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RESIDUES OF LAMBDA-CYHALOTHRIN IN /ON ORANGE FRUITS AND ITS EFFECT ON SOME QUALITY PROPERTIES

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ABSTRACT: ***Pesticides are known to interfere with the biochemical processes of plants, lowering their food quality. Therefor, this study was designed to evaluate persistence of Lambda-cyhalothrin in / on fresh orange fruits and investigate its effect on fruit quality. The insecticide residues were determined using GC- ECD system. Also, the biochemical parameters were determined using spectrophotometric techniques. The results showed that a waiting period of 7days after application on orange is enough to reduce the Lambda-cyhalothrin residues to below the maximum residue limits (MRL). Lambda-cyhalothrin rapidly disappeared with half-life (t ½) of 1.6 days on orange fruits. Furthermore, the ascorbic acid content and dry matter percentage were significantly reduced however, total protein content, acidity (%), moisture(%) and total soluble solids (T.S.S,%) were significantly increased in Lambda-cyhalothrin treated compared to untreated orange fruits.***

Key words: ***Orange, Lambda-cyhalothrin, quality properties, dissipation, Half-life.***

INTRODUCTION

Pesticides are biologically active compounds used in the world for the protection of food, fiber, and human health (Malhat *et al*., 2015). After application, pesticides tend to degrade, with their residues remaining not only in the plants but also in various environmental matrices, like water, soil or sediments. Pesticides have been reported to cause toxic effects on humans, ranging from short term effects such as headaches and nausea to chronic effects like cancer, reproductive damage and endocrine disruption (Berrada *et al*., 2010; Claeys *et al*., 2011; Malhat *et al*., 2014a). Humans main exposure route is via food. Therefore, through the diet the exposure to pesticide residues is assumed to be five times more than other routes, such as air and drinking water (SurasKeet., 2009; Claeys *et al*., 2011; Malhat *et al*., 2014b). Pesticides contaminated food and associated with severe effects on the human health. (It is therefore rather important to work out strategies to enhance safe application of pesticide use. Maximum residues levels (MRLs) are useful parameters that promote food safety by restricting the concentration of pesticide residue permitted on a commodity (Berrada *et al*., 2010; Chen *et al*., 2011; Claeys *et al*., 2011).

Pyrethroids are axonic poisons that affect the nerve fiber by binding to a protein that regulates the voltage–gated sodium channel (Burr and Ray 2004). Lambda-cyhalothrin [(R,S) -α-cyano -3-phenoxy benzyl –(Z) – (1R,3R)-3-(2-chloro-3,3,3 –trifluropropenyl) -2,2-dimethyl-cyclopropane -carboxylate], has been widely used to control chewing and

sucking insect pests in field crops, beside it's wide use in public health (Davey *et al*. 1992; Roberts *et al.,* 1993; Dikshit *et al*. 2000; Mathirajan *et al*. 2000). Information about the dissipation rate of pesticide after application is a valuable tool for assessing the level of residues and estimating the pre-harvest interval (PHI) (Malhat *et al*., 2014a). The orange is one of the most important fruits in Egypt.It is liable to be attacked by a variety of insect pests, the warm temperatures and long growing season are very favorable for insects. Consequently some form of insect control is often necessary to protect the orange from severe damage.

The objectives of this work include: (1) studying the persistence of Lambda-cyhalothrin in oranges, to determine a safety period (time between pesticide application and consumption of the orange) (2) investigating the side-effects of the insecticide on the orange quality.

MATERIALS AND METHODS

Field Experiment:

The field trial was conducted in faculty of Agriculture farm, Menoufia University, Egypt. The trial was conducted in a randomized complete block design with three replicates (each = m^2). The orange trees at the fruiting stage were spraying with insecticide Lambda-cyhalothrin (10% Wp) which supplied from CHEMA company. The insecticide was applied at the recommended rate (20 cm^3/100 L. water) according to Egyptian Ministry of Agriculture. Untreated control plot was sprayed with water only. All agricultural management practices were done as usually practiced in commercial production.

