J. Plant Prot. and Path., Mansoura Univ., Vol. 10 (5): 281- 287, 2019

Degradation of Azoxystrobin, Lufenuron and Fenpyroximate Residues in/on Grape Fruits under Field Conditions.

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ABSTRACT

Fungal infection and pests attack are very serious problems that facing grapes growers in Egypt. Fungicide azoxystrobin, (Azostar® 25%SC), insecticide lufenuron, (Cymax® 5%EC) and acaricide fenpyroximate (Ortus super® 5%EC) are the most common pesticides used to control such pests (downy mildew, grape fruit worm *Eudemis botrana* and red spider mite, respectively) in Egypt. The present study was carried out to assess persistence Vs. degradation behavior of the mentioned pesticides when sprayed on foliage of grape plants under field conditions during fruiting stage at the recommended and double the recommended rates of application during the season of 2017 in Adam village, El-Nobaria district, El-Behaira Governorate, Egypt. Fruit samples were collected randomly, two hours (initial time) and 1, 3, 7, 14 and 21 days after application. Samples of treated and untreated (control) grape fruits were prepared, extracted, cleaned-up by QuEChERS analytical method before quantification by high performance liquid chromatography with diode array detector (HPLC-DAD) and gas chromatography extended by electron capture detector (GC). The corresponding values for dissipation of the mentioned pesticides initial deposits, degradation percentages of residues, Residual Lifetime 50% (RL_{50}), Residual Lifetime 90% (RL_{90}) and pre-harvest intervals (PHIs) of the tested pesticides were determined. Results revealed that grape fruits remained higher initial amounts by (2.93 and 3.97), (0.82 and 1.14) and (1.74 and 1.94) mg kg^{-1} azoxystrobin, lufenuron and fenpyroximate for both doses, respectively. As for RL_{50}, RL_{90} and PHIs, values showed (3.22, 1.73, 1.85 days) and (9.71, 4.22 and 6.31 days) and (5, 6.89, 4.05 days) when the recommended doses were applied and also, (3.80, 10.4 and 6.85 days) and (1.91, 5.02 and 7.12 days) and (2.58, 6.09 and 5.24 days) at the double recommended rates of application, in/on grape, respectively. In general, azoxystrobin, lufenuron and fenpyroximate residue in/on grape fruits had low persistence. In addition, the grape fruits could be consumed safely after 5, 6.89, 4.05 days, respectively from treating by the recommended rate of azoxystrobin, lufenuron and fenpyroximate when compared by the Maximum Residue Limits (MRLs) of the Codex Alimentarius Commission or the European Union (2, 0.01 and 0.01 mg kg^{-1}), respectively.

Keywords: Pesticides Residues, Behavior, Degradation, Persistence, Azoxystrobin, Lufenuron, Fenpyroximate, Grapes

INTRODUCTION

Grape (*Vitis vinifera* L.) is a power house of antioxidants; it contains high levels of phytonutrients that help in maintaining heart health and preventing cancers. Grape is one of the most common types of fruits wide spread in the world. According to the FAOSTAT (2016) 71% of the grape around the world is produced for wine, 27% as table fruits and about 2% as dried fruits. Grapes are normally attacked by mites such as red spider or grape fruit worm (*Eudemis botrana*) or fungi such as downy mildew (*Plasmopara viticola),* gray mould (*Botrytis cinerea*), anthracnose (*Elsinoe ampelina*) and black rot (*Aspergillus niger*). Fruits infection reduces both quality and quantity of fruit yield and vine. Pesticides are the main way to reduce the damage of these pathogenic pests. Azoxystrobin, lufenuron and fenpyroximate are applied to control pests that infect grapes worldwide (Teixeira *et al.,* 2004 and Likas *et al.,* 2007).

Azoxystrobin, a β-methacrylate compound, is a systemic fungicide that inhibits electron transport in fungi, a systematic analog of the fungal metabolites of the strobilurins and oudemansins (Schirra *et al.,* 2002). While, lufenuron is a benzoylphenylurea insecticide that inhibits chitin synthesis in the cuticle layer of the insects (Tomlin, 2000). On the other hand, fenpyroximate is one of the phenoxypyrazole group acaricide with selective activity on phytophagous species (Hamaguchi *et al*. 1990). Relatively few data are available regarding fate of fenpyroximate under field conditions (Naik *et al*., 2009; Sherif *et al*., 2012).

