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Dissipation of chlorpyrifos-methyl and lufenuron in and on tomato fruits infested with the cotton leafworm *Spodoptera littoralis* (Lepidoptera: Noctuidae) under the field conditions

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Abstract:

Organophosphates and IGR have captured the popular choice among other groups of insecticides being used against the Egyptian cotton leafworm, *Spodoptera littoralis* (Boisduval) (Lepidoptera: Noctuidae), in Egypt. This study was designed to estimate the residue levels of two insecticides belonging to two different groups with different modes of action, chlorpyrifos-methyl and lufenuron in/on tomato fruits infested with *S. littoralis* in the field. The experiment was designed in randomized block design. Samples of tomatoes were randomly collected from treated and un-treated plants after a time interval of zero time, 1, 3, 7, 10, and 15 days for both insecticides. The technique was validated for chlorpyrifos-methyl and lufenuron at different fortification levels (0.01, 0.5, and 0.1 µg/kg) in/on tomato fruits. The mean recoveries were from 90% to 111%. The insecticide residues extracted by an optimized QuEChERS coupled with the gas chromatographic analysis technique (GC) in the case of chlorpyrifos-methyl, and the high-performance liquid chromatographic (HPLC) analysis combined with diode array detection for lufenuron. HPLC and GC analytical systems were characterized by high accuracy and acceptable sensitivity to meet the requirements for monitoring insecticides in/on local tomato cultivation. Under the optimized condition, the residues in/on tomato fruits were below the codex maximum residue limit (MRL) (1 and 0.4 mg/kg) after pre-harvest intervals (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 its half-life values were 1.03 and 1.50 days, respectively.

Introduction

Nowadays, the cultivation of tomato fruits is widespread around the world and cultivated over a large area in Egypt. Tomato production is one of the most economic industries due to their nutritional content, either used as a fresh product or canned for later use (El-Nabarawy and Abou-Dania, 1992). Tomato cultivation was obstructed by many pests. The Egyptian cotton leafworm, *Spodoptera littoralis* (Boisduval) (Lepidoptera: Noctuidae) proved to be the most important pest destructing Tomato fruit fields in Egypt. The use of chemical pesticides such as organophosphorus (Ops) and insect growth regulators insecticides in/on tomato fruits agriculture is still progressive because of the efficacy of Ops and IGR in reducing insect infestation (Prabhaker *et al.,* 1985).

The Successive use of these synthetic insecticides might cause serious problems such as resistance development, environmental pollution, and detrimental hazards to non-target organisms (Hamama and Fergani, 2019). One of these problems is a remaining residue in fresh consumed edible crops as vegetables and fruits that hazards to human health (Zidan *et al.,* 1996). Over 20 pesticide residues and their degradation metabolites have been determined in different food products by Abdel-Gawad and Shams El-Deen (1989). Inadequate use and failure to comply with pre-harvest intervals can cause the occurrence of residues above MRL. Therefore, different countries and international organizations have included several laws to regulate pesticide residues in food sources that are required to protect the health of consumers (Wang *et al.* 2015). Field evaluations should control the unwise use of insecticides in/on tomato crops that may cause accumulation of pesticide residues more than the permitted levels.

Accurate measurements of dissipation or degradation rates of various insecticides under field conditions to ensure that the established pre-harvest interval (PHI) residues level were below the maximum residue limit (Malhat *et al*., 2011). In recent decades, the QuEChERS ‘‘Quick, Easy Cheap, Effective, Rugged and Safe’’ method is one of the most distinctive AOAC (AOAC, 2000) official protocols for quantitation of pesticide residues in food matrices (Lehotay, 2007). Also, choosing the appropriate methodology for sample preparation methods greatly influences the reliability and accuracy of food analysis (Seddik *et al.,* 2012).

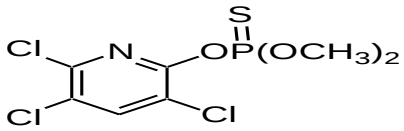
The main objectives of this study were to estimate the residue levels of Chlorpyrifos-methyl and Lufenuron and in tomato fruits cultivation infested with *S. littoralis* in the field using PHL and $t_{1/2}$ parameters which suggested as one of the most important registration requirement using the QuEChERS method coupled with (HPLC) connected with photodiode array detector (DAD) and (GC) analysis technique.

