J. of Plant Protection and Pathology, Mansoura Univ., Vol. 11 (7):327-332, 2020

Journal of Plant Protection and Pathology

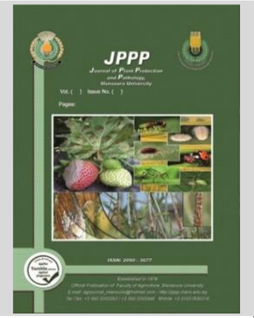
Journal homepage: www.jppp.mans.edu.eg
Available online at: www. jppp.journals.ekb.eg

Dissipation of some Pesticide Residues in Tomato (*Lucopersicon esculentum* L.) Fruits Using QuECHERS Methodology under the Egyptian Field Conditions

Cross Mark

Reham M. Abdelfatah*; A. A. Saleh; R. A. Elgohary Laila and S. E. Negm

Pesticides Dept., Faculty of Agriculture, Mansoura University, Egypt



ABSTRACT

The residual levels of abamectin, spinosad, and acetamipride were determined by HPLC-DAD moreover, penconazole, diniconazole and fipronil determined by using GC-ECD in tomato fruit under field conditions using QuEChERS methodology (Quick, Easy, Cheap, Effective, Rugged and Safe). The dissipation half-life time of abamectin, spinosad, acetamipride, diniconazole, penconazole and fipronil residues in tomato fruits were 3.91, 0.36, 1.19, 0.71, 4.19 and 1.78 days, respectively. Depending on the maximum residue limits (MRL), the pre-harvest interval (PHI) of abamectin, spinosad, acetamipride, diniconazole, penconazole, and fipronil were 10, 1, 1, 10,5 and 21daysafter the application, respectively. This recommended that the use of tomato fruits treated with these pesticides were safe for consumption after these intervals.

Keywords: Pesticides, half-lives, tomato, dissipation, residues.

INTRODUCTION

Pesticides have a significant role to increase agricultural production; however, their wide use has made environmental problems and health hazards to human.

Tomato (*Solanum lycopersicum* L.) is one of the most important and popular vegetables cultivated in the world (Doraiset *al.*, 2008). Egypt almost produces seven million tons of tomato each year (Malhatet *al.*, 2012), and considered the fifth country among tomato producers around the world (FAO, 2011). Tomato considered a basic element of the human diet in several countries in the world as, it is used raw and cooked.

In Egypt, tomato crop is attacked by a lot of insects, fungi, virus, bacteria, and mites. Therefore, more than 100 synthetic and natural pesticides from different chemical groups have been recommended to control different pests and pathogens (APC, 2010). Thus, the residue analysis of pesticides in tomato fruits has to be monitored frequently (Fenollet *al.*, 2009).The residues of pesticides on the commodity must be toxicologically acceptable and their levels are lower than the acceptable limits. The degradation of pesticides after application affected by many factors like the application rate, type of formulation, insecticide chemical structure, plant species, the number of applications, application method, climatic conditions, volatilization and photodegradation(Garau *et al.*, 2002). Moreover, it is an important method for the valuation of the pre-harvest interval (PHI) (Fenoll *et al.*, 2009).

In general this work aimed to investigate the persistence of abamectin, spinosad, acetamiprid, diniconazole, penconazole and fipronil residues on and in tomato fruits beneath field conditions and determines the residue half-life period (T ½), dissipation rate and pre-harvest interval (PHI) for the tested pesticides.

MATERIALS AND METHODS

A. Experimental and pesticide treatments:

Tomato *Lucopersicon esculentum* Var. "saria" was planted at faculty of agriculture Mansoura University, Egypt, on March 24, 2018. The field was exposed to normal agricultural services. Seven treatments were used containing six pesticides and the control. Four replicates (48 m^2 each) were used. Treatments were organized in completely randomized blocks design, and were remote from each other by passages. A Knapsack sprayer with one nozzle was used. Plants were sprayed with the recommended rate of pesticides for two times; May 8 and July 18 of 2018.

1. Sampling:

Samples were randomly collected from all treatments after one hour, 1, 3, 5, 7, 10, 15 and 21 days of application, to provide a representative sample and the plants in the border were avoided.

Table 1. Pesticides used:

Common name	Trade name	Empirical Formula	Pesticide group	Field recommended rate
Abamectin	Gold 1.8% E.C.	$C_{48}H_{72}O_{14}$ (B1a) $C_{47}H_{70}O_{14}$ (B1b)	Avermectin	40 cm^3/100 L
Spinosad	Tracer 24 % S.C.	$C_{41}H_{65}NO_{10}$ (A); $C_{42}H_{67}NO_{10}$ (D)	spinosyn	50 cm^3/fed.
Acetamiprid	Molan 70% W.G.	$C_{10}H_{11}ClN_4$	Neonicotinoid	50 g /fed.
Diniconazole	Sumi-eight 5 % E.C.	$C_{15}H_{17}Cl_2N_3O$	Triazole	50 cm^3/100 L
Penconazole	Penazole 10 % E.C.	$C_{13}H_{15}Cl_2N_3$	Triazole	25 cm^3/100 L
Fipronil	Ferogen 80 % WDG.	$C_{12}H_4Cl_2F_6N_4OS$	Fiprole	0.75 L/fed.

