SUMMARY

Pesticides occupy a unique position among the many hazardous chemicals that man and animals encounter daily .Pesticides are intentionally introduced into the environment to enhance agricultural production, to reduce pest damage in crops and to control disease vectors .The greatly increased uses of pesticides in agriculture beside their vital role in public health, have introduced a serious and novel hazards to human and their environment.

Strawberry ***(Fregariax ananassa)*** is one of the most widely grown vegetable crops in the world .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 .

Tomato crop plays a very useful role in various industries and nutritional aspects for humans. In Egypt, this crop is going to be one of the economic vegetable crops and the cultivated area is increasing from year to another. The rapid increase in the acreage is mostly related to its high price and good yield in comparison with other crops as well as it is considered an export crop

Abamectin insecticide and acaricide used for controlling motile stage of mites ,leaf miners, coloradobedles, etc .on many vegetables and fruits crop .Several methods have been described determination of abamectin .While the triazole fungicide diniconazole is recommended for controlling powdery mildew and berry rot according to pest control program (**Mohamed and Eissa 2007**) determined diniconazole residues in field-sprayed and house hold processed cucumber and pepper fruits .Methomyl has been recommended to control many pests of strawberry, these pests include Egyptian cotton leaf warm, Red pumpkin bettle, squash bettle and others are attacked strawberry .

The present study aimed to investigate the following points:

1- Persistence of abamactin, diniconazole and methomyl residue on and in strawberry and tomato fruits in open field.

2- Determine the dissipation rate, half-life values (RL_{50}) and pre-harvest interval (PHI) for the tested pesticide.

3- Investigate the impact of some environmental factor i.e., different degree of temperature, sunlight and ultra -violet rays on the persistence of tested pesticide.

4- Identification of the photo degradation products of diniconazole after exposure to U.V using GC-MS .

The obtained results could be summarized as follows:

1. Persistence of abamactin, diniconazole and methomyl in and on strawberry and tomato fruits:

1.1. Residue of abamactin:

1.1.1. Strawberry:

The initial deposit of abamectin on and in strawberry fruits was 0.51 ppm one hour after application .The residue of abamectin in strawberry fruits within the first one day after application decreased to 0.26 ppm with 49.01 %loss .The rapid degradation continued for abamactin to reach 0.10 ppm with 80.39 %loss after 3 days from application .The decrease in the amounts of abamectin recovered 5 days after application continued to be 0.03 ppm with 94.11 loss . After 7 days, there was a small decline to 0.01 ppm, with 98.03 %loss .At 10 day of this experiment, residue of abamectin was not detected .The obtained residual half-life value (RL_{50}) of abamactin on and in strawberry fruits was 1.02 days .The data show that strawberry fruits could be safely consumed after 7 days of application according to the recommended maximum residue limit (MRL) for Abamectin in strawberry (0.02 ppm) .The maximum residue limits (MRL) of abamectin was established in ***(Codex.2009)*** for strawberry fruits.

1.1.2. Tomato:

The initial deposit of abamectin on and in tomato fruits was 0.34 ppm one hour after application .The residue of abamectin in tomato fruits within the first one day after

application decreased to 0.16 ppm with 52.94 %loss .The rapid degradation continued for abamactin to reach 0.08 ppm with 76.47 %loss within 3 days from application .The decrease in the amounts of abamectin recovered 5 days after application continued to be 0.01 ppm with 97.05 %loss . After7 day of this experiment, residue of abamectin was not detected . The obtained residual half-life value (RL_{50}) of abamactin on and in strawberry fruits was 0.98 days .The data show that tomato fruits could be safely consumed after 5 days of application according to the recommended maximum residue limit (MRL) for Abamectin in tomato (0.02ppm) .The maximum residue limits (MRL) of abamectin was established in ***(Codex.2009)*** for tomato fruits.

1.2. Residue of diniconazole:

1.2.1. Strawberry

The initial deposit of diniconazole was 2.47 ppm one hour after application then decreased to 2.20, 1.6, 0.46, 0.29, 0.16, 0.07and 0.02ppm indicated the rate loss were 10.39, 35.22, 81.37, 88.25, 93.25, 97.16 and 99.19 % after 1, 3, 5, 7, 10, 12 and 15 days respectively .The half-life value of diniconazole was 4.25 days .The data indicated that strawberry fruits could be consumed a safely after 15 days after application, where (MRL) of diniconazole residue in strawberry was 0.05ppm according to ***(European Union 2005).***

1.2.2. Tomato:

The initial deposit of diniconazole was 2.21 ppm one hour after application then decreased to 1.87, 1.27, 0.52, 0.33, 0.14, 0.06 and 0.03 ppm indicated the rate loss were 15.74, 42.53, 76.47, 85.06, 94.09, 97.28 and 98.64 % after 1, 3, 5, 7, 10, 12 and 15 days respectively .The half-life value (RL_{50}) of diniconazole was 3.4 days .The data indicated that tomato could be consumed a safely after 14 days after application, where (MRL) of diniconazole residue in tomato was 0.05ppm according to ***(European Union 2005).***

1.3. Residue of methomyl:

1.3.1. 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 (RL_{50}) of Methomyl was 3.97 days .The data indicated that strawberry fruits could be consumed a safely after 15 days after application, where (MRL) of methomyl residue in strawberry was 0.05ppm according to (European Union2005).

