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Estimation of effectiveness and residues of pyridalyl, methomyl, emamectin-benzoate and lufenuron against *(Spodotera Littoralis)* on tomato fruits under field conditions.

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ABSTRACT

A Field study was conducted at EL-Beheira Governorate, Egypt to determine the insecticidal activities of pyridalyl, methomyl, emamectin benzoate, and lufenuron on tomato plants against the cotton leaf-worm *(Spodotera Littoralis)*. Data obtained showed that a pyridalyl compound has the highest toxicity against the cotton leaf worm followed by methomyl then emamectin benzoate while the lufenuron has the lowest toxicity. The insecticide residue on the fruits of treated tomato fruits was extracted using QuEChERS method before analysis by HPLC-UV.
The validation method for extraction and quantitative analysis of tested pesticides residue in tomato fruits using HPLC-UV, at fortification levels of 0.1, 0.5, and 1.0 mg/kg in tomato fruits was performed. The results suggest that the pyridalyl, methomyl, emamectin benzoate, and lufenuorn dissipation curves and its half-lives in tomatoes were 1.16, 1.38, 1.80 and 1.20 days for pyridalyl, methomyl, emamectin benzoate, and lufenourn, respectively. The residues in tomato were below the (MRL) and the safety time was 1, 5, 7 & 7 days for pyridalyl, methomyl, emamectin benzoate, and lufenuron, respectively. In conclusion, pyridalyl, methomyl, emamectin benzoate, and lufenuron insecticide are useful in controlling cotton leaf-worms in tomato fields and safe for human consumption.

INTRODUCTION

The *Spodoptera littoralis* (Boisd) cotton leaf worm is one of the most significant insect pests in Egypt. Cotton, vegetables, and ornamentals are all at risk. To manage this dangerous pest, many farmers use the organophosphorus chemicals chlorpyrifos-methyl and profenofos as well as carbamate, and methomyl (**Tomlin, 2000**). Due to its rapid reproductive rate and significant crop losses, the cotton leaf worm *Spodoptera littoralis* (Boisd.) is one of Egypt's most devastating phytophagus insect

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pests. It is a highly polyphagous species that consumes 87 economically significant kinds of plants from 40 different families of plants (**Kandil, et al. 2020**). The prolific and extremely polyphagous *Spodoptera littoralis* (Boisd.) cotton leaf worm belongs to the Lepidoptera family (Noctuidae). Since it infects a wide variety of host plants, it is regarded as a major pest with significant economic significance in many nations. The main impact is defoliation since the larvae (caterpillars) primarily eat leaves and have a habit of burrowing into and feeding inside of fruits like tomatoes, young melons, and peppers that are close to or rest on soil (**Ali et al. 2015**). A novel bio-insecticide called emamectin benzoate was discovered by the fermentation of the soil microbe *Streptomyces avermitilis*. Biochemistry causes paralysis by promoting the release of aminobutyric acid, an inhibitory neurotransmitter (**Raslan et al. 2009**). **Abdel-Rahim, 2011**, employed the traditional insecticide methomyl to suppress lepidopterous bugs. The environmental friendliness of pyridalyl flowable has been confirmed, and it is ideal for use in integrated pest management (IPM) system. It has a high level of safety for people, animals, and fish, without any effect on both natural pest predators and pollinating insects (**Dahi, et al. 2011**).

When one of the target pests crosses the economic threshold, lufenuron and abamectin may be used often (**Freitas and Bueno, 2004**). In Egypt, one of the most significant solanaceous vegetable crops is the tomato (Lycopersicon esculentum Mill). There are numerous harmful bugs currently infesting tomato plants (**Natwick, 2010)** Between 2000 and 2002, the QuEChERS method was created as a new sample-preparation technique for pesticide multi-residue analysis (**Anastassiades et al. 2003**).

Pre-Harvest Interval (PHI) of tomatoes treated with tested pesticides was to be determined. The current experiment focused on the dissipation rate and residue levels of included pyridalyl, methomyl, emamectin benzoate, and lufenuron insecticide in tomato fruits under field settings.