Materials and methods

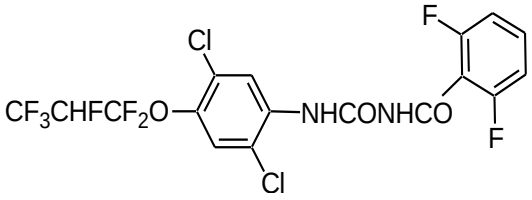
1. Chemicals:

Two different groups were purchased locally and used for a field experiment in this work at the recommended dose:

1.1. Chlorpyrifos-methyl (insecticide, acaricide), organophosphate IUPAC name *O, O*-dimethyl *O*-3, 5, 6-trichloro-2-pyridyl phosphorothioate, *O, O*-dimethyl *O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate, 50 % EC**,** at rate 1000 cm^3/ 100 litters.



1.2. Lufenuron (insecticide, acaricide) benzoylurea, *RS*)-1-[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]-3-(2,6-difluorobenzoyl)urea 5% EC. at 1000 cm^3/ 100 litters.



2. Field trials:

The experiments were carried out at Etai El-Barood Agricultural Research Station, El-Beheira, March 2020 Egypt. Tomato seedling [*Solanum Lycopersicum* Mill.) cv. Malika]. The experiments were designed in the following ways: plot size, 7 x 6 m; plot to plot distance, 1.5 m; plant to plant distance, 0.4 m for a row to row distance 1 m. Treatment plots were arranged in a randomized complete block design with three replications. Cultural practices were made according to the recommended crop schedule. To ensure the reliability of the experimental results, the field trials were previously investigated to be free of the pesticide. A hand-operated knapsack sprayer (20 liters) was used to apply the tested insecticides to the tomato plants. The recommended formulation used by sprayer volume of 1L/feddan (1feddan=4.200 m^2) for Chlorpyrifos-methyl 50% EC (Burodan) and 50cm^3/100Lwater for lufenuron (Granda). The spray was done in June 2020.

3. Reagent and chemicals:

Analytical standards of Chlorpyrifos-methyl and Lufenuron (≥99.9% purity) were obtained from Dr. Ehrestorfer Augusburg, Germany. All organic solvents used in this study were of HPLC grade and purchased from Scharlau (Barcelona, Spain). The suitability of solvents was ensured by running a reagent blank along with actual analysis. Sodium chloride of analytical grade was purchased from El Naser Pharmaceutical Chemicals Co. (Cairo, Egypt). Anhydrous magnesium sulfate of analytical grade, purchased from Merck (Germany), was activated by heating at 400°C for 4 hours in a muffle furnace, then cooled and kept in a desiccator before use. Primary secondary amine (PSA, 40 µm Bondesil) was obtained from Supelco (Bellefonte, PA).

4. Preparation of standard solutions:

The stock solution containing 100 µg/ml of the analyte was prepared using acetonitrile as a solvent and kept in a refrigerator at 4°C. The working standard solutions (0.001, 0.01, 0.05, and 0.1 µg/ml) were prepared through a series of dilutions of a standard stock solution in acetonitrile. Meanwhile, a matrix-matched standard solution was similarly produced with blank tomato extract added to each diluted solution using the same calibration graph. The standard calibration curves of used insecticides were constructed by plotting analyte concentrations versus peak area.

5. Residue analysis:

5.1. Sampling and extraction:

After a spray of the tested insecticides, samples of treated and un-treated tomato fruits were collected randomly from each replicate at intervals of zero time (2h after application),1, 3, 7, 10, 15 days for all treatments. Samples were transferred to the laboratory and stored at –20 ºC until using for analysis. One kilo of each sample was chopped into small cubes and homogenized for 5 min at high speed in a laboratory homogenizer and extracted according to the procedure described and modified by Lehotay *et al*. (2010). Ten grams of each homogenized sample was weighed into a 50 ml Teflon-Tube, extraction, and cleaned-up were done extracted by an optimized QuEChERS method (Anastassiades *et al.*, 2003) by blending with 10 ml of 1.0% acidified acetonitrile with acetic acid and shake vigorously for 1 min, the whole extract decanted through a glass wool plug in a glass funnel containing 4 g of anhydrous magnesium sulfate and 1 g of sodium chloride then shake vigorously for 1 min. one gram sodium citrate dehydrate, and 0.5 g

disodium hydrogen citrate sesquihydrate were added. The filtrate then vigorously shaken for 1 min using a vortex mixer at maximum speed. Afterward, 4 g of anhydrous MgSO4, 1 g of NaCl, 1 g sodium citrate dehydrate, and 0.5 g disodium hydrogen citrate sesquihydrate were added, then extract by shaking vigorously on vortex for 2 min and centrifuged for 10 min at 5,000 rpm. An aliquot of 3 ml was transferred from the supernatant to a new clean 5-ml centrifuge tube and cleaned by dispersive solid-phase extraction with 75 mg of PSA and 500 mg of magnesium sulfate. Afterward, centrifugation was carried out at 6,000 rpm for 5 min. An aliquot (2 ml) from the supernatant was filtered through a 0.2-µm PTFE filter (Millipore, USA) and then analyzed by Agilent 1100 HPLC-DAD.