These pesticides are registered in pest control programs in Egypt and applied at specific concentrations that recommended by the Egyptian Ministry of Agriculture and Land Reclamation so as not to exceed the limits that cause harm to human health. The frequent use of pesticides has increased their accumulation within edible parts of plant. Pesticide residues in food commodities should not exceed the Maximum Residue Limits (MRLs) of the International Codex Committee Standard which characterized by a low mammalian toxicity (Codex Alimentarius Commission, 2010). Residues remain in food may pose potential health hazards to consumers, field dissipation studies on pesticide persistence in foodstuffs and studies of pesticide residue behavior in agricultural fields are needed (Malhat *et al.,* 2014). Recently, the production of grapes required for export has been considerable emphasis (Mansour, 2005). However, there are many concerns that hinder the export of grapes due to pesticide residues and adequate monitoring programs (EU, 2007). Exceeded MRLs are the indicators for any violation of the permissible limits (Nasreddine and Parent-Massin, 2002). Over doses of pesticides in agriculture may be hazardous to human, animal and plant health (Mansour, 2007).

Limited data are available on the dissipation rates of the mentioned pesticides under field conditions. Hence, the present study aimed to determine the residues of azoxystrobin, Lufenuron and fenpyroximate in/on grape fruits when both the recommended and double the recommended doses were applied, detect the initial deposits, the percent of residues degradation (RL_{50} and RL_{90}) as well as calculate the pre-harvest intervals (PHIs) for the previous pesticides to protect public health and expand the local and global market.

MATERIALS AND METHODS

Tested pesticides and application rates:

Azoxystrobin, (Azostar® 25 % SC; methyl (E) - 2- { 2- [6-(2- cyanophenoxy) pyrimidin- 4 -yloxy] phenyl}-3-methoxyacrylate), lufenuron, (Cymax® 5%EC; (RS) 1 - [2,5 - dicloro - 4- (1,1,2,3,3,3- hexafluoropropoxy)phenyl]-3-(2,6-difluorobenzoyl) urea and fenpyroximate, (Ortus super® 5%EC; tert-butyl (E)-alpha-(1,3)- dimethyl-5-phenoxy-1H-pyrazol-4-yl methylene amino-oxy) -para-toluate) were purchased from Star Chemical Company, Giza Governorate, Egypt.

Field applications:

The experiment was carried out in open field eighteen plots ($200m^2$/each plot; 20x10 m) at Adam village, El-Nobaria district, El-Behaira Governorate, Egypt. Two rates of the azoxystrobin, lufenuron and fenpyroximate pesticides; recommended doses (40 cm^3, 50 cm^3 and $50cm^3$ / 100 L water) and double recommended doses ($80cm^3$, $100cm^3$ and $100cm^3$ / 100 L water) respectively, were applied on grape plants (Crimson seedless *cv*.) at May 15th, 2017 (when the first symptoms of downy mildew and smooth worm insect pest infections were appeared or five adult spiders were seen on the leaves lower surfaces. Pesticides were sprayed using snake sprayer fit with one nozzle. Trees of one plot were sprayed with water instead of chemicals as check control and for recovery target. Experiment was arranged in a complete randomized block design.

Fruit samples:

Three replicates of treated and untreated grape fruit samples were randomly taken at initial time; two hours and also 1, 3, 7, 14 and 21days after applications. Samples were frozen immediately at -20°C till pesticides residue analysis.

Extraction and clean up:

Pesticides were extracted and cleaned up from grape fruit samples according to the method stated by QuEChERS (European Union Reference Laboratory in Pesticide residues analysis pesticide Residue; 2013) as well as (Anastassiades *et al.,* 2003).

Determination of lufenuron and fenpyroximate residues

Residues of lufenuron and fenpyroximate were determined using high performance liquid chromatograph (Agilent 1100 series HPLC system) with photo diode array detector and chromatographic column (150 x 4.6 mm id, x 5 µm film thickness OSD). Flow rate of mobile phase: Acetonitrile (35%) + Methanol (65%) was one ml per minute and injection volume was 20 µl. Detection wave lengths 230 nm and 210 nm with retention time 2.87 min and 3.26 min were set for lufenuron and Fenpyroximate, respectively.