Sampling:

A weight of 1kg of mature orange fruit sample was taken from each replicate at different times of 0,1,3,5,7,10 and 14 days after the insecticide spraying. The sample of zero time was taken at 1 hour after treatment. Control samples were taken at the same time the samples of different times were used to determine the insecticide residues whereas, the biochemical parameters were measured in samples obtained at 14 th day.

Chemicals:

All solvents used in this study were analytical grade and purchased Scharlau (Barcelona, Spain). Primary secondary amine (PSA, 40 mm, Bondesil), anhydrous magnesium sulfate (analytical reagent grade) was purchased from Merck (Germany) and was activated by heating at 450 ºC for six hours and kept in desiccators. Sodium Acetate Anhydrous was purchased from El Naser Pharmaceutical Chemicals Company (Egypt).

Analytical procedures for insecticide residues:

Extraction of the insecticide from samples was done by using (QuEChERS) method; this method is known as quick, easy, cheap, effective, rugged and safe method for pesticide residues in vegetables and herbs. A sub-sample (10 g) was taken to extract. After homogenization, 15 g of homogenized fruits was extracted by 15 ml acetonitrile, followed by a liquid-liquid partitioning step performed by adding 6 g anhydrous MgSO4 plus 1.5 g NaCl. After centrifugation at 3500 rpm for 10 min, the organic layer was decanted into a tube containing 300 mg primary secondary amine (PSA) sorbent plus 1.8 g anhydrous $MgSO_4$, which constituted a cleanup procedure called dispersive solid–phase extraction (dispersive–SPE). After a second shaking centrifugation step, the acetonitrile extract was transferred to auto sampler vials for con current analysis by GC-ECD system. The half–life (t½) value was calculated using equation by Moye *et al*. (1987).

Instrumental analysis:

Lambda-cyhalothrin was determined using the GC-ECD system consisted of a Hewlett Packard 6890 network GC system equipped with Ni^{63} micro electron capture detector (μ-ECD). The analyze was separated on a HP-5MS capillary column (30 m length x 0.32 mm (i.d) x 0.25 μm film thickness, Agilent Technologies, Santa Clara, CA, USA). The injector and detector temperatures were maintained at 280 and 300℃, respectively. The column oven temperature was held at 160℃ for 2 min, which was raised to 260℃ at 3℃/min and then held for 5 min. Nitrogen, was used as carrier gas flow at 4ml/min.1 μL injection volume was injected at split less mode.

Recovery studies:

The efficiency of the chromatographic analysis for determination of Lambda-cyhalothrin in orange fruit was run by adding known amount of the insecticide to untreated fruit sample before the extraction immediately. After, clean up the residue was determined as followed in the applied method. The recovery value was calculated according to the following formula:

$$\text{Recovery(\%)} = \frac{\text{mg insecticide determined/g. sample}}{\text{mg insecticide added /g. sample}} \times 100$$

The average recovery value was used to correct all obtained values of Lambda–cyhalothrin residues in orange.

Calculated half-life values: The half-life value t ½ in days were calculated according to Moye *et al*. (1987).

$$RL_{50} = \frac{Ln2}{K} = \frac{0.6932}{K}$$

$$K = \frac{1}{T_X} \times \ln \frac{a}{b_X}$$

Were:

K = Rate of decomposition Tx= Time in days

bx = Residue at × time a= Initial concentration

Biochemical analysis:

To evaluate the side effect of Lambda-cyhalothrin on the quality of orange fruits. The chemical quality parameters was carried out for treated and untreated orange fruits at 14 days after application. The dry matter and total protein content were determined according to the methods of Gabal *et al*. (1984). The total soluble solids (T.S.S.), acidity % and vitamin "C" (as L- ascorbic acid) were determined according to (AOAC, 1995).

Statistical Analysis:

The statistical analysis was performed using Costat program (version 6.31). The experimental data are presented as mean ± SD. Analysis of variance (ANOVA) of the data was conducted and means property values were separated ($P \leq 0.05$).