2. Analytical procedure:

Residues of six pesticides; Abamectin, spinosad, acetamiprid, diniconazole, penconazole, and fipronil were determined on and in tomato fruits (*Lucopersicon esculentum)* by HPLC-DAD for abamectin, spinosad, and acetamiprid pesticides and GC-ECD for diniconazole, penconazole and fipronil pesticides.

* **Corresponding author.**
E-mail address: reham_227@yahoo.com
DOI: 10.21608/jppp.2020.108835

a. Extraction:

The tomato samples were extracted using the QuEChERS methodology reported by (Anastassiades *et al.*,2003) with little modulation. 10 g of the homogenized tomato samples were weighed and added to 10ml of acetonitrile containing 1.0% acetic acid in a 50 ml centrifuge tube, and the tube was shaken for 1min vigorously using a vortex mixer. After that, 1g of sodium chloride and 4 g of anhydrous magnesium sulfate were added, then shaking vigorously 10min by hand, and centrifuged at 4000 rpm for 10min.

b. clean up:

Four milliliters from the supernatant were put in a clean centrifuge tube (15ml) and shaken with 100 mg primary secondary amine (PSA), 300 mg of magnesium sulfate, and 20 mg graphite carbon black (GCB), Thereafter, centrifuged at 4000 rpm for 10min. Then, one milliliter of the supernatant was filtered over a 0.45 µm PTFE Filter, (Anastassiades *et al.*, 2003).

c. Chromatographic analysis and Determination:

a. Abamectin, spinosad, and acetamipride:

Agilent 1100 High-performance liquid chromatography (HPLC) equipment with a diode array detector (Agilent, USA) was used for the determination of abamectin, spinosad, and acetamiprid residues at the conditions presented in table (2).

Table 2. High performance liquid chromatography (HPLC) conditions for abamectin, spinosad, and acetamiprid.

Analytical parameter	Technical material		
	Abamectin	**Spinosad**	**Acetamiprid**
UV wavelength	254 nm	250 nm	230 nm
Mobile phase	90% methanol +10% water	60% acetonitril + 30% methanol + 10% water	65% acetonitril + 35% methanol
Flow rate	1 mL/min	1 mL/min	1 mL/min
Absolute retention time	3.9 min	6.9 min 7.8 min	2.6 min
Column	C18 Hypersil (150 mm length x 4 mm (i.d))		

b. diniconazole, penconazole, and fipronil:

Agilent 6890 gas chromatograph equipped with a Ni^{63} – electron capture detector (ECD) was used to determine the residues of diniconazole, penconazole, and fipronil at the next conditions.

GC conditions: HP-5 (J and W Scientific) capillary column (30m length x 0.32 mm internal diameter x 0.25 µm film thickness), Injection port and Detector temperatures were 300°C and 320°C, respectively. The initial column temperature was initial oven temperature, 200°C for 2 min, raised at 5°C/min. After that, held at 270°C for 10 min. Carrier gas: nitrogen at a flow rate of 4 ml/min. The retention time values were 2.9, 4.7 and 3.1 minutes for diniconazole, penconazole, and fipronil, respectively.

B. Recovery studies:

Untreated samples of tomato fruits were spiked by adding a known amount of each pesticide standard solution (0.5, 1.0 and 2.0 mg/kg (ppm)). The efficacy of extraction and clean-up methods for spiked samples were estimated for each pesticide. The recovery percent of abamectin, spinosad, acetamiprid, diniconazole, penconazole and fipronil were calculated by the equation of % Recovery = ((µg) present / (µg) added) x 100.

Spiked levels were 0.5, 1.0 and 2.0 mg/kg(ppm). The results were corrected depending on the recovery rate.

Data in Table (3) showed that the average recovery percentages ranged from 92.58 to 96.14%, 88.71 to 91.20%, 92.85 to 97.86%, 90.52 to 93.67%, 95.80 to 99.15%, 88.47 to 92.75%, for abamectin, spinosad, acetamiprid, diniconazole, penconazole and fipronil, respectively.

Table 3. Recovery rates of abamectin,spinosad, acetamiprid, diniconazole, penconazole and fipronilat spiked levels 0.5, 1.0 and 2.0 ppm.

Spiked level (ppm) (n=3)	Recovery percentage of Pesticides					
	abamectin	**spinosad**	**acetamiprid**	**diniconazole**	**penconazole**	**fipronil**
0.5	93.21	88.71	94.36	91.44	97.33	89.25
1.0	92.58	89.45	92.85	90.52	95.80	88.47
2.0	96.14	91.20	97.86	93.67	99.15	92.75

n) replicates number

C. Calculation of the Half-life (RL_{50}):

The Rate of degradation of the tested pesticides and their half-life periods (RL_{50}) in tomato fruits were calculated by the equation of (Moye*et al*., 1987).

D. Calculation of the residues:

The residues were calculated by using the equation of (Mollhoff, 1975).

RESULTS AND DISCUSSION

Persistence of pesticides used on and in Tomato fruits:

A. Abamectin residues:

Residues, rate of degradation, pre-harvest interval (PHI) and half-life time of abamectin in tomato fruits were presented in table (4).