Determination of Azoxystrobin residue

Residue of Azoxystrobin was determined by gas chromatograph (Agilent series 6890N), extended by electron capture detector. The column was PAS-5, (30m x 0.25mm x 0.25 µm film thickness) and the injection port temperature was 290°C, initial temperatures 220°C for 2 min, 10 min, up to 280°C and the detector temperature was 300°C. The carrier gas was nitrogen at a flow rate of 3 ml/min with retention time 6.24 min.

Recovery of field experiment samples:

Four levels (0.5, 1, 2 and 2.5 µg) of azoxystrobin, lufenuron and fenpyroximate were added to one gram of control fruit samples to assess the percentages of recovery. Extraction and clean-up processes were performed and determined using the chromatographic method as described before. The average recovery percentages in grape fruits for the target pesticides were 91.11^a, 89.98^b, 92.48^c and 90.52^d % Azoxystrobin / fruit and 87.76^a, 88.14^b, 90.18^c and 91.09^d % lufenuron / fruit and 84.19^a, 89.87^b, 90.26^c and 93.98^d % fenpyroximate / fruit for the four tested levels, respectively (Table 1). All obtained results in this study were corrected according to the recovery percentages.

The degradation constant (K) and degradation periods (RL_{50} and RL_{90}) of azoxystrobin, lufenuron and fenpyroximate levels were calculated as follows:

Rate of degradation (K) = 2.303 × slope

The half-life period RL_{50} = 0.693/K (Gomaa and Belal, 1975).

Table 1. Recovery percentages (%) of azoxystrobin, lufenuron and Fenpyroximate from spiked samples of grape fruits.

Spiked Samples	Grape fruits			
Azoxystrobin	91.11^a	89.98^b	92.48^c	90.52^d
Lufenuron	87.76^a	88.14^b	90.18^c	91.09^d
Fenpyroximate	84.19^a	89.87^b	90.26^c	93.98^d

Values in the table represent the average of three replicates.
Spiked sample levels (a, b, c and d represent 0.5, 1, 2 and 2.5 µg gm^{-1}, respectively).

RESULTS AND DISCUSSION

1. Residue of azoxystrobin in/on grape fruits

Residue and degradation percentage of azoxystrobin in/on grape fruits at the recommended and double the recommended rates were illustrated in Table (2) and Figures (1 and 2). The initial deposits, which remained in/on unwashed grape fruits; two hours after application, were found to be 2.93 and 3.97 mg kg^{-1}. These amounts decreased to 2.21 and 3.48 mg kg^{-1} one day after the application indicating degradation percentages of 24.57 and 12.34%. Residues of azoxystrobin in/on grape fruits was gradually decreased to 1.98, 0.47, 0.17 and 0.02 and 2.34, 0.78, 0.61 and 0.02 mg kg^{-1} for recommended and double recommended rates with corresponding degradation percentages of 32.42, 83.95, 94.19 and 99.31 and 41.05, 80.35, 84.63 and 99.49% for recommended and double recommended rates after 3, 7, 14 and 21 days of application, respectively. The degradation of pesticide residues in/on edible parts of plants were varied according to the plant species, climatic conditions, type of application, dosages, time between applications and harvest date (Khay *et al.* 2008). Estimated measurements represented by the regression lines, *i.e.* slope, degradation constant (K) and RL_{50}, RL_{90}, showed decrease in the persistence behavior of the tested fungicide (Table 2). The azoxystrobin degradation constant (K) values were -0.476 and -0.641 in/on grape fruits. As for RL_{50}, RL_{90} and PHIs values, azoxystrobin recorded (3.22 and 3.80), (9.71 and 10.40) and (5.00 and 6.85) days in/on grape fruits. These results indicated that the different rates of azoxystrobin fungicide have the same degradation behavior in/on grape

fruits. In the present study, the low residue half-life for azoxystrobin fungicide in/on grape fruits was 3.22 days, concerning health aspects; it was noticed that this value was less than the maximum residue limit (MRL) of azoxystrobin residues in/on grape according to Codex Alimentarius Commission (2009) which was 2mg kg^{-1}. Consequently, grape fruits can be consumed safely after 5 days when the recommended rate of azoxystrobin was applied. These results were supported by Chen *et al.* (2004) who found the deposits of azoxystrobin residue on apple at 12 days after application was 0.15 ppm. The initial deposits of azoxystrobin (Amistar 25% SC) in/on grape fruits treated with recommended dose was 1.86 ppm then residues declined to 0.12 ppm on fruit after 10 days of application, the corresponding values for dissipation, half-life (t0.5) and PHI were 93.55%, 2.8 days and 6 days after application of (Montasser and Mahmoud, 2009). Also, these data are in agreement with those obtained by Bursi *et al*. (2007) who cited that the residues of azoxystrobin in cucumber samples collected 7 days after treatment were below the MRL. Based on the present study, when the recommended rate of azoxystrobin was applied on grape, the levels of residues in/on fruit samples after 5 days was clearly below the established MRL value of Codex Alimentarius Commission (2009) causing no problems in terms of food safety to avoid health hazards and facilitate the national and international trade.