RESULTS AND DISCUSSION

1. Lambda-cyhalothrin residues in/on orange fruits.

1.1. Dissipation of tested insecticide.

Orange trees were sprayed at fruit stage with Lambda-cyhalothrin using a recommended field rate to study the persistence of the insecticide at different time intervals. The insecticide residues in /on orange fruits in the study period are presented in (Table 1).

The obtained data showed that the initial deposits of insecticide for orange fruits was 1.02 mg/kg, a rapid dissipation of insecticide residues was observed, 48.92% dissipation was recorded at 3rd day after application. Also, the dissipation percentage within the first week reached to 93.72% furthermore, by the end of experiment (two weeks), the fruits contained negligible residues (about 100% dissipation) for Lambda-cyhalothrin.

Table (1): Residues of Lambda-cyhalothrin in/on orange fruit at different time intervals.

Time (Days after treatment)	Residues (mg/kg)	% Dissipation
0	1.02	-
1	0.963	5.59
3	0.521	48.92
5	0.201	80.29
7	0.064	93.72
10	0.015	98.53
14	ND	*100

ND= Not detected, * =about 100%

Table (1) indicated that the residues of Lambda-cyhalothrin in/on investigated orange fruits were reduced from 0.963 mg/kg at 1st day to 0.201 mg/kg at 5 Th day from the treatment. Therefore, the dissipation percentage was increased from 5.59 to 80.29% at the same time intervals. The disappearance curve of Lambda-cyhalothrin exhibited in Fig (1) indicating that the first week after spraying was critical, showing the highest rate of dissipation at 10th day.

1.2. The half-life of tested insecticide:

The insecticide residue was negligible; hence the residue at 14th day was not detected. The half-life value of Lambda-cyhalothrin in/on orange was calculated using the first order equation:

Ct = C0e - Kt, where K = apparent rate constant, C0= initial concentration, Ct=concentration after t, and t= time in days. t½ = ln2/K =0.6932/k.

According, it was recorded the t½ Lambda-cyhalothrin in/on orange was 1.6 days (Table 2). Moreover, it was recorded that 0.064 mg/kg of Lambda-cyhalothrin was detected on orange fruit, Lambda-cyhalothrin at 7days after application, this indicate that at 7th day after application, this illustrates that a 7-days period was long enough to reduce the insecticide (Lambda-cyhalothrin) to below the permissible residue limits on orange fruits. Therefore, it was suggested that the PHI of Lambda-cyhalothrin in/on orange under the same condition is 7 days.

In addition, the literature indicated that the Codex MRLs to be 0.2mg/kg in/on citrus fruits (Anonymous, 2013).

The obtained results of this study show that Lambda-cyhalothrin residues on orange fruits are comparable to those reported in earlier studies. The residues of Lambda-cyhalothrin in grape were lost with pre-harvest intervals (PHI) of 12 and 15 days corresponding to the applications at 25 and 50 g a.i.ha^{-1} respectively. Banerjee *et al*. (2006). Malhat *et al*. (2016) found that Lambda-cyhalothrin half-life in tomato was 3.12 days and harvest time was 14 days after final application, the remaining residue of Lambda-cyhalothrin were below codex MRL Also, it was reported that Pre-harvest period of 21 days after application of pirimiphos-methyl or fenitrothion on grapes is enough to

reduce residues to below the MRLS (Radwan *et al*. 2001). The occurrence of four pesticide residues, were assessed in several fruits (orange, tangerines, water melons, and date plums) from the). Concentration of imidacloprid, carbendazin, methiocarb, and hexythiazox ranged from 0.02 to 0.75 mg/kg in 184 samples of orange, tangerines, watermelon and date plums. Nineteen samples containing methiocarb or hexythiazox residues that exceeded the maximum residue limits (Blasco *et al*. 2005).

2. Effect of Lambda-cyhalothrin on some biochemical parameters in orange fruits:

Since our knowledge about the effect of tested insecticide on the quality attributes in orange is quite meager. It is of interest to investigate the effect of this compound on moisture, dry weight, T.S.S., total protein percent, acidity percent and vitamin "C" as ascorbic acid in orange fruits (Table 3).