The initial residue of abamectin on and in tomato fruits was 5.80 ppm after one hour of treatment then reduced to 4.30, 3.97, 3.45 and 1.65 ppm indicated that the rates of loss were 25.86, 31.55, 40.52 and 71.55 % after 1, 3, 5 and 7 days of treatment respectively. Abamectin was not found in tomato fruits after 10 days of treatment. The rate of degradation (K) was 0.1772 day^{-1}, the half-life (RL_{50}) time value of abamectin in tomato fruits was 3.911 days. Data showed that tomato fruits could be consumed safely after 10 days of the treatment depending on the maximum residue limit (MRL) of abamectin in tomato (0.09 ppm) (EU 2018).

The results are in harmony with the findings of (Abd-Alrahman*et al.*, 2014) who found that the residue of abamectin in potatoes was below the maximum residue limit after 10 days. Half-life of abamectin was 3.5 days. The recovery of abamectin was 89% at three levels of fortification. (Reddy*et al.*, 2007a) determined the residue of abamectin in tomato and sweet pepper planted in open field and greenhouse and found that both of them could be consumed safely after 10 days. Also, (Badawy*et al.*, 2020) assessed the dissipation rate of abamectin in pods of green beans under field conditions in Egypt; they reported that the pre-harvest time was 10 days however the half-life value was one day. (Abdellseid and Rahman, 2014) found that the half-life of abamectin residues in tomato was 2.4 days, and the pre-harvest time was 8 days.

On the other hand, (Abd-Alrahman*et al.*, 2012) found that the half-life of abamectin residue in tomato was 1.06 days. Pre-harvest interval for abamectin was 6 days. Also, (Ramadan*et al.*, 2016) investigated the residual behavior of abamectin under Egyptian field conditions in tomato fruits, and found that the half-life was 4.1 days. The results suggested that tomato fruits could be consumed safely after 7 days. Recoveries amounts ranged from 85% to 130% at two fortified levels.(Mahmoud *et al.,* 2010) studied the residual level of abamectin in strawberry beneath the Egyptian field condition, and found that the half-life time was 1.02 days, while the pre-harvest time (PHI) was 7 days. (Xie*et al.,* 2011) found that the recoveries of abamectin in vegetables ranged from 83.2% to 123.7%.

B. Spinosad residues:

Residues, rate of degradation, pre-harvest interval (PHI) and half-life time of spinosad in tomato fruits were presented in table (4).

The initial residue of spinosad on and in tomato fruits was 1.92 ppm after one hour of treatment then reduced to 0.29 ppm indicated that the rates of loss were 84.89 % after 1 day of treatment. Spinosad was not found in tomato fruits after 5 days of treatment. The rate of degradation (K) was 1.8901 day^{-1}, the half-life (RL_{50}) time value of spinosad in tomato fruits was 0.3667 days. Data showed that tomato fruits could be consumed safely after 1 day of treatment depending on the maximum residue limit (MRL) for spinosad in tomato (0.7 ppm) (EU 2015).

In fact, the present results were in harmony with several studies, (Ramadan*et al.,* 2016) who investigated the residual behavior of spinosad in tomato fruits in Egyptian field conditions. The half-life of spinosad was 1.7 days. The results suggested that tomato fruits could be consumed safely after <1d of treatment at recommended rates. Recoveries were between 85% and 130% at two fortified levels. (Kashyap and Sharma, 2015) estimated spinosad residue in tomato planted in India, and they found that the half-life time of spinosad was 1.20 days. The safety interval was 1.92 days. While, recoveries were in the range between 80.6 to 91.4 %. Also, (Drozdzynski and Kowalska, 2009) found that recoveries of the spiked samples of spinosad were ranged between 67% and 108%.

One the other hand, (Sharma*et al.,* 2007) evaluated the persistence of spinosad in cauliflower and cabbage at two application rates; at 35.0 g/ha, spinosad continued up to 10 days. But, at 17.5 g/ha, spinosad continued up to 7 days. The half-live times of spinosad residues were calculated as 2.0 and 2.6 days for the 35 g/ha application, and as 2.8 and 1.5 days respectively for the 17.5 g/ha application. (Adak and Mukherjee, 2016) studied the dissipation of spinosad in and on tomato in Indian field conditions. The results showed that spinosad remains were less than the determination limit after 15 days of application for the recommended dose. The half-life time of spinosad was ranged between 3.18 to 3.74 days. (Sikorska-Zimny*et al.,* 2017) studied the persistence of spinosad in onion, cabbage, and carrot. The highest level of the pesticide after 7 days remained in carrot. The amount of spinosad on day 7 found in cabbage and onion was equal to the Maximum Residue Level.

C. Acetamiprid residues:

Residues, rate of degradation, pre-harvest interval (PHI) and half-life time of acetamiprid in tomato fruits were presented in table (4).

The initial residue of acetamiprid on and in tomato fruits was 1.10 ppm after one hour of treatment then reduced to 0.500, 0.340, 0.143, 0.005 and 0.004 ppm indicated that the rates of loss were 54.55, 69.09, 87.00, 99.55 and 99.64 % after 1, 3, 5, 7 and 10 days of treatment respectively. Acetamiprid was not found in tomato fruits after 15 days of treatment. The rate of degradation (K) was 0.5804 day^{-1}, the half-life (RL_{50}) time value of acetamiprid in tomato fruits was 1.1943 days. Data showed that tomato fruits could be consumed safely after 1 day of treatment depending on the maximum residue limit (MRL) of acetamiprid in tomato (0.5 ppm) (EU 2019).