Table 2. Residues degradation (%) and persistence (%) of azoxystrobin detected in/on grape fruits.

	The recommended dose			Double The recommended dose		
Days after application	**Residues mg kg^{-1}**	**Degradation %**	**Days after application**	**Residues mg kg^{-1}**	**Degradation %**	**Days after application**
Initial (2 hrs)	2.93	–	100	3.97	–	100
1	2.21	24.57	75.42	3.48	12.34	87.65
3	1.98	32.42	67.57	2.34	41.05	58.94
7	0.47	83.95	16.04	0.78	80.35	19.64
14	0.17	94.19	5.80	0.61	84.63	15.36
21	0.02	99.31	0.68	0.02	99.49	0.51
K		-0.476			-0.641	
RL_{50}		3.22			3.80	
RL_{90}		9.71			10.4	
PHI		5			6.85	
MRL	2mg kg^{-1} Codex, 2009					

ND*: Not detectable (LOD): Limit of detection 0.02 mg kg^{-1}. K= ln(2)/t1/2

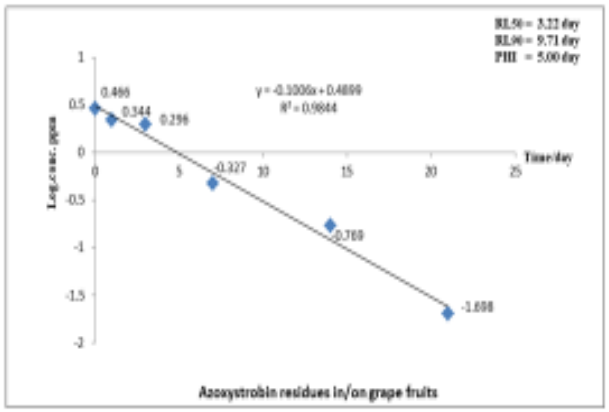

Fig. 1. Log. Residue – day regression line of azoxystrobin at the recommended dose detected in/on grape fruits.

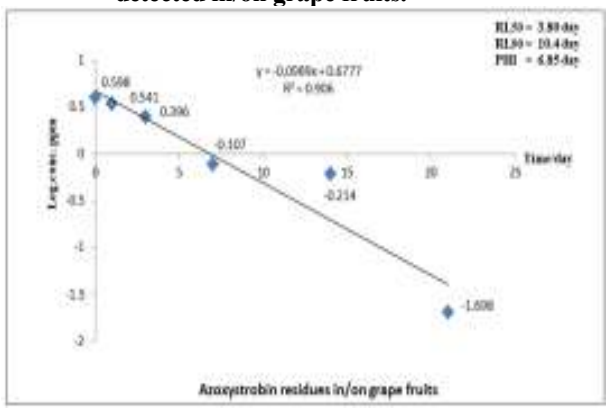

Fig. 2. Log. Residue – day regression line of azoxystrobin at the double recommended dose detected in/on grape fruits.