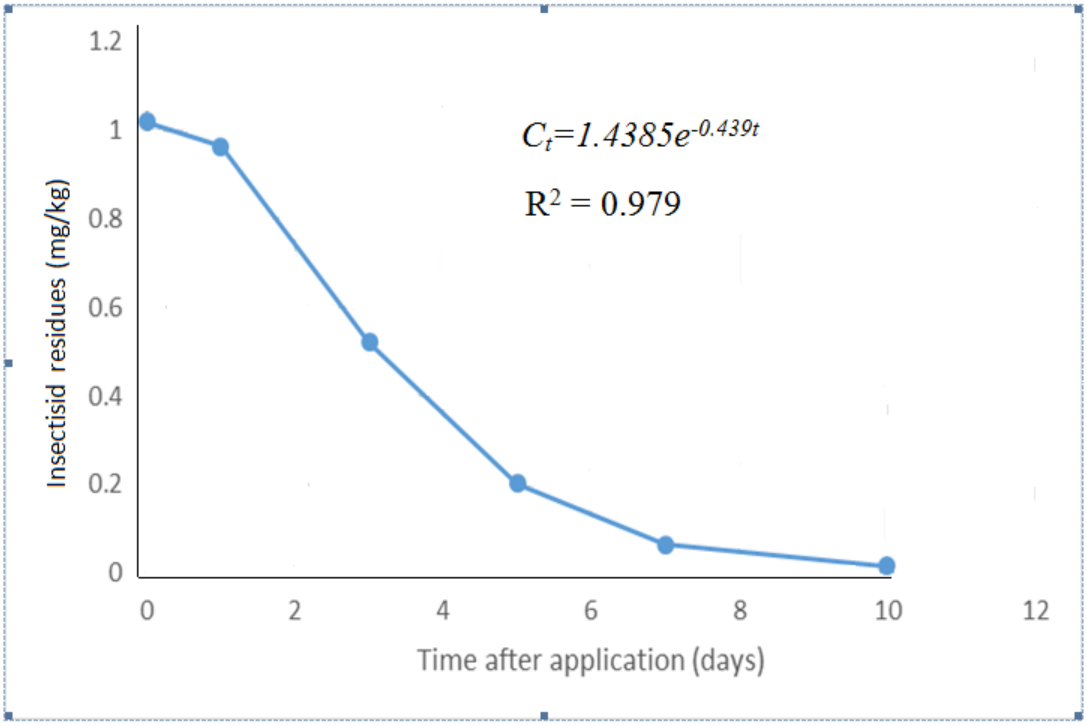

Fig (1): Disappearance curve of Lambda-cyhalothrin residues in/on orange at different time intervals.

Table (2): Calculated the half-life (t½) Codex Alimentarius (MRL) and International food standards and pre-harvest interval (PHI) of Lambda-cyhalothrin in/on orange.

t½	MRL mg/kg	PHI (Days)
1.6	Lambda-cyhalothrin	7

MRL =Maximum residue limit

Table (3): Effect of Lambda-cyhalothrin on quality parameters of orange fruits and its relative changes (RC %).

Parameters	Treatment	Control	% RC
Ascorbic Acid (mg/100g)	$41.366^{b} \pm 0.152$	$41.666^{a} \pm 0.115$	- 0.720
Total Protein (g/g100)	$0.84^{a} \pm 0.072$	$0.73^{b} \pm 0.64$	+ 15.068
Acidity%	$8.51^{a} \pm 2.224$	$8.86^{a} \pm 2.172$	- 3.950
TSS%	$8.0^{a} \pm 0.2$	$7.5^{a} \pm 0.4$	+ 6.666
Dry matter%	$11.57^{b} \pm 0.005$	$12.49^{a} \pm 0.01$	-7.36
Moisture%	$88.42^{a} \pm 0.22$	$87.51^{b} \pm 0.16$	+ 1.039

Each value in the treatment is a mean of three replicates ± SD Means followed by the same letter in each raw are not significantly different (ANOVA, LSD Test P.≤ 0.05).