This work aimed to study the dissipation rate and residue levels of pyridalyl, methomyl, emamectin benzoate, and lufenuron insecticide in tomato fruits under Egyptian field conditions. As well as provide some insight into how well the pyridalyl, methomyl, emamectin benzoate, and lufenuron insecticides worked against worm cotton leaves. Also, determine the harvest intervals (PHI's) and minimize health risks.

2-MATRIALS and METHODS

2.1. Field trials and sample collection

The field trials were achieved in El-Beheira Governorate, Egypt. The tomato plants were grown in 1m rows with a distance of 0.5 m between plants. The experimental area was divided into five plots, one plot for control samples and other plots for treatment by (Pyridalyl) Billio 50% EC with a rate of 100 cm^3/feddan, the second plot for treatment by (Methomyl) Methu-Neo 40 % SP with rate 675 g/feddan, another plot for treatment by (Emamectin benzoate) Tiknubist 5.7% WDG with rate 60 g./ feddan, and the last one for treatment with (Lufenuron) Aksudus 5% EC with rate 160cm3/Feddan for each plot. After application, two kilograms of tomato fruits were collected randomly from both control and applied plots, and at intervals of 1 h after application (1 h, as initially), 1, 3, 7, 10, and 15 days, respectively. Fruit samples were stored in a freezer at -20ºC until extraction.

2.2. Insect rearing:

Egg masses of *S. littoralis* field strain were collected from cotton fields of Etay-El-Baroud, Beheira Governorate, which did not receive any insecticidal treatments before egg masses collection. The egg masses were transferred to the laboratory and maintained under conditions of 25 ± 2 °C, 65 ± 5 RH, and 14:10, L: D, photoperiod even developed into 4th instar larvae; then used in the test. The larvae were fed on fresh leaves of the castor bean, *Ricinus communis*, as described by **El-Defrawi et al. (1964).**

2.3. Pesticides bioassay:

The experiments were performed under laboratory conditions of 25 ± 2°C, 70 ± 5 RH,

and 14:10, L: D, photoperiod. Five *S. littoralis* 4th instar larvae were put in a 500 ml plastic pot and covered with a clean piece of muslin cloth, representing one replication. Ten replications were made for each treatment at each date of feeding. The sprayed tomato leaves were picked up immediately after one h from spray (zero time), and then after 1, 2, 4, and 6 days post spray and transferred directly to the laboratory for feeding the selected larvae. After 24 h of feeding on treated leaves, the survived larvae were transmitted to new and clean 500 ml plastic pots and were fed on untreated cotton leaves till pupation. The number of dead larvae and percentage of mortality were recorded after 1, 3, and 7 days post-treatment. The larva was considered dead if no movement was observed when it was touched with a small brush. Larval duration, percentages of normal and deformed pupae, and percentages of normal and malformed adult emergence were estimated. The mortality of larvae was counted and recorded 24 hrs later after feeding and corrected for natural mortality by using Abbot's formula (1925).

2.4. Standards and reagents

Pyridalyl, Methomyl, Emamectin benzoate, and Lufenuron reference standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany), with > 99% purity (Fig. 1).

All other reagents and solvents were obtained from Sigma Aldrich and were HPLC grade. Stock solutions of tested pesticides were prepared at a concentration of 100 µg/ml in acetonitrile and kept in a refrigerator (4°C). Calibration standard and working solutions concentrations ranging from 0.01 to 5.0 µg /ml were prepared by serial dilution of the stock solutions.

QuEChERS salts 4 g $MgSO_4$, 1 g NaCl, 1 g trisodium citrate dihydrate, 0.5 g disodium hydrogen citrate sesquihydrate, and d-SPE salts were purchased from Agilent Technologies (Wilmington, DE, USA).