2. Residues of lufenuron in/on grape fruits.

Residues and degradation percentage of lufenuron in/on grape fruits were illustrated in Table (3) and Figures (3 and 4) at the recommended and double recommended rates, respectively. The initial residue deposits in/on grape fruits, two hours after application, were found to be 0.82 and 1.14 mg kg^{-1}, these amounts decreased to 0.71 and 0.92 mg kg^{-1} one day after application indicating degradation percentages of 13.41 and 16.92%. Residues of lufenuron in/on grape fruits were gradually decreased to 0.04 and 0.02 mg kg^{-1} and 0.49 and 0.04 mg kg^{-1} for recommended and double recommended rates corresponding degradation percentages of 95.12 and 97.56 and also, 57.01 and 96.49% for recommended and double recommended rates after 3 and 7 days of application, respectively. On the other hand, lufenuron residues were not detected after 14 and 21 days of application with both doses. Estimated measurements represented by the regression lines, *i.e.* slope, degradation constant (K) and RL_{50}, RL_{90}, showed gradually decrease in the persistence behavior of the tested insecticide (Table 3). The lufenuron degradation constant (K) values were 0.1450 and 0.046 in/on grape fruits. As for RL_{50}, RL_{90} and PHIs values, lufenuron showed (1.73 and 1.91), (4.22 and 5.02) and (6.89 and 7.12) days in/on grape fruits. These results indicated that the different rates of lufenuron insecticide have the same degradation behavior in/on grape fruits. In the present study, the low residue half-life for lufenuron insecticide in/on grape fruits was 6.89 days, concerning health aspects; it was noticed that this value was less than the maximum residue limit (MRL) of lufenuron residues in/on grape according to EU (2005) which was 0.01mg kg^{-1}. So, the fruits of grape can be consumed safely after

approximately 7 days of application by the recommended rate. These results are in agreement with Montasser and Mahmoud (2009) who found that the initial concentration of lufenuron on grape fruits was 0.58 ppm after one hour of application with reduction in the residues level to 0.01 ppm after 6 days and also, lufenuron wasn't detected in samples after 15 and 21days of application. They results showed that lufenuron residues were decreased rapidly by time on fruits with half life time ($t_{0.5}$) value of lufenuron was 1.7 days. Also, agreed with Lo´pez- Lo´pez, *et al.* (2003) who found that PHI value was 7 days for grapes treated with lufenuron with recommended rate. These results were closed to Hassan *et al.* (2013) who showed that the initial deposit, and $t_{0.5}$ of lufenuron in grape fruit were observed to be 1.85mg kg^{-1} and 2.79 days at single application recommended rate with reduction in lufenuron residue to 1.76mg kg^{-1} one day after treatment and 4.86% loss of the initial deposits. The MRL value of lufenuron at recommended rate on grapes according to EU (2005) was 0.01mg kg-1. Based on the present study, when the recommended rate of lufenuron was applied on grape, the levels of residues in/on fruit samples after 6.89 days was clearly below the established MRL value of EU (2005) indicating food safety that avoid health hazards and facilitate the national and international trade.

Table 3. Residues degradation (%) and persistence (%) of lufenuron in/on grape fruits.

	The recommended dose			Double The recommended dose		
Days after application	**Residues mg kg^{-1}**	**Degradation %**	**Days after application**	**Residues mg kg^{-1}**	**Degradation %**	**Days after application**
Initial (2 hrs)	0.82	–	100	1.14	–	100
1	0.71	13.41	86.59	0.92	19.29	80.70
3	0.04	95.12	4.87	0.49	57.01	42.98
7	0.02	97.56	2.43	0.04	96.49	3.51
14	ND*	100	00	ND*	100	00
21	ND*	100	00	ND*	100	00
K		0.1450			0.046	
RL_{50}		1.73			1.91	
RL_{90}		4.22			5.02	
PHI		6.89			7.12	
MRL	0.01mg kg^{-1} EU 2005					

ND*: Not detectable Limit of detection (LOD) 0.02 mg kg^{-1}. K= ln(2)/t1/2

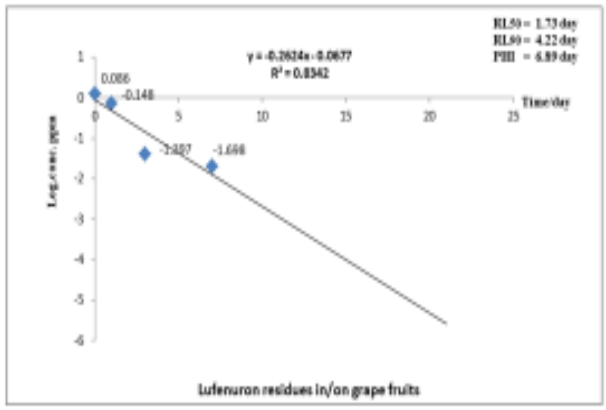

Fig. 3. Log. Residue – day regression line of lufenuron at the recommended dose detected in/on grape fruits.