The results are in coordination with the findings of (Ahmed *et al.,* 2004) who analyzed acetamiprid residues in green pepper and cucumber which planted under plastic greenhouse conditions. Acetamiprid residues in samples of both fruits and in all tested periods were lower than the MRL. Who reported also, the fresh fruits could be marketed with apparent safety for human consumption at one day after acetamiprid spray. The RL_{50} was 51.19 h for pepper and 19.80 h for cucumber. In the same trend,(El-Din*et al.,* 2012) investigated the rate of loss of acetamiprid residue in cucumber and tomato fruits. The half-life times of acetamiprid were 1.18 and 1.04 days in cucumber and tomato fruits, respectively.,and became near to the acceptable maximum residue limits after 3 days of application.

On the other hand, (Singh, and Kulshrestha, 2005) studied the dissipation and residues of acetamiprid in okra fruits, and it was observed that residues were beneath the detectable limits on the 7th day after treatment. Moreover, the half-life of acetamiprid was 2.3 days. Also, (Park *et al.,* 2011) determined acetamiprid residues in zucchini planted in greenhouse. Recovery percentage ranged between 85.7 to 92.2%. The half-life of acetamiprid was 1.9 days. No residues were found after 7 days after treatment. (Cara *et al.,* 2011) determined the residue of acetamiprid in cucumber under greenhouse conditions. They found that the pre-harvest time (PHI) was determined to be 7 days. The recoveries of spiked samples ranged from 80 to 92%. (Lazić*et al.,* 2015) determined the residues of acetamiprid in tomato after the treatment at the recommended dose. The results indicated that the half-life time of acetamiprid was 4.33 days. Residues in tomato were at MRL after 6 days of treatment. (Varghese *et al.,* 2015) studied the residues of acetamiprid on chili fruits. The half-life value of acetamiprid was 2.27 days, while a waiting period was 7.18 days. (Lazić*et al.,* 2016) investigated the dissipation of acetamiprid in tomato and pepper fruits under greenhouse conditions. The half-life time of acetamiprid in tomato samples (4.3 days) and pepper (3.9 days). PHI for acetamiprid in tomato and pepper was 14 days.

Table 4. Residues, rate of degradation, pre-harvest interval (PHI) and half-life time of abamectin, spinosad and acetamiprid in tomato fruits:

Time after application (days)	Residues					
	abamectin		spinosad		acetamiprid	
	Residues (ppm)**	% loss	Residues (ppm)**	% loss	Residues (ppm)**	% loss
Initial*	5.80	00.00	1.92	00.00	1.100	00.00
1	4.30	25.86	0.29	84.89	0.500	54.55
3	3.97	31.55	ND	100	0.340	69.09
5	3.45	40.52	ND	100	0.143	87.00
7	1.65	71.55	ND	100	0.005	99.55
10	ND	ND	ND	100	0.004	99.64
15	ND	ND	ND	100	ND	100
21	ND	ND	ND	100	ND	100
K	0.1772		1.8901		0.5804	
RL_{50}(days)	3.911		0.3667		1.1943	
MRL(ppm)	0.09(EU 2018)		0.7(EU 2015)		0.5(EU 2019)	
PHI(days)	10		1		1	

***: Samples were taken after one hour of treatment. N.D. = Not detectable.**
****: Average of four replicates.**

D. Diniconazole residues:

Residues, rate of degradation, pre-harvest interval (PHI) and half-life time of diniconazolein tomato fruits were presented in table (5).

The initial residue of diniconazole on and in tomato fruits was 0.700 ppm after one hour of treatment then reduced to 0.150, 0.024, 0.021 and 0.020 ppm indicated that the rates of loss were 78.57, 96.57, 97.00 and 97.14 % after 1, 3, 5 and 7 days of treatment respectively. Diniconazole was not found in tomato fruits after 10 days of treatment. The rate of degradation (K) was 0.9684 day^{-1}, the half-life (RL_{50}) time value of diniconazole in tomato fruits was 0.7158 days. Data showed that tomato fruits could be consumed safely after 10 days of the treatment depending on the maximum residue limit (MRL) of diniconazole in tomato (0.01 ppm) (EU2013).

Our results are correlated with the findings of (Mahmoud *et al.,* 2010) who studied the residual behavior of diniconazole in strawberry fruits in Egypt. The half-life was 4.25 days, and the pre-harvest time was determined to be 15 days. (Mahmoud and Eissa, 2007) determined the residual behavior of diniconazole following the treatment of greenhouse-grown pepper and cucumber fruits. The results of this study indicated that the half-life was 20.71 and 73.79 hoursin pepper and cucumber fruits, successively. It was recorded that pre-harvest interval (PHI) is more than 15 daysfor treated pepper and cucumber fruits and therefore it is not recommended to use diniconazole on the greenhouse-grown cucumber.(Din *et al.,* 2015) studied the persistence of diniconazole in broad bean pods, seeds, peels and soil. They found that the recoveries were in the range between 81–99 %. The results showed that the half-life times of diniconazole in pods, seeds, peels and soil were 2.4, 5.2, 2.2, and 5.5 days, respectively. The pre-harvest interval (PHI) of pods was 9 days.

On the other hand, (Amer*et al.,* 2007) determined residues and the rate of degradation of diniconazole in tomatoes and green beans fruits. They conclude that the half-life was 3 days for diniconazole. Residues were not found in fruits after 21 days of treatment.