1.3.2. Tomato:

The initial deposit of methomyl was 2.87 ppm one hour after application then decreased to 2.14, 1.72, 1.05, 0.65, 0.12 and 0.02 ppm indicated the rate loss were 25.43, 40.06, 63.41, 77.35, 95.81 and 99.30 % after 1, 3, 5, 7, 10 and12 days respectively .The half-life value (RL_{50}) of methomyl was 4.80 days .The data indicated that tomato fruits could be consumed a safely after 7 days after application, where (MRL) of methomyl residue in tomato was 1 ppm according to (**Codex.2009**)

2. Effect of some environmental factors on the degradation of abamactin, diniconazole and methomyl:

2.1. Direct Sunlight:

Data showed that the percent of loss for abamectin, diniconazole, and methomyl wree29.90, 19.35 and 22.31% after one hour of exposure to direct sunlight. The decomposition percentages of abamectin were rapidly increased to 44.77, 67.32, 76.65, 87.31 and 97.64% after 3, 6, 9, 12 and 24 hours of exposure to direct sunlight. While these values were 31.79, 53.93, 66.18, 78.63, 88.82% and 39.19, 57.84, 73.32, 82.75, 94.06% when diniconazole and methomyl were exposed to direct sunlight for the same periods of exposure respectively.

The calculated half-life values (RL_{50}) of abamactin, diniconazole and methomyl were 3.65, 5.60 and 4.65 hours, respectively.

2.2. Effect of UV-rays on the pesticides tested:

The percent of loss for abamectin, diniconazole and methomyl were 14.99, 12.07 and 13.23% after one hour of exposure to UV-rays. The decomposition percentages of

abamectin increased to24.58, 37.29, 56.88, 71.07 and 88.23% after 3, 6, 9, 12 and 24 hours of exposure to UV-rays, respectively. While these values were 19.08, 28.29, 42.13, 57.48, 79.89% and 22.17, 32.24, 50.58, 67.96, 84.36% when diniconazole and methomyl were exposed to UV-rays for the same periods of exposure, respectively.

The calculated half-life values of abamactin, diniconazole and methomyl were 7.93, 10.18 and 8.91 hours, respectively.

2.3. Effect of different temperature degrees:

2.3.1. Abamactin:

Data summarize the effect of four different temperature levels (35, 40, 45 and 50 ˚C) on stability and degradation of abamactin .The results clearly indicated that the persistence of abamactin was influenced by temperature and period of exposure .It is evident that there is a positive relationship between the degree of temperature and the rate of degradation.

The data demonstrated thermal decomposition of abamactin for 3 hours at 35 and 40 ˚C were 8.08 and 11.23 %respectively, while the percentage losses were 11.79 and 13.27 % at 45 and 50 ˚C, respectively .

Thermal decomposition of abamactin continued to reach 11.55 and 14.99 %loss after 6 hours of exposure to temperature of 35and 40 ˚C, respectively .The decline in abamactin amounts continued after 12 hours to give 16.22 and 18.23 % loss at 35 and 45 ˚C, respectively .The decline in the amounts of abamactin continued after 24 hours to be 21.89 and 23.37 % loss at 35and 40 ˚C .

The decrease in the amounts of abamactin recovered 48, 96 and 144 hours after exposure to temperature of 35˚C became slower and gradual with an increase in percent loss and tendency to become close .However, the amounts of abamactin decreased from 48 to 144 hours and reached 59.69 % loss after exposure to temperature at 40 ˚C.

Also data indicated that the amounts of abamactin decreased from zero to 12 hours of exposure to temperature of 45 and 50˚C, to give 19.19 and 26.68 % loss, respectively .The

decrease in the residue of abamactin continued after 24 hours to be 28.65 and 35.53 % loss at 45 and 50 ˚C.

The percent loss of abamactin was 51.11 and 69.93 %after 96 hours of exposure to temperature of 45 and 50 ˚C, respectively .The result of 144 hours was 69.78 and 78.68 % loss at 45 and 50 ˚C, respectively.

The statistical half-life times for abamactin were 143.59, 112.67, 107.35 and 49.50 hours at 35, 40, 45 and 50 ˚C, respectively.