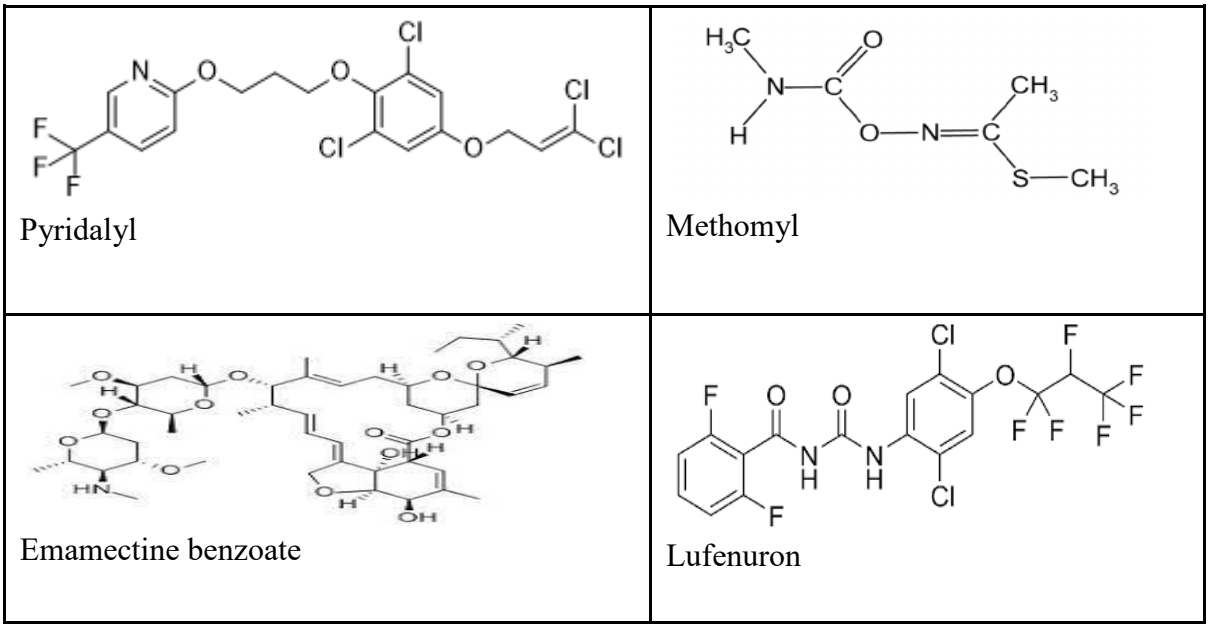

Fig (1): Structures of tested pesticides

2.5. Sample preparation:

Extraction and cleanup were carried out according to the official method presented by **Anastassiades et al. (2003)**, 10 gram of the homogenized sample was weighed into a 50 mL centrifuge tube, and extraction and cleanup were achieved using a QuEChERS extraction salt packet and dispersive kits for cleanup. The analytical procedure was done as follow: (1) adding a 10 g of sample into a centrifuge tube; (2) adding 10 mL of acetonitrile, then well-shacked by vortex, QuEChERS extraction salts were added in each tube, the tubes were closed and vigorously shaken by hand for 1 min., and centrifuging at 3,500 rpm for 5 min; (3) transferring 1 mL of acetonitrile extract to a 15 mL centrifuge tubes containing 25 mg PSA and a 150 mg of anhydrous $MgSO_4$. The tube was vortexed for 1 min and then centrifuged for 5 min at 3500 rpm. The supernatants were filtered using a 0.2 µm PTFE filter (Millipore, Billerica. MA) into auto-sampler glass vials for HPLC-UV analysis. Fortified samples were prepared by spiking different standard solution concentrations to 10 g of control samples of tomato in three levels of 0.1 to 1.0 mg/kg. The fortified samples were left for 30 min at room temperature to allow the pesticide to penetrate the matrix before extraction and the solvent evaporates. Each fortification level was analyzed through five replicates with the same processes.

2.6 Instruments and apparatus

The chromatographic analysis was performed using the HPLC system, an Agilent 1260 series equipped with a quaternary pump, variable wavelength ultraviolet (UV) and an analytical column (Nucleosil C_{18}) (30 mm×4.6 mm id, × 5 µm, a flow rate of mobile phase (acetonitrile 60% + water 40 %) was 1ml/min. and wavelength was set at 205 nm for Pyridalyl. The retention time for Pyridalyl was 5.35 min., while the flow rate of the mobile phase (acetonitrile 90% + water 10 %) was 1ml/min for Methomyl and the wavelength was set at 220 nm. The retention time for methomyl was 2.47 min., while the flow rate of mobile phase (acetonitrile 65% + water 35 %) was 0.8 ml/min for Emamectin benzoate and wavelength was set at 220 nm. The retention time for Emamectin benzoate was 5.03 min. while the flow rate of the mobile phase (acetonitrile 90% + water 10 %) was 0.8 ml/min for Lufenuron and the wavelength was set at 254 nm. The retention time for Lufenuron was 9.24 min.