E. Penconazole residues:

Residues, rate of degradation, pre-harvest interval (PHI) and half-life time of penconazolein tomato fruits were presented in table (5).

The initial residue of penconazole on and in tomato was 0.239 ppm after one hour of treatment then reduced to 0.210, 0.191, 0.080, 0.047, 0.038 and 0.0247 ppm indicated that the rates of loss were 12.13, 20.08, 66.53, 80.33, 84.10 and 89.67 % after 1, 3, 5, 7, 10 and 15 days of treatment respectively. Penconazole was not found in tomato fruits at 21 days of treatment. The rate of degradation (K) was 0.1650 day^{-1}, the half-life (RL_{50}) time value of penconazole in tomato fruits was 4.199 days. Data showed that tomato fruits could be consumed safely after 5 days of the treatment depending on the maximum residue limit (MRL) of penconazole in tomato (0.5 ppm) (EU 2019).

Similar results were found by (Ahmed *et al.,* 2004) who analyzed penconazole residues in green pepper and cucumber which planted under plastic greenhouse conditions. Penconazole residues reached a safe level for marketing after 4 days in cucumber fruits. Penconazole residue half-lives values were 31.63 h for pepper and 10.19 h for cucumber. (Barakat *et al.,* 2006) studied the persistence of penconazole residue in tomato, cucumber and green pepper fruits under greenhouse conditions. The initial residues of penconazole in tomato, cucumber and green pepper fruits were 0.09, 0.13 and 0.24 ppm, respectively. the assessed half-life times of penconazole for these crops were 1.5, 3.3 and 4.97 days.

On the other hand, (Romeh*et al.,* 2009) found that the tomato fruits can be harvested safely after 3 days of treatment by penconazole. (Abd-Alrahman and Ahmed, 2012) studied the penconazole residues in tomatoes. The half-life value and pre-harvest interval of penconazole were 5.61 and 15 days, respectively. Also, (Abd-Alrahman and Ahmed 2013) evaluated the dissipation of penconazole in peach, apricot, mango, and plum fruits. The residues dissipated below the maximum residues limit after 15, 10, 21 and 7 days for peach, apricot, mango, and plum, respectively. The half-life time and pre-harvest (PHI) of penconazole were 7.2 (12), 1.53 (7), 4.54 (21) and 2.48 (12) days for peach, apricot, mango, and plum, respectively.

F. Fipronil residues:

Residues, rate of degradation, pre-harvest interval (PHI) and half-life time of fipronil in tomato fruits were presented in table (5).

The initial residue of fipronil on and in tomato was 2.890 ppm after one hour of treatment then reduced to 1.220, 0.717, 0.664, 0.440, 0.160, 0.090 and 0.004 ppm indicated that the rates of loss were 57.79, 75.19, 77.02, 84.78, 94.46, 96.89 and 99.86 % after 1, 3, 5, 7, 10, 15 and 21 days of treatment respectively. The rate of degradation (K) was 0.3891 day^{-1}, the half-life (RL_{50}) time value of fipronil in tomato fruits was 1.7813 days. Data showed that tomato fruits could be consumed safely after 21 days of the treatment depending on the maximum residue limit (MRL) of fipronil in tomato (0.005 ppm) (EU 2019).

Similar results were found by (Xavier *et al.,* 2014) who determined the dissipation of fipronil on chili fruits after the spraying at double and single dose. The half-life time of fipronil at double and single dose in fresh chili pepper was 4.32 and 4.22 days and the waiting periods were 30.6 and 25.9 days, respectively. (Kumar *et al.,* 2013) reported the persistence of fipronil in and on chili fruits following spraying at double and recommended doses. No residues of fipronil were found in chili fruits after 20 days. Half-life of fipronil on fruits was in the range of 1.71-1.57 days. (Duhan *et al.,* 2015) studied the dissipation of fipronil in cauliflower. Residues of fipronil were less than the detectable level before 30 days of treatment. A safe waiting interval was 15 days. (Kaur *et al.,* 2015) determine residues of fipronil in different vegetables (tomato, brinjal, cauliflower, cabbage, okra, and capsicum). The recoveries obtained for fipronil at different spiking levels in all samples were determined to be above 85%.

On the other hand, (Reddy*et al.,* 2007b) studied the residues of fipronil on chilies in India. Half-life time for fipronil was 16.8 days. The suggested waiting period was 5 days. (Gupta *et al.,* 2007) studied the dissipation of fipronil in eggplants. The residues persisted beyond 10 days. The half-live was 2.5 days. The suggested waiting time was 7 days. In addition, (Gupta *et al.,* 2009) studied the dissipation of fipronil in okra fruits. The residues remained up to 10 days with half-life time 0.65-1.12 days. The suggested waiting period was 3 days. (Reddy and Reddy, 2013) found that fipronil was dissipated to below detectable residues at 10 days after the fourth spray in green chili pods. The waiting period was 7.26 days in green chili pods. The half-life value for fipronil was 3.26 days. Also, (Haiqun*et al.,* 2005) used GC to analyze the residue of fipronil in tomatoes. The average recovery values were 82.36-90.38% in tomato samples. (Yan*et al.,* 2005) found that the half-life times of fipronil in vegetables were 10.4 days.