2.3.2. Diniconazole:

The obtained data summarize the effect of four different temperature levels (35, 40, 45 and 50 ˚C) on stability and degradation of diniconazole .Also it is clearly evident that thermal decomposition of diniconazole is positively correlated with temperature and period of exposure .The data demonstrated that the percentage losses of diniconazole after 3 hours of exposure were 4.29, 9.97, 14.92 and 19.78 % at 35, 40, 45 and 50 ˚C, respectively . Thermal decomposition of diniconazole continued to reach 9.37 and 18.48 % loss after 6 hours of exposure to temperature of 35 and 40˚C respectively .The decline in diniconazole amounts continued after 12 hours of exposure to temperature to give 16.23 and 23.07 % loss at 35 and 40 ˚C, respectively .The decline in the amounts of diniconazole continued after 24 hours to be 22.08 and 37.45 % loss at 35 and 40˚C .At the last day of this experiment (144 hours) the percent losses of diniconazole were 54.22 and 66.99 % after exposure to temperature at35 and 40˚C.

Data also indicate that the amounts of diniconazole decreased from zero to 12 hours of exposure to temperature of 45 and 50 ˚C to give 44.35 and 59.87 % loss, respectively .The percent loss of diniconazole was 48.94 and 68.77 % after 24 hours of exposure to temperature of 45 and 50˚C, respectively .The results of 144 hours were 76.27 and 89.95 % loss at 45 and 50 ˚C, respectively.

The statistical half-life times for diniconazole were 134.33, 90.78, 28.50 and 8.19 hours at 35, 40, 45 and 50 ˚C, respectively.

2.3.3. Methomyl

Data summarize the effect of four different temperature levels (25, 35, 40, 45 and 55 ˚C) on stability and degradation of methomyl and clearly indicated that the persistence of methomyl was influenced by temperature and period of exposure .It is evident that there is a positive relationship between the degree of temperature and the rate of degradation . Methomyl showed less persistence when exposed to temperature than that of abamactin and diniconazole .The data demonstrated that the percentage losses of methomyl after 3 hours of exposure were 2.28, 4.87, 14.57 and 16.37 % at 35, 40, 45 and 50 ˚C .Thermal decomposition of methomyl continued to reach 6.18, 8.98, 19.47 and 26.32 % loss after 6 hours of exposure to temperature of 35, 40, 45 and 50 ˚C, respectively.

Thermal decomposition of methomyl continued to reach 11.23 and 20.67 % loss after 12 hours of exposure to temperature of 35 and 40˚C respectively .The decline in diniconazole amounts continued after 24 hours of exposure to temperature to give 20.09 and 31.78 % loss at 35 and 40 ˚C, respectively .The decline in the amounts of diniconazole continued after 48 hours to be 29.12 and 38.21 % loss at 35 and 40˚C .At the last day of this experiment (144 hours) the percent losses of diniconazole were 65.00 and 74.11 % after exposure to temperature at35 and 40˚C.

Data also indicate that the amounts of methomyl decreased from zero to 12 hours of exposure to temperature of 45 and 50 ˚C to give 29.41 and 38.21 %loss, respectively .The percent loss of diniconazole was 51.53 and 71.47 %after 24 hours of exposure to temperature of 45 and 50˚C, respectively .The results of 144 hours were 99.2 and 99.8 % loss at 45 and 50 ˚C, respectively.

The statistical half-life times for methomyl were 120.32, 108.01, 22.86 and 15.60 hours at 35, 40, 45 and 50 ˚C, respectively.

3. Identification of the photo degradation products of diniconazole after exposure to UV light using GC-MS:

The results of GC/MS analysis of extracts of diniconazole after exposure to UV-radiation showed that, at zero time unchanged diniconazole was found .The proportion detected by GC/MS of diniconazole after exposure to UV-radiation decreased with time.

The total ion chromatogram and mass spectrum at fig (17)showed a molecular ion peak ($M^{+\bullet}$)at m/z 294, and fragment 264, 178, 164, 151, 136, 123, 109, 95, 81, 67 and 55 which are corresponding to the formula ($C_{13}H_{10}N_3OCL_2$)which suggested to be ((1E-)-1-(2,4-dichlorophenyl-)-2-(1H-1,2,4-triazol-1-yl)penta-1,4-dien-3-ol.).

The other founded compound are of M-2 at m/z 279 and fragment 268, 231, 221, 207, 193, 179, 167, 157, 149, 132, 122, 113, 104, 93, 83, 71 and 57, which are corresponding to the formula ($C_{14}H_{13}NOCL_2$) which are suggested to be in fig.(18).

And this compound which suggested to be the major degadates of diniconazole when exposure to UV-radiation according to (**Krishan and Shyam 199**7).