2.7 Method validation.

According to **SANTE/11312/2021** laboratory method validation was performed to prove the effectiveness of the extraction and quantitative determination of tested pesticides in tomatoes. The method was validated following a conventional validation procedure that included the following parameters: linearity, multi-level calibration of tested pesticide residues in tomato was diluted either with a pure solvent in series at (5, 1, 0.5, 0.1,0.05, 0.01) µg/ml for HPLC analysis, (matrix effect) comparing the response produced from the tested pesticide residues in pure solvent solution with the samples were first extracted and then spiked with a tested pesticide in the same solvent at the same concentration level,(selectivity and sensitivity) determined limit of quantification (LOQ), trueness (bias) five replicates were used to check the recovery at the levels (1, 0.5, and 0.1) mg/kg and repeatability precision (RSD%)

3. RESULTS:

Table (1) showed the mortality percentages of four insecticides pyridalyl, methomyl, emamectin benzoate, and lufenuron against the second and fourth instars of cotton leafworm larvae in different exposure periods 1, 3, and 7 days under laboratory conditions.

Table 1. Toxicity of pyridalyl, methomyl, emamectin benzoate, and lufenuron against 2nd and 4th instar larvae of *S. littoralis* after different exposure times.

Pesticides	% Larvae Mortality (days)								
	1			3			7		
	2nd	4th	Average	2nd	4th	Average	2nd	4th	Average
Pyridalyl	100.0	92.34	96.17	73.50	100	86.75	100.0	68.50	84.25
Methomyl	98.45	91.33	94.89	84.56	76.00	80.28	78.25	76.90	77.57
Emamectin Benzoate	94.10	80.55	87.32	90.25	69.75	80.00	75.50	70.40	72.95
Lufenuron	88.76	83.87	86.31	79.75	73.90	76.82	66.25	62.75	64.50

Table 2. Mean recovery percentages and repeatability precision of pyridalyl, methomyl, emamectin benzoate and lufenuron from spiked samples of tomato fruits

Spiked Samples	0.1 ppm	RSD%	0.5 ppm	RSD%	1 ppm	RSD%
pyridalyl	90.24±0.92	1.25	95.84±1.12	1.11	99.82±1.42	1.20
methomyl	88.30±1.07	2.02	92.47.30±1.31	1.29	95.45±1.95	2.08
emamectin benzoate	85.45±1.55	1.94	89.61±1.89	1.62	93.88±1.73	1.99
lufenuron	92.44±1.11	1.55	96.59±1.04	1.48	99.69±1.66	1.43

The average recovery percentages in tomato fruits for the target pesticides were presented in Table (2) for the three tested levels, respectively. All obtained results in this study were corrected according to the recovery percentages.

Table 3. Residue levels and dissipation behavior of pyridalyl in tomato under open field conditions.

Time after treatment (days)	Pyridalyl Residues (mg/kg)±SD	Methomyl Residues (mg/kg)±SD	Emamectin benzoate Residues (mg/kg) ± SD	Lufenuron Residues (mg/kg) ±SD
Initial*	1.82±0.20	4.53 ± 1.32	1.01±0.13	2.58±0.26
1	1.04±0.15	2.89±0.65	0.73±0.11	1.51±0.55
3	0.87±0.11	1.05±0.25	0.09±0.018	0.94±0.22
7	0.44±0.12	0.31±0.04	0.02±0.012	0.32±0.195
10	0.10±0.041	0.10±0.022	0.007±0.0014	0.17±0.019
15	0.05±0.025	0.04±0.012	ND	0.02±0.012
$t_{1/2}$ (days)	1.16	1.38	1.80	1.20
MRL	1.5 ppm (EU2021)	1 ppm (codex2009)	0.02 ppm(EU 2022)	0.4 ppm (codex2016)
PHI (days)	1	5	7	7

$t_{1/2}$: Half-life period. MRL: Maximum residue level. PHI: Pre-harvest interval. ND: Not detected.