From the above, we can conclude that the different results are due to the degradation rate of pesticides after application, which affected by many factors like the applied dose, type of formulation, insecticide chemical structure, plant species, the number of applications, application method, climatic conditions, volatilization and photodegradation (Garau*et al.,* 2002). Also, it is a key for the estimation of (PHI) the pre-harvest interval (Fenoll*et al.,* 2009).

Table 5. Residues, rate of degradation, pre-harvest interval (PHI) and half-life time of diniconazole, penconazole and fipronil in tomato fruits:

Time after application (days)	Residues					
	diniconazole		penconazole		fipronil	
	Residues (ppm)**	% loss	Residues (ppm)**	% loss	Residues (ppm)**	% loss
Initial*	0.700	00.00	0.239	00.00	2.890	00.00
1	0.150	78.57	0.210	12.13	1.220	57.79
3	0.024	96.57	0.191	20.08	0.717	75.19
5	0.021	97.00	0.080	66.53	0.664	77.02
7	0.020	97.14	0.047	80.33	0.440	84.78
10	ND	100	0.038	84.10	0.160	94.46
15	ND	100	0.0247	89.67	0.090	96.89
21	ND	100	ND	100	0.004	99.86
K	0.9684		0.1650		0.3891	
RL_{50}(days)	0.7158		4.199		1.7813	
MRL(ppm)	0.01(EU 2013)		0.1(EU 2019)		0.005(EU 2019)	
PHI(days)	10		5		21	

***: Samples were taken after one hour of treatment. N.D. = Not detectable.**
****: Average of four replicates.**

REFERENCES

Abd-Alrahman, S.H. and Ahmed, N. (2012). Dissipation of penconazole in tomatoes and soil. *Bulletin of Environmental Contamination and Toxicology*, 89(4):873–876.

Abd-Alrahman, S. H. and Ahmed, N. (2013). Dissipation of penconazole in peach, plum, apricot, and mango by HPLC–DAD. *Bulletin of Environmental Contamination and Toxicology*, 90(2):260–263.

Abd-Alrahman S.H.A.; Almaz, M.M. and Ahmed, N.S. (2012). Dissipation of fungicides, insecticides, and acaricide in tomato using HPLC-DAD and QuEChERS methodology. *Food Analytical Methods*, 5(3):564–570.

Abd-Alrahman, S. H.; Elhalwagy, M. E.; Salem-Bekhit, M. M. and Abdel-Mageed, W. M. (2014). Evaluation of degradation kinetics for abamectin in potatoes. *Journal of Animal and Veterinary Advances*, 13(9):608-611.

Abdellseid, A., and Rahman, T. A. (2014). Residue and dissipation dynamics of abamectin in tomato fruit using QuEChERS methodology. In *International Conference on Food, Biological and Medical Sciences Bangkok*, 1-9.

Adak, T., and Mukherjee, I. (2016). Dissipation kinetics of spinosad from tomato under sub-tropical agro-climatic conditions. *Environmental Monitoring and Assessment*, 188(5):299.

Ahmed, N. S.; El-Bouze, M. F. R. and El-Aziz, S. A. A. (2004). Residual behaviour of penconazole and acetamiprid pesticides on and in green pepper and cucumber fruits under plastic house conditions. *Arab Univ. J. Agric. Sci., Ain Shams Univ.,Cairo*, 12 (2): 795 - 806.

Amer, M. M.; Shehata, M. A.; Lotfy, H. M.and Monir, H. H. (2007). Determination of tetraconazole and diniconazole fungicide residues in tomatoes and green beans by capillary gas chromatography. *YakugakuZasshi*, 127(6): 993-999.

Anastassiades, M.; Lehotay, S. J.; Štajnbaher, D. and Schenck, F. J. (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. *Journal of AOAC international*, 86(2), 412-431.

APC. 2010. Pesticides registration. Agricultural Pesticide Committee (APC), Ministry of Agriculture, Cairo, Egypt.

Badawy, M. E.; Mahmoud, M. S. and Khattab, M. M. (2020). Residues and dissipation kinetic of abamectin, chlorfenapyr and pyridabenacaricides in green beans (Phaseolus vulgaris L.) under field conditions using QuEChERS method and HPLC. *Journal of Environmental Science and Health*, Part B, 17(2):1-8.

Barakat, D. A.; Nasr, I. N.; El-Mahy, S. A. and El-Hefny, D. E. (2006). Persistence of the fungicides tetraconazole and penconazole residues on and in some vegetables grown in the greenhouse and under different environmental conditions. *Bulletin of Faculty of Agriculture, Cairo University*, 57(3):511-529.

Cara, M.; Vorpsi, V.; Harizaj, F.; Merkuri, J. and Vladi, V. (2011). Degradation of the insecticide Acetamiprid in greenhouse cucumbers and an estimation of the level of residues. *Journal of Environmental Protection and Ecology*, 12(1):74-81.

Din, S. E.; Azab, M. M.; El-Zaher, T. R. A.; Mahmoud, H. A. and Sleem, F. M. (2015).Persistence of diniconazole and etoxazole in broad bean pods, peels, seeds and its planted soil. *Journal of Plant Protection and Pathology*, 6(5), 859-870.

Dorais, M.; Ehret, D.L. and Papadopoulos, A.P. (2008). Tomato (Solanumlycopersicum) health components: from the seed to the consumer. *Phytochemistry Reviews*, 7(2):231-250.

