>
</tr>
<tr>
<td>Flow rate</td>
<td>1ml/min</td>
<td>0.7ml/min</td>
</tr>
<tr>
<td>Absolute retention time</td>
<td>3 min</td>
<td>3.4min</td>
</tr>
</tbody>
</table>

Table 2: Residues levels of abamactin, diniconazole and methomyl at different time intervals:

<table>
<thead>
<tr>
<th>Time after application</th>
<th>Abamectin</th>
<th>Diniconazole</th>
<th>Methomyl</th>
</tr>
</thead>
<tbody>
<tr>
<td>932</td>
<td>0.51 ppm</td>
<td>2.47 ppm</td>
<td>3.26 ppm</td>
</tr>
<tr>
<td>934</td>
<td>0.26 ppm</td>
<td>0.46 ppm</td>
<td>0.78 ppm</td>
</tr>
<tr>
<td>935</td>
<td>0.10 ppm</td>
<td>0.29 ppm</td>
<td>1.21 ppm</td>
</tr>
<tr>
<td>936</td>
<td>0.03 ppm</td>
<td>0.16 ppm</td>
<td>0.47 ppm</td>
</tr>
<tr>
<td>937</td>
<td>0.01 ppm</td>
<td>0.07 ppm</td>
<td>0.17 ppm</td>
</tr>
<tr>
<td>938</td>
<td></td>
<td>0.02 ppm</td>
<td>0.03 ppm</td>
</tr>
<tr>
<td>(days)</td>
<td>Residue**</td>
<td>Loss (%)</td>
<td>Residue**</td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>0</td>
<td>0.51</td>
<td>0.00</td>
<td>2.47</td>
</tr>
<tr>
<td>1</td>
<td>0.26</td>
<td>49.01</td>
<td>2.01</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>80.39</td>
<td>1.60</td>
</tr>
<tr>
<td>5</td>
<td>0.03</td>
<td>94.11</td>
<td>0.46</td>
</tr>
<tr>
<td>7</td>
<td>0.01</td>
<td>98.03</td>
<td>0.29</td>
</tr>
<tr>
<td>10</td>
<td>ND</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td>12</td>
<td>ND</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td>15</td>
<td>ND</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>21</td>
<td>ND</td>
<td>-</td>
<td>ND</td>
</tr>
<tr>
<td>RL50(day)***</td>
<td>1.02</td>
<td>4.25</td>
<td>3.97</td>
</tr>
<tr>
<td>MRL****</td>
<td>0.02</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>PHI*****</td>
<td>7</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

*: samples were taken one hour after application.
**: Each value represents an average of three replicates.
***: Residue half-life values
****: Maximum residue limits.
*****: Pre-harvest intervals
ND: Not detected.

The present study also indicated that the residues of abamectin on strawberry fruits were rapidly decreased more than diniconazole and methomyl. The obtained results are in accordance with some scientists[14,16,17].

REFERENCES

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