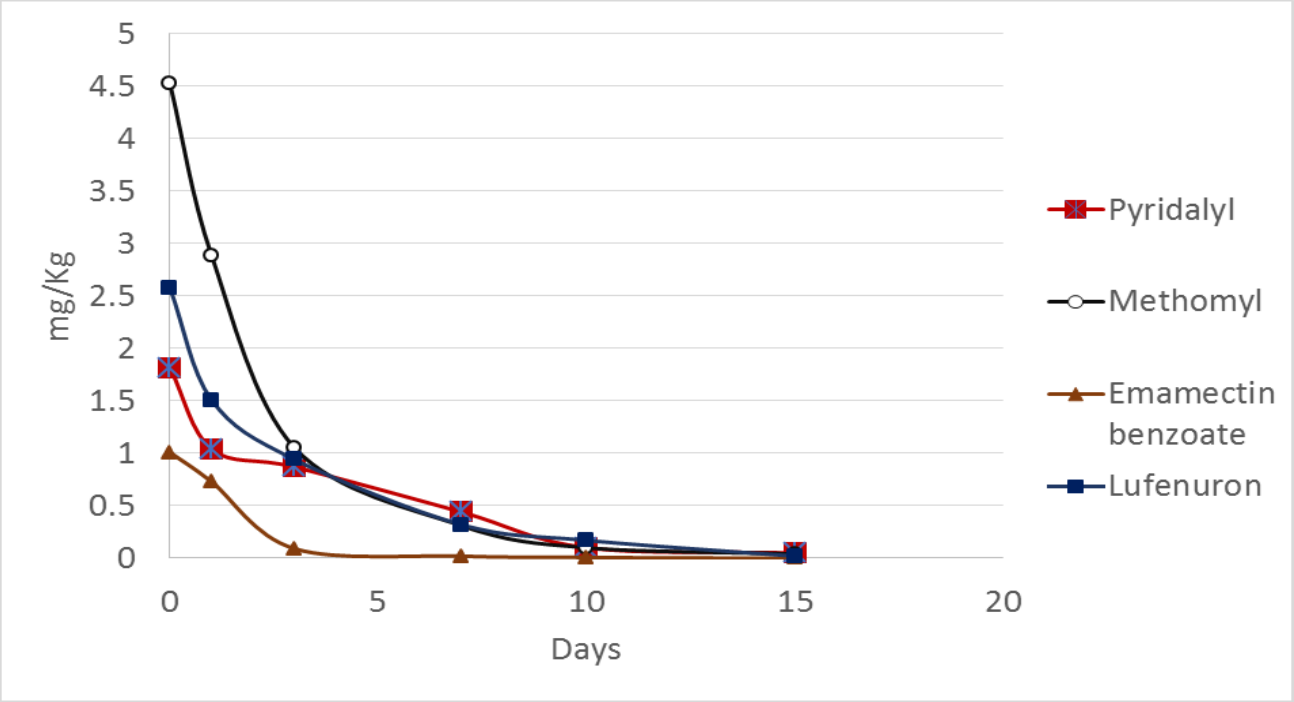

Table 3. Demonstrate the determination of pyridalyl, methomyl, emamectin benzoate, and lufenuron residues in tomato fruits under field conditions using HPLC-UV analysis under field conditions

4. DISCUSSION

Results in table (1) showed the mortality percentages of four insecticides pyridalyl, methomyl, emamectin benzoate, and lufenuron against the second and fourth instars of cotton leafworm larvae in different exposure periods 1, 3, and 7 days under laboratory conditions. The second instar larvae were more susceptible to all treatments than the fourth instar larvae and pyridalyl was the most toxic against the larvae of the cotton leaf-worm, followed by methomyl then followed by emamectin benzoate and lufenuron was the least toxic one, respectively.