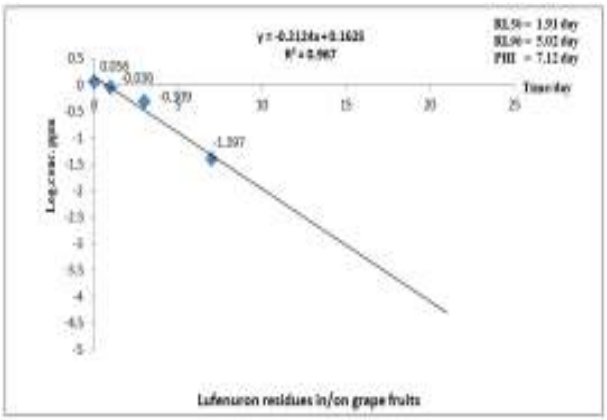

Fig. 4. Log. Residue – day regression line of lufenuron at the double recommended dose detected in/on grape fruits.

3. Residues of fenpyroximate in/on grape fruits.

Residues and degradation percentage of fenpyroximate in/on grape fruits were illustrated in Table (4) and Figures (5 and 6) at the recommended and double recommended rates, respectively. The initial residue deposits, which remained in/on unwashed grape fruits, two hours after application were found to be 1.74 and 1.94 mg kg^{-1}. These amounts decreased to 1.15 and 1.17 mg kg^{-1} one day after the application indicating degradation percentages of 33.90 and 39.69 %. Residues of fenpyroximate in/on grape fruits were gradually decreased to 0.56, 0.05 and not detected (ND) and also, 0.57, 0.07 and 0.02 mg kg^{-1} for recommended and double recommended) rates corresponding degradation percentages of 67.81 and 97.12 and 100% and also, 70.62, 96.39 and 98.96% for recommended and double recommended rates after 3, 7 and 14 days of application, respectively, while fenpyroximate residues were not detected after 21 days of application with both doses. Estimated measurements represented by the regression lines, *i.e.* slope, degradation constant (K) and RL_{50}, RL_{90}, showed decrease in the persistence behavior of the tested acaricide (Table 4). The fenpyroximate degradation constant (K) values were 0.077 and 0.254 in/on grape fruits. As for RL_{50}, RL_{90} and PHIs values, fenpyroximate showed (1.85 and 2.58), (6.31 and 6.09) and (4.05 and 5.24) days in/on grape fruits. These results indicated that the different rates of fenpyroximate acaricide have the same degradation behavior in/on grape fruits. In the present study, the low residue half-life for fenpyroximate acaricide in/on grape fruits was 4 days, concerning health aspects; It was noticed that this value was less than the prescribed maximum residue limit (MRL) of fenpyroximate residues

in/on grape according to Codex Alimentarius Commission (2018) which was 0.1 mg kg^{-1}. Consequently, grape fruits can be consumed safely after 4.05 days of treatment by recommended rate of application was used.

These data was agreed with Sherif *et al.* (2012) who reported that the initial deposit of fenpyroximate residue on grape fruits was 0.49 mg kg^{-1} after 7 days of application then degraded to 0.08 mg kg^{-1} (83.6%). They added that PHI and half-life were 3 days and 1.56 days for grape fruits when fenpyroximate applied at the recommended dose. Also, Malhat *et al.* (2014) reported that fenpyroximate residue in grapes was declined from 0.5 mg kg^{-1} (2 h after application) to 0.05 mg kg^{-1} (15 days after application) at the recommended dose and from 0.998 to 0.06 mg kg^{-1} at double the recommended dose, which indicated that 83.3% and 90% reduction in fenpyroximate residue occurred in grapes at the two doses, respectively, The half-lives ($t_{0.5}$) for both treatments were approximately 3.5 days for fenpyroximate on grapes in open field. Their founding's were below the MRL on day 10, 0.1 mg kg^{-1} (Codex Alimentarius Commission, 2011).

In general, there are many characteristics factors influence pesticides persistence Vs. degradation behavior such as overall stability either parent compound or metabolites, volatility, solubility, formulation and method and site of application (Cabras *et al*., 1989). Furthermore, several environmental factors as temperature, precipitation, humidity and air movement (Gennari *et al*., 1985) and plant properties factors as plant species, the nature of the harvested crop, structure of cuticle, stage and rate of growth, treated plant surface and the general condition around plant (Khay *et al*., 2008; Tewary *et al*., 2005; Malhat 2012; Malhat *et al*., 2014).