5.2. Determination:

5.2.1. Chlorpyrifos-methyl:

Determination of Chlorpyrifos-methyl residues was performed using the Gas chromatographic (GC) analytical system. After extraction 0.5 mL of the cleaned supernatant was transferred into a screw cap vial and1.0 µL of the solution was injected into (G.C) Agilent-GC analysis. Chlorpyrifos-methyl (Hewlett Packard GC Model 6890) equipped with Ni^{63} electron capture detector (ECD). The gas chromatography conditions HP-5MS capillary column (30m length x 0.32 mm internal diameter (i.d) x 0.25 µm film thickness). Operating temperatures were: column temperature was programmed: initial oven temperature, 40 ^{0}C to 220^{0}C at 30^{0}C /min then to 240^{0}C at 5 ^{0}C /min and detector temperature 320 ^{o}C with nitrogen carrier gas flow at 1.0 ml/min. all compounds were identified by their retention times compared to known standards.

5.2.2. Lufenuron:

Lufenuron residues were determined by the HPLC system. The chromatographic conditions were as follows: an Agilent 1100 series equipped with an analytical column (150 mm×4.6 mm id, × 5 µm ODS) attached to a photodiode array detector. The flow rate of mobile phase methanol 80 % + water 20 %) was 0.8ml/min and the injection volume were 20 µl. the detection wavelength was set at 255nm. Residues were estimated by comparison of peak area of standards with that of the unknown or spiked samples run under identical conditions

6. Recovery studies:

According to SANCO/1257/2013 (SANCO, 2013) within laboratory method validation was performed to provide evidence that the method is fit for the extraction and quantitative determination of Chlorpyrifos-methyl and Lufenuron in/on tomato fruits. The method was validated following a conventional validation procedure that included the following parameters: (Linearity) multilevel calibration of Chlorpyrifos-methyl and Lufenuron was diluted either with pure solvent in series at (5, 2.5, 1, 0.5, 0.2, and 0.01) µg/ml, (Matrix effect) comparing the response produced from the Chlorpyrifos-methyl and Lufenuron in a pure solvent solution with the samples were first extracted and then spiked with Chlorpyrifos-methyl and Lufenuron in the same solvent at the same concentration level, (Selectivity and Sensitivity). Determining limit of quantification (LOQ), the limit of detection (LOD), Trueness (bias) five replicates were used to check the recovery at the levels (1, 0.5, and 0.01) mg/ and Repeatability Precision (RSD).

7. Half-life Calculation:

Half-life times ($t_{1/2}$) of recovery of chlorpyrifos-methyl and Lufenuron residues were calculated mathematically according to Moye *et al*. (1987). The dissipation kinetics of both insecticide residues were determined by plotting residue concentration against elapsed time after application and the equation of best curve fit with maximum coefficients of determination (R^2) was

determined. For dissipation of targeted insecticide in tomato, an exponential relationship was found to be applied corresponding to the general first-order kinetics equation:

$C_t = C_0 e^{-kt,}$

Where C_t represents the concentration of the pesticide residue at the time of *t*, C_0 represents the initial deposits after application, and *k* is the constant rate of pesticide disappearance per day. From this equation, the dissipation half-life periods ($t_{1/2} = ln\ (2)/k$) of the studied insecticide.

8. Statistical analysis:

Data were subjected to analysis of variance (ANOVA) followed by the least significant difference (CoStat Statistical Software, 1998-2005) The Dissipation and Persistence values were calculated according to the following formula:

Dissipation%= [(initial residue residues found at different time) /initial residue] x100

Persistence=100- Dissipation%

Results and Discussion

To confirm the safe treatment of tomato fruits in fields with the tested insecticides, low residues of insecticides should be detected, and their pre-harvest intervals (PHI), i.e. the time (in days) required for dissipation of the initial residue levels to below their corresponding maximum residue limits (MRL) (Codex Alimentarius Commission for Pesticides residues, 2013) with highly selective, sensitive, and accurate analytical methods.