This studies similar to that recorded by **Raslan et al. (2009**) data obtained showed a promising use emamectin benzoate in the integrated control programs of cotton leaf worms. The obtained results found in agreement with that of (**Kandil, et al. 2020**) who noted that emamectin benzoate (EMB) are effective insecticide for controlling the cotton leaf worm, Spodoptera. This result was confirmed by **Abdel-Rahim (2011**) who found that the bio-residual activity of two compounds, pyridalyl, and methomyl against the second and fourth instar larvae of a laboratory strain of the cotton leafworm, *Spodoptera littoralis* was evaluated under laboratory and semi-field conditions.

Table (2) demonstrate the average recovery percentages of four studied pesticides in tomato fruits which were corrected according to the recovery percentages. The lowest concentration at which detected insecticide corresponding to a signal/noise ratio of 3:1 was taken as the LOD. The LOQ of the method was set by determining the pesticides at different concentrations at which the chromatographic peaks could be determined in samples corresponding to a signal/noise ratio of 10:1 was taken as the LOQ [**SANTE/11312/2021**]. LOD and LOQ were calculated and found to be 0.01 and 0.1 mg/kg, respectively, low detection and quantification limits of the proposed method allow its application for the accurate determination of pesticide residues in tested crops.The % ME could be negative or positive: no matrix effect (between -20% and 20%), medium matrix effect (between -50% and -20%), and strong matrix effect (below -50% or above 50%). **Saber *et al.* (2016)** and

Ferrer *et al.* (2011). The matrix effect ranged from -10.24 to 15.85% for tested pesticides which indicated that no interfering endogenous peak appeared and did not significantly suppressor enhance the response of the instrument.

The linearity of the method was determined by constructing calibration curves prepared by triple injection (n= 3) for each of the six concentrations of tested pesticides, i.e. 0.01 to 5.0 mg/kg. All tested pesticides showed good linearity with a determination coefficient (R^2) ranging 0.978 to 0.992 and the matrix-matched calibration also showed good linearity with determination coefficients $R^2 > 0.976$.

Determination of tested pesticides in/on tomato fruits using HPLC-UV analysis.

Table (3) showed the determination of pyridalyl, methomyl, emamectin benzoate, and lufenuron residues in tomato fruits under field conditions using HPLC-UV analysis under field conditions. The initial deposit of pyridalyl, methomyl, emamectin benzoate, and lufenuron in tomato was 1.82±1.20, 4.53 ± 2.32, 1.01±1.03 and 2.58±1.26 ppm, respectively one hour after application. Then gradually decreased within one day to 1.04 ± 1.50, 2.89 ± 1.65, 0.73 ± 1.11, and 1.51±1.55 ppm, respectively. The residues gradually decreased to reach 0.05±0.55, 0.04±1.19, ND, and 0.02±1.07 ppm, respectively after 15 days of application for pyridalyl, methomyl, emamectin benzoate, and lufenuron. The half-life of pyridalyl, methomyl, emamectin benzoate, and lufenuron were 1.16, 1.38, 1.80, and 1.20 days, respectively. Estimated PHI values according to EU (2021) and Codex (2009) for tested pesticides were 1, 5, 7, and 7 days, respectively.

Our results agreed with **Soliman and Fergani (2021**) who found that the residues in/ on tomato fruits were below the Codex maximum residue limit (MRL) which were 1 and 0.4 mg/ kg (EU, 2022) after the pre-harvest interval (PHI) were 3 and 8 for chlorpyrifos-methyl and lufenuron respectively. The limit of quantitation and detection for chlorpyrifos-methyl were 0.1 and 0.02 while for lufenuron were 0.01 and 0.003 mg/kg, respectively. The results suggest that the chlorpyrifos-methyl and lufenuron dissipation curves followed the first-order kinetics and their half-life values were 1.03 and 1.50 days, respectively. **Ramadan et al. (2016**) found that the residue concentrations of pyridalyl on leaves and fruits, two hours after a single application of the insecticide were 1.007 and 0.815 mg a.i./kg, respectively. The insecticide residues on fruits were 0.707, 0.569, and 0.474 mg a.i./kg after 1, 2, and 3 days and reached 0.2 mg a.i./kg after 14 days. The corresponding residues on leaves were 0.808, 0.646, 0.637, and 0.284 mg a.i./kg after 1, 2, 3, and 14 days. The rates of degradation (k values) were 0.100 and 0.115 on leaves and fruits, respectively. The corresponding half-life times ($t_{1/2}$) were 6.95 and 6.05 days on leaves and fruits, respectively. The residues on tomato fruits were below the maximum residual level (MRL) value reported by the European Food Safety Authority (**EFSA, 2013**).