Drozdzynski, D. and Kowalska, J. (2009). Rapid analysis of organic farming insecticides in soil and produce using ultra-performance liquid chromatography/tandem mass spectrometry. *Analytical and Bioanalytical Chemistry*, 394(8):2241-2247.

Duhan, A.; Kumari, B. and Duhan, S. (2015). Determination of residues of fipronil and its metabolites in cauliflower by using gas chromatography-tandem mass spectrometry. *Bulletin of Environmental Contamination and Toxicology*, 94(2):260-266.

El-Din, A. M. S.; Azab, M. M.; El-Zaher, T. R. A.; Zidan, Z. H. A. and Morsy, A. R. (2012). Persistence of acetamiprid and dinotefuran in cucumber and tomato fruits. *American-Eurasian Journal of Toxicological Sciences (AEJTS)*, 4(2):103-107.

European Union. (2013). Maximum residue limits for insecticides.

European Union. (2015). Maximum residue limits for insecticides.

European Union. (2018). Maximum residue limits for insecticides.

European Union. (2019). Maximum residue limits for insecticides.

FAO. (2011). FAOSTAT. Food and Agriculture Organization of the United Nations (FAO), Rome, Italy. Available at http://faostat3. fao.org/home/E.

Fenoll, J.; Ruiz, E.; Hellín, P.; Lacasa, A. and Flores, P. (2009). Dissipation rates of insecticides and fungicides in peppers grown in greenhouse and under cold storage conditions. *Food Chemistry*, 113(2): 727-732.

Garau, V. L., Angioni, A., Del Real, A. A., Russo, M., and Cabras, P. (2002). Disappearance of azoxystrobin, pyrimethanil, cyprodinil, and fludioxonil on tomatoes in a greenhouse. *Journal of Agricultural and Food Chemistry*, 50(7): 1929-1932.

Gupta, S.; Sharma, R. K.; Gupta, R. K.; Sinha, S. R.; Rai, S.and Gajbhiye, V. T.(2009). Persistence of new insecticides and their efficacy against insect pests of okra. *Bulletin of Environmental Contamination and Toxicology*, 82(2):243-247.

Gupta, S.; Sharma, R. K.; Sinha, S. R.; Gupta, R. K. and Gajbhiye, V. T.(2007). Persistence of some new insecticides in brinjal and their efficacy against brinjal leafhopper and borer. *Pesticide Research Journal*, 19(2):205-209.

Haiqun, C., Yanhong, S., and Rimao, H. (2005). Study on analytical method of fipronil residue in tomato and soil. *Journal of Anhui Agricultural University*.

Kashyap, L., and Sharma, D. C. (2015). Dissipation behaviour of spinosad in polyhouse grown tomato under mid-hill conditions of Himachal Pradesh, India. *Environmental monitoring and assessment*, 187(3): 75.

Kaur, R.; Mandal, K.; Kumar, R. and Singh, B. (2015). Analytical method for determination of fipronil and its metabolites in vegetables using the QuEChERS method and gas chromatography/mass spectrometry. *Journal of AOAC International*, *98*(2), 464-471.

Kumar, A.; Mukherjee, I.; Singh, M. K. and Kumar, A.(2013). Persistence of cypermethrin and fipronil in/on chilli (Capsicum annuum Linn.). *Pesticide Research Journal*, *25*(2), 174-176.

Lazić, S.; Šunjka, D. and Vuković, S. (2016). Safe use of neonicotinoids in some vegetables in terms of residues. In *III International Congress," Food Technology, Quality and Safety", 25-27 October 2016, Novi Sad, Serbia. Proceedings* (pp. 311-315). University of Novi Sad, Institute of Food Technology.

Lazić, S.; Šunjka, D.; Jovanov, P.; Grahovac, N.; Mojašević, M. and Stojanović, I. (2015). Determination of acetamiprid residues in selected vegetable and fruit. In *Proceedings of the 7th Congress on Plant Protection" Integrated Plant Protection-a Knowledge-Based Step Towards Sustainable Agriculture, Forestry and Landscape Architecture". November 24-28, 2014, Zlatibor, Serbia* (pp. 343-348). Plant Protection Society of Serbia (PPSS).

Mahmoud, H. A. and Eissa, F. I.(2007).Diniconazole residues in field-sprayed and household processed cucumber and pepper fruits. Annals of Agricultural Science (Cairo), 52(1):253-260.

Mahmoud, H.A.; Arief, M.M.H.; Nasr, I.N. and Mohammed, I.H. (2010). Residues and half-lives of abamectin, diniconazole and methomyl on and in strawberry under the normal Field conditions. *Journal of Applied Sciences Research*, 6(8): 932-936.

Malhat, F.; Abdallah, H. and Nasr. I. (2012). Estimation of etofenprox residues in tomato fruits by QuEChERS methodology and HPLCDAD. *Bulletin of Environmental Contamination and Toxicology*, 88(6):891-893.

Mollhoff, E. (1975). Method for gas chromatographic determination of residues of Tokuthion and its oxon in plants and soil samples. *Pflanzenschutz Nachrichten* Bayer, 28(3):382-387.