1. Residual behavior of chlorpyrifos-methyl:

The method for the determination of chlorpyrifos-methyl was based on the use of reverse-phase (HPLC) analysis. The obtained data in (Table 2 and Figure 1) showed that the residue levels in/on tomato fruits treated with chlorpyrifos-methyl significantly decrease with time elapsing. The maximum amount of detected residues levels of chlorpyrifos-methyl was after two hours (Zero time) after treatment where it reached 1.13 mg kg^{-1}. One day post-treatments significant dissipation was recorded as the level of residues decreased to 0.83 mg kg^{-1} corresponding to 26.54% dissipation. The lowest number of residues was detected after one week (0.04 mg kg^{-1}) with a significantly maximum dissipation rate was recorded as 96.46%. After ten days, no residues were detected in all samples. The same pattern for dissipation was recorded for organophosphate insecticides (Abdalla *et al*., 1993 and Al-Eed, 2006). The dissipation rate of tomato fruit exhibited first order kinetics. The half-life of chlorpyrifos- methyl calculated in/on tomato fruit treated at recommended dose was 1.03 days. The pre-harvest interval (PHI), during which the residue level was below the maximum permitted residues level (MRL) (EU, 2009) was three.

2. Residual Behavior of lufenuron:

The data in (Table 2 and Figure 1) showed that the concentration of lufenuron residues detected two hours after treatment was significantly at the maximum level of 4.31 mg/kg. However, rapid dissipation levels were recorded after one-day post-treatment (58.19) where the residue level significantly decreased to 1.8 mg/kg. The residual level of lufenuron dissipated by 91.39 % on the seventh day with an average deposit of 0.37 mg kg-1. The residues of lufenuron were dissipated in/on the tomato to undetectable limits ten days after treatments. The calculated half-life time of lufenuron was 1.5days. The pre-harvest interval (PHI) of lufenuron was 8 days. The residue levels of lufenuron tended significantly to decrease with time (Fig1) and these results were in line with (Malhat *et al*., 2012).

The limit of quantification was 0.1 mg/kg and 0.01 mg/kg, far below the MRLs established for chlorpyrifos-methyl and lufenuron, respectively. The acceptable recovery range ranged between 70 and 120% while the RSD was ≤20% according to EU

method validation guide lines (SANTE/11813/2017, 2017). Mean recoveries between 90 and 111% were obtained during method development. A relative standard deviation of ≤20% is also feasible with this method (Table 2). The recovery results fully comply with the EU method validation guidelines (Table 1). Different dissipation rates of both insecticides might due to the difference between their chemical structure and physiochemical characters under the field conditions that almost affect their persistence in the field with different climatic parameters and through the different processing procedures of tomato products.

Table (1): Recoveries and relative standard deviations for chlorpyrifos-methyl and lufenuron in/on tomato fruits at various fortification levels.

Spike level (mg/kg) (n*=3)	Chlorpyrifos-methyl			Lufenuron		
	Recovery ±SD	Average%±SD	RSD%	Recovery ±SD	Average%±SD	RSD%
0.10	90±5.16		5.10	99±4.24		4.21
0.50	99±1.2	97.3±6.66	1.1	105±7.03	105±6.00	6.99
0.01	103±4.3		3.99	111±4.24		4.1

*** Number of replicates**

Table (2): Determination of chlorpyrifos-methyl and lufenuron in/on tomato fruits at different time intervals from the application.

Days after treatment	Chlorpyrifos-methyl			Lufenuron		
	Residues (mg/kg)	Dissipation %	Persistence %	Residues (mg/kg)	Dissipation %	Persistence %
Z	1.13 ^{a} ± 0.14	0.00 ^{d} ± 0.00	100.00 ^{a} ± 0.00	4.31 ^{a} ± 0.58	0.00 ^{d} ± 0.00	100.00 ^{a} ± 0.00
1	0.83 ^{b} ± 0.26	26.54 ^{c} ± 3.58	73.46 ^{b} ± 5.78	1.8 ^{b} ± 0.12	58.19 ^{c} ± 3.28	41.81 ^{b} ± 4.83
3	0.25 ^{c} ± 0.17	77.87 ^{b} ± 6.51	22.13 ^{c} ± 3.43	0.93 ^{c} ± 0.21	78.37 ^{b} ± 5.04	21.63 ^{c} ± 2.99
7	0.04 ^{d} ± 0.02	96.46 ^{a} ± 10.89	3.54 ^{d} ± 0.82	0.37 ^{d} ± 0.09	91.39 ^{a} ± 12.16	8.61 ^{d} ± 3.14
10	ND			ND		
15	ND			ND		
MRL(ppm)	1			0.4		
$t_{1/2}$ (day)	1.03			1.50		
PHI	3			8		

Z: two hours after the insecticide application (zero time). MRL: acceptable maximum residue limit Rec: Mean recovery t1/2: Half-time PHI: Pre-harvest interval ND: Not detected. LOQ limit of quantification

Values within the same row having the same letters are non-significant, p>0.05.