Table 4. Residues degradation (%) and persistence (%) of fenpyroximate in/on grape fruits.

	The recommended dose			Double The recommended dose		
Days after application	**Residues mg kg^{-1}**	**Degradation %**	**Persistence %**	**Residues mg kg^{-1}**	**Degradation %**	**Persistence %**
Initial (2 hrs)	1.74	–	100	1.94	–	100
1	1.15	33.90	66.09	1.17	39.69	60.30
3	0.56	67.81	32.18	0.57	70.62	29.38
7	0.05	97.12	2.87	0.07	96.39	3.60
14	ND*	100	0.00	0.02	98.96	1.03
21	ND*	100	0.00	ND*	100	0.00
K		0.077			0.254	
RL_{50}		1.85			2.58	
RL_{90}		6.31			6.09	
PHI		4.05			5.24	
MRL	0.1mg kg^{-1} (Codex, 2018)					

ND*: Not detectable Limit of detection (LOD) 0.02 mg kg^{-1}. K= ln(2)/t1/2

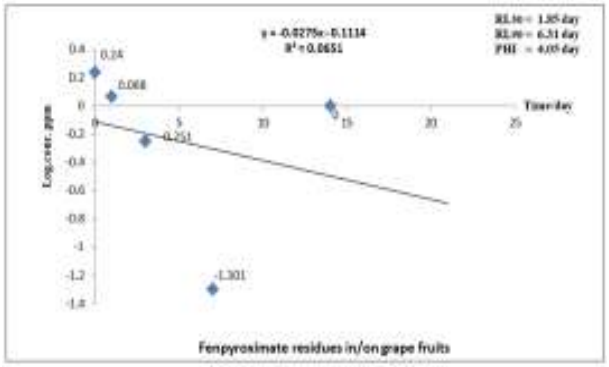

Fig. 5. Log. Residue – day regression line of fenpyroximate at the recommended dose detected in/on grape fruits.

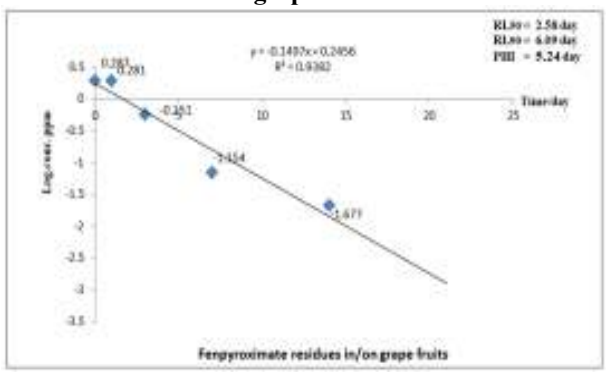

Fig. 6. Log. Residue – day regression line of fenpyroximate at the double recommended dose detected in/on grape fruits.

CONCLUSION

Dissipation study showed that the half-life ($t_{0.5}$) of azoxystrobin, lufenuron and fenpyroximate on grape fruits was approximately (3.22 and 3.80), (1.73 and 1.91) and (1.85 and 2.58) days, at both recommended and twice the recommended dosage respectively, in/on grape fruits in open field.

The present study revealed that after PHIs were determined, it was noted that azoxystrobin, lufenuron and fenpyroximate did not exceed the recommended MRLs for grape fruits (2, 0.01 and 0.1 mg kg^{-1}) at 5, 6.89 and 4.05 days. Therefore, it might be recommended that growers harvest grape after 5, 7 and 4 days, respectively, after spraying mentioned pesticides in accordance with good agricultural practices for safety and quality fruits.

Finally, studies need to be carried out in open-field due to the dissimilar behavior of all pesticides applied in different ways.