Moye, H.A.; M.H. Malagodi; J. Yoh; G.L. Leibee; C.C. Ku and P.G. Wislocki (1987). Residues of avermectin B1a in rotational crops and soils following soil treatment with [14C] avermectin B1a. *Journal of agricultural and food chemistry*, 35(6), 859-864.

Park, J.; Choi, J.; Kim, B.; Park, J.; Cho, S.; Ghafar, M. W.; El-Aty, A. M. A. and Shim, J. (2011). Determination of acetamiprid residues in zucchini grown under greenhouse conditions: application to behavioral dynamics. *Biomedical Chromatography*, 25(1/2):136-146.

Ramadan, G.; Shawir, M.; El-Bakary, A. and Abdelgaleil, S. (2016). Dissipation of four insecticides in tomato fruit using high performance liquid chromatography and QuEChERS methodology. *Chilean Journal of Agricultural Research*, 76(1):129-133.

Reddy, C. N. and Reddy, D. J. (2013). Persistence and dissipation certain insecticides on chilli pods and soil. *Progressive Research*, 8(2):245-247.

Reddy, K. D.; Reddy, K. N.; Mahalingappa, P. B. (2007b). Dissipation of fipronil and profenofos residues in chillies (*Capsicum annum* L.). *Pesticide Research Journal*, 19(1):106-107.

Reddy, S. G. ; Sharma, D.; Kumar, N. K. (2007a). Residues of insecticides on sweet pepper and tomato grown under greenhouse and open field cultivation. *Pesticide Research Journal*, 19(2):239-243.

Romeh, A. A.; Mekky, T. M.; Ramadan, R. A. and Hendawi, M. Y. (2009). Dissipation of profenofos, imidacloprid and penconazole in tomato fruits and products. *Bulletin of Environmental Contamination and Toxicology*, 83(6):812-817.

Sharma, A., Srivastava, A., Ram, B., and Srivastava, P. C. (2007). Dissipation behaviour of spinosad insecticide in soil, cabbage and cauliflower under subtropical conditions. *Pest Management Science: formerly Pesticide Science*, *63*(11), 1141-1145.

Sikorska-Zimny, K. M.; Wedzisz, A.; Rogowska, M.(2017).Spinosad decay dynamics and mineral content of some elements in chosen vegetables. *Journal of Elementology*, 22(2):737-746.

Singh, S. B. and Kulshrestha, G. (2005). Residues of thiamethoxam and acetamiprid, two neonicotinoid insecticides, in/on okra fruits (*Abelmoschusesculentus* L). *Bulletin of Environmental Contamination and Toxicology*, 75(5):945-951.

Varghese, T. S.; Mathew, T. B.; George, T.; Beevi, S. N. and Xavier, G.(2015). Persistence and dissipation of neonicotinoid insecticides on chilli fruits. *Quality Assurance and Safety of Crops & Foods*, 7(4):487-491.

Xavier, G.; Chandran, M.; George, T.; Beevi, S. N.; Mathew, T. B.; Paul, A.; Arimboor, R.; Vijayasree, V.;Pradeepkumar, G.T. and Rajith, R.(2014). Persistence and effect of processing on reduction of fipronil and its metabolites in chilli pepper (*Capsicum annum* L.) fruits. *Environmental Monitoring and Assessment*, 186(9):5429-5437.

Xie, X.; Wang, X. and Zhao, L. (2011). A fast, simple, and reliable high-performance liquid chromatography (HPLC) method for determining abamectin residues in vegetables and fruits. *Food Analytical Methods*, 4(2):203-211.

Yan, C.; Liu, X.; Yu, X.; Zhang, C.; Wang, D.; Li, J. (2005). Application of ELISA in degradation analysis of fipronil. *Jiangsu Journal of Agricultural Sciences*, 21(2):113-117.

اختفاء متبقيات بعض مبيدات الآفات في ثمار الطماطم باستخدام طريقةQuECHERS تحت ظروف البيئة المصرية

ريهام محمد عبد الفتاح*، عادل عبد المنعم صالح، ليلى رجب على الجوهرى و سلوى السعيد نجم
قسم المبيدات - كلية الزراعة - جامعة المنصورة- مصر

تم تقدير متبقيات ومعدل اختفاء كل من مبيداتالأبامكتين ، والاسبينوساد ، والأسيتاميبريدفى ثمار الطماطم باستخدام جهاز الكروماتوجرافى السائل عالى الاداء وكذلك مبيدات الداينيكونازولوالبينكونازولوالفيبرونيل باستخدام جهاز الكروماتوجرافى الغازى تحت الظروف الحقلية باستخدام طريقة QuEChERS. وكانت فترة نصف العمر للأباماكتين ، الاسبينوساد،الأسيتاميبريد، الداينيكونازول، البينكونازول و الفيبرونيل في ثمار الطماطمهى 3.91 و 0.36 و 1.19 و 0.71 و 4.19 و 1.78 يوم على التوالي. وكانت فترة ما قبل الحصاد هى10 و 1 و 1 و 10و 5 و 21 يومًا بعد التطبيق، على التوالي وذلك تبعًاللحدودالقصويللمتبقيات. وهذا يشير إلى أن استخدام ثمار الطماطم المعامله بهذه المبيدات اصبحت آمنة للاستهلاك بعد هذه المدة. قد تكون هذه الدراسة مفيدة لمنع المشاكل الصحية لبقايا المبيدات على المستهلكين.