2.1 Effects on moisture and dry weight:

Obtained data (Table 3) revealed that Lambda-cyhalothrin caused significant increase in moisture (88.42%) compared to with untreated samples (87.51%). In contrast, the dry weight of fruits was lower significantly (11.57%) than that in untreated fruits (12.49%). These results are in agreement with those obtained by Shalaby and Gad (2016).IT indicated that pesticides; chlorpyrifos, carbosulfan, betacyfluthrin and acetamiprid caused increase in fresh while, caused decrease in dry weigh in tomato fruits compared to with untreated plants.

2.2 Effects on total soluble solids (T.S.S.) and total protein:

Data in (Table 3) indicated that the TSS (%) and total protein content percent of orange fruits were 7.5% and 0.73 g/100g in untreated samples whereas, 8.0% and 0.84 g/100g in treated samples, respectively. Clearly, the insecticide Lambda-cyhalothrin increased significantly both TSS and total protein content in orange fruits. Similar results have been obtained by Chauhan *et al*. (2013) who reported that protein content increased in the imidacloprid treated potato samples.

2.3 Effects on acidity percentage and ascorbic acid concentration:

The obtained data revealed that Lambda-cyhalothrin significantly reduced the ascorbic acid concentration (41.366 mg/100g) compared to that in untreated samples (41.666 mg/100g).It was reported that the vitamin c(as ascorbic acid) is an antioxidant and necessary to several metabolic processes (Griffiths and Lunce 2001).

In addition, the statistical analysis indicated that in significant difference in acidity percentages was obtained between Lambda-cyhalothrin treated and untreated orange fruits. However, about 0.35% of acidity was detected as a difference between treated and untreated samples. Chauhan *et al*. (2013) reported that pesticides are known to interfere with the biochemical processes of plants, lowering their food quality. However, Gad and Hassan (2013) found that cobalt significantly increased total protein, total soluble solids and vitamin" C " compared with control. In fact, increasing of biochemical constituents improve the quality of fruits.

Conclusion:

It could be concluded that the dissipation rate of insecticide Lambda-cyhalothrin in/on orange fruits was rapid. Consequently, the dissipation percentage within the first week after spraying reached to 93.72%. Furthermore, the t½ value of the tested insecticide was 1.6 days. In addition, it could be suggested that the PHI of Lambda-cyhalothrin in/on orange fruits is 7days. Moreover, depends on the investigation of the insecticide side effects on the biochemical parameters, the tested insecticide in general is safe to apply on the orange fruits.

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متبقيات مبيد اللامبادا سيهالوثرين علي وداخل ثمار البرتقال وتأثيراته على بعض خصائص الجوده

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الملخص العربى:

تم دراسه ثبات متبقيات مبيد لامبادا سيهالوثرين (مبيد حشري ، مجموعه البيرثرويد) علي وداخل ثمار البرتقال وعلاقة ذلك بالتأثير علي بعض صفات جودة الثمار. أوضحت النتائج أن متبقيات المبيد إنخفضت خلال الأسبوع الأول بعد الرش إلي مستوي أقل من القيم المرجعية للحدود المسموح بها وكذلك وجد أن فترة نصف العمر للمبيد المختبر علي البرتقال هي 1.6 يوم وعلي ذلك يمكن القول أن فترة ماقبل قطف ثمار البرتقال بعد الرش هي 7 ايام. وبدراسه تأثيرمتبقيات مبيد لامباداسيهالوثرين علي صفات جودة ثمار البرتقال اتضح أن المعامله بالمبيد قد أدت إلي نقص معنوي في تركيز حمض الأسكوربيك وأيضا النسبة المئوية للماده الجافة. وعلي العكس من ذلك فقد ظهرت زياده معنوية في محتوي البروتين الكلي ، النسبه المئويه للحموضة ،النسبة المئوية للرطوبة وكذلك النسبة المئوية للمواد الصلبة الذائبة الكلية وذلك بالمقارنة مع ثمار غير معاملة بالمبيد. وعموما فهذه النتائج تدل علي أن مبيد لامباداسيهالوثرين مناسب للإستخدام علي أشجار البرتقال مع الأخذ في الإعتبار فترة ماقبل قطف الثمار.

أسماء السادة المحكمين

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