Thus, tomato fruits could be safely harvested for human consumption and processing purposes. **Ahmed and Hassanein (2005)** showed the determination of the insecticidal activities of chlorpyrifos-methyl, profenofos, and methomyl on tomato plants against the cotton leaf-worm (*Spodotera littoralis*). Data showed a high initial mortality (100, 100, and 100%) against the second and the fourth instars larvae with reasonable persistence**.** The residues of these insecticides on fruits of the sprayed and contaminated tomato plants were determined by GLC and HPLC, with recoveries of 100, 100, and 94.58%, respectively. The initial deposits of chlorpyrifos-methyl, profenofos, and methomyl were 2.10, 2.58, and 20.11ppm, while decreased to 0.19, 1.41, and 0.33ppm after 3,1 and 13 days from spraying, respectively, such residue levels are below the maximum residue level (MRL). The estimated half-life values ($t_{1/2}$) were 0.49, 1.03, and 1.19 days for the same insecticides, respectively. **El -Hefny et al. (2019)** investigate the dissipation of methomyl (a common insecticide) used mainly on tomato fruits. LC-MS/MS coupled with the QuEChERS method was used for the determination of methomyl. The results showed that the recovery using matrix-

matched standards ranged from 87.8 to 101.3%, with a relative standard deviation of 2.5 to 7.5%. Residue half-life calculated using kinetic rate ranged from 1.95 to 1.63 days in tomato and soil, respectively. From the results, it was concluded that tomato fruits can be safely harvested for consumption after 15 days of application based on the estimated preharvest interval (PHI). It is advisable to re-estimate the PHI regularly owing to data from the EU (2022) and Codex (2016). On other hand, **Shalaby et al. (2022)** studied the residues and dissipation rates of emamectin benzoate and the results revealed that the initial amounts of emamectin benzoate in leaves and fruits were 1.721, and 0.215, respectively. Loss percentages in residues were higher in tomato fruits than in leaves. The half-life (t½) values of emamectin benzoate were 0.973, and 1.16 days in tomato fruits and leaves, respectively. Contaminated tomatoes could be consumed safely after 3 days for unwashed and washed fruits contaminated with the tested pesticide according to the maximum residues limit (MRL) of the EU pesticides database - European Commission.

Pesticides' persistence vs. degradation behavior is generally influenced by a variety of factors, including the general stability of the parent component or its metabolites, volatility, solubility, formulation, application method, and site (**Cabras et al. 1989**). Additionally, there is several environmental factors, such as temperature, precipitation, humidity, and air movement, as well as factors related to plant properties, such as plant species, the type of crop harvested, cuticle structure, stage of growth, rate of growth, treated plant surface, and the general environment around the plant (**Gennari et al. 1985, Khay et al. 2008; Tewary et al. 2005; Fenollet et al. 2009; Malhat, 2012; Malhat et al. 2014).**

CONCLUSION

In conclusion, pyridalyl compound has the highest toxicity against cotton leaf-worm followed by methomyl, followed emamectin benzoate while the lufenuron has the lowest toxicity. The results suggest that the pyridalyl, methomyl, emamectin benzoate, and lufenuorn dissipation curves and their half-life were 1.16, 1.35, 1.80, and 1.20 days for pyrida -lyl, methomyl, emamectin benzoate and lufenourn in tomato, respectively. Generally, the residues in tomato were below the MRL while, the safety time was 1 and 5 days for pyridalyl and methomyl, respectively, as well as 7 days for emamectin benzoate and lufenuron. In addition these pesticides, are safe for human consumption.

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