



ISSN 2357-0725

<https://jsasj.journals.ekb.eg>

JSAS 2022; 7(2): 127-137

Received: 16-09-2022

Accepted: 04-10-2022

Gaber, S.S.**Abd El-Latif, A.O.****Sallam, A.A.**

Plant Protection Department

Faculty of Agriculture

Sohag University

Sohag

82524

Egypt

El-Hefny, D. S.

Pesticide Residues and

Environmental Pollution

Department

Central Agriculture Pesticide

Laboratory

Agriculture Research Center

Egypt

Corresponding author:**Gaber, S.S.**salmasalahgaber@gmail.com

Dissipation kinetics study of acetamiprid, metalaxyl-M and fenpyroximate in the ecosystem of tomato fruits under field and greenhouses conditions

Gaber, S.S., El-Hefny, D. S., Abd El-Latif, A.O. and Sallam, A.A.

Abstract

Extreme pesticide use in tomato growing could have negative impact on the environment and human health. In this study, the rate of dissipation of three commonly used pesticides for growing tomatoes, acetamiprid, metalaxyl-M, and fenpyroximate was assessed. Within two weeks after the application of pesticides, tomato samples were collected from field and greenhouses and the pesticide residues were extracted using QuEChERS technology and quantified using high-performance liquid chromatography and diode array detection (HPLC-DAD). Recovery assays were performed in the levels of 0.1, 0.5 and 1.0 mg/kg. The recovery rates for acetamiprid, metalaxyl-M, and fenpyroximate were 87.71 ± 1.33 %, 92.08 ± 2.35 % and 91.77 ± 1.06 %, respectively. The Preharvest intervals (PHI) for these pesticides in greenhouse and field tomato plants ranged from 5 to 7 days. The half-lives of these pesticides were determined to be 1.80, 0.80 and 1.75 days, respectively, for acetamiprid, metalaxyl-M, and fenpyroximate in tomato samples taken from open fields, and to be 1.48, 2.27 and 1.36 days, respectively, in tomato samples taken from greenhouses. The amount of detected pesticide residues remained in the treated tomato fruits are affected by cooking. Pesticide residues were essentially undetectable in tomato paste.

Keywords:

Pesticides, Dissipation, QuEChERS, Preharvest interval, Tomato, HPLC-DAD

INTRODUCTION

The use of pesticides is a significant step in the management of pests in agricultural crops. More than 1000 pesticides are employed globally to defend crops against various pests. These pesticides are used both before and after harvest to reduce crop loss. Approximately one-third of agricultural products are produced using pesticides (Tudi *et al.*, 2021). Pesticide residues are present in food due to the application of pesticides (Boobis *et al.*, 2008, Nougadère *et al.*, 2012). The use of pesticides has increased many folds during the past few decades. More than 5 billion pounds of pesticides are used worldwide annually, so it is critical to spread the idea of safe use of pesticides, about 250,000 to 370,000 human deaths, most of them were noticed in developing countries (Shalaby *et al.*, 2022). One of the most significant health issues in the globe is the pesticide residues that persist in or on food products. When dumping exceeds MRL, these residues can be dangerous to humans and result in a variety of ailments. (Zhang *et al.*, 2011; Oliva *et al.*, 2017 and Soydan *et al.*, 2021). A balanced and nutritious diet must contain both fruits and vegetables. They are known to include elements that have a variety of health-promoting effects (including pre-biotic, vitamins, vital minerals, and antioxidants) (fibers). Also, harmful compounds like pesticide residues can be found in fruits and vegetables. (Mermer *