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هدم متبقيات مبيدات الأزوكسيستروبين واللوفنيورون والفينبيروكسيمات في/على ثمار العنب تحت الظروف الحقلية

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يهدف هذا العمل إلى دراسة هدم متبقيات مبيدات الأزوكسيستروبين، اللوفنيورون، والفينبيروكسيمات في/على ثمار عنب المائدة تحت الظروف الحقلية شائعة الإستخدام فى مصرحيث تم تقدير معايير الميل، ثابت الإنهيار (K)، معدلات الإنهيار لـ 50% (RL_{50})، 90% (RL_{90})، تحديد فترات ما قبل الحصاد (PHIs). أجريت الدراسة بقرية آدم، النوبارية، محافظة البحيرة أثناء موسم 2017. أخذت العينات بعد تطبيق المبيدات المختبرة على المجموع الخضرى أثناء فترة الإثمار وذلك بعد ساعتين، 1، 3، 7، 14، 21 يوماً من الرش بالجرعة الموصى بها وضعفها. تم التقدير باستخدام أجهزة GC لمبيد الأزوكسيستروبين و HPLC لمبيدى اللوفنيورون، والفينبيروكسيمات. دلت النتائج المتحصل عليها أن المتبقيات الأولية المتواجدة بعد ساعتين من المعاملة بالرش كانت (2,93 و 3,97) و (0,82 و 1,14) و (1,74 و 1,94) جزء فى المليون على الترتيب للجرعة الموصى بها وضعف الجرعة. ودلت مستويات المتبقيات على انخفاض متبقيات الأزوكسيستروبين في/ على ثمار العنب تدريجياً الى 2,21، 1,98، 0,47, 0,17، 0,02 جزءاً في المليون و3,48, 2,34, 0,78, 0,61, 0,02 جزءاً في المليون بعد 1، 3، 7، 14، 21 يوم على الترتيب للجرعة الموصى بها وضعف الجرعة. كما إنخفض متبقي المبيد الحشري اللوفنيورون تدريجياً الى 0,71، 0,04، 0,024 جزءاً في المليون و 0,92، 0,49 ، 0,04 بعد 1، 3، 7 يوم على الترتيب للجرعة الموصى بها وضعف الجرعة فى حين أن متبقى مبيد اللوفينورون بعد 14، 21 يوم من إجراء عملية الرش كان تحت حدود التقدير المسموحة لكلا الجرعتين وأيضاً فقد انخفض متبقي المبيد الأكاروسى الفينبيروكسيمات تدريجياً الى 1,15، 0,56، 0,05 جزءاً في المليون و 1,17، 0,57 ، 0,07 جزءاً في المليون بعد 1، 3، 7 يوم من المعاملة على الترتيب للجرعة الموصى بها وضعف الجرعة فى حين أن متبقى مبيد الفينبيروكسيمات بعد 14 يوم انخفض الى 0,02 و كان تحت حدود التقدير المسموحة بعد21 يوم من إجراء عملية الرش بالجرعة الموصى بها, فى حين أن متبقى مبيد الفينبيروكسيمات بعد 14، 21 يوم من إجراء عملية الرش فى حالة ضعف الجرعة كان تحت حدود التقدير المسموحة. ومن ناحية أخرى فقد أثبتت نتائج المعايير المدروسة والمتمثلة في الميل، وثابت الإنهيار (K) ومعدلات الإنهيار لـ 50% (RL_{50})، 90% (RL_{90}) تشابه نتائج التحلل الإنهياري وسلوك ثبات المبيدات موضع الدراسة في/على ثمار العنب وكانت نتائج قيم RL_{50}, RL_{90}، PHIs لمبيد الأزوكسيستروبين (3,22، 9,71، 5 يوم) و مبيد اللوفنيورون (1,73، 4,22، 6,89 يوم) و مبيد الفينبيروكسيمات (1,85، 6,31, 4,05 يوم) بالنسبة للجرعة الموصى بها على الترتيب، بينما قيم RL_{50}, RL_{90}، PHIs لمبيد الأزوكسيستروبين (3,80، 10,4، 6,85 يوم) و مبيد اللوفنيورون (1,91، 5,02، 7,12) و مبيد الفينبيروكسيمات (2,58، 6,09، 5,24 يوم) على الترتيب بالنسبة لضعف الجرعة الموصى بها. وتدل هذه النتائج على أنه من الرغم من إنخفاض قيم فترات نصف العمر لبقايا مبيدات الأزوكسيستروبين و اللوفنيورون و الفينبيروكسيمات في/على ثمار عنب المائدة 3,22، 1,73، 1,85 يوم فإنه يمكن الإستهلاك الآمن للثمار بعد 5، 7، 4 يوم من المعاملة على الترتيب، وذلك بالإعتماد على القيم القصوى المسموح بها من المتبقيات في/على ثمار العنب (2، 0,01، 0,1 جزء فى المليون وفقاً لهيئة الدستور الغذائى و منظمة الإتحاد الأوروبى.