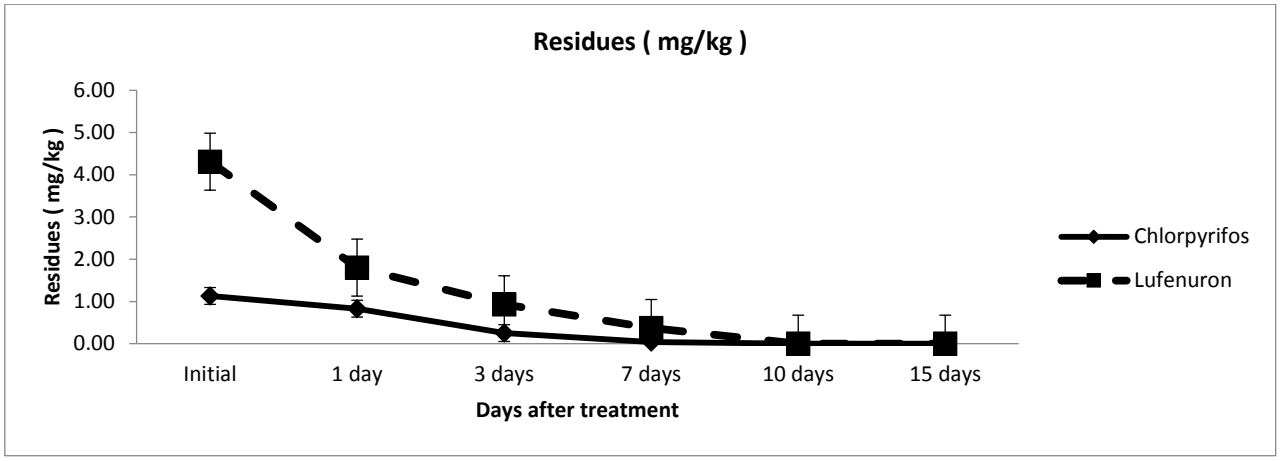


Figure (1): Decline rate of chlorpyrifos-methyl and lufenuron in/on tomato fruits after different time intervals of application.

Tomato fruits are considered one of the economic vegetables in the world. It is one of the main sources of national agricultural income, which occupies an important position in export to attract foreign exchange to the Egyptian economy. Tomato contains multi- nutrients such as vitamin A, vitamin C, potassium, phosphorus, magnesium, and calcium (USDA, 2009). *S littoralis* is one of the most known pests infesting tomato cultivation all over the year. The integrated pest management strategies aimed mainly to reach good agricultural practices including reduction of pesticide usage to reduce the most environmentally dangerous pesticides. Monitoring of pesticide residues is one of the main targets of integrated pest management to predict adequate concentrations and the pre-harvest interval should be estimated. To certify the quality of both Chlorpyrifos-methyl and Lufenuron residue results should align with standard limits. The limits of quantification (LOQ) in both insecticides were lower than MRLs established by Codex Committee and Switzerland (EU, 2008). The QuEChERS method showed good recoveries, and the analytical method allowed good separation of the tested insecticides. Based on these results of this study that residue levels will be acceptable when applied to tomatoes in Egypt due to their relatively low cost and their lack of bioaccumulation in the ecosystems, these results were in agreement with Prabhaker *et al.* (1985). Also, their lower toxicity to non-target species, very short half-life time in the tomato plant. The obtained results suggest that if tomatoes are destined to be sold as a fresh product, it may be advisable to lower the dose of the treatments with lufenuron. Also, because washing the fruit does not seem to guarantee a significant decrease of residues that were in line with (Gambacorta *et al.*, 2005).

Several concerns should be taken when using pesticides in the tomato fruits cultivations under field conditions because tomato production is intended exclusively for fresh consumption. Monitoring of pesticides is very important for defining pesticide residues. The proposed method has been validated with good recoveries and low LOQs. The MRLS of chlorpyrifos-methyl and lufenuron were lower than MRLs, fulfilling the Codex Committee and (EU) criteria. The results obtained in this study confirm that the proposed methods are easy and reliable for the determination of the analyzed Chlorpyrifos-methyl and Lufenuron insecticide residues in/on tomato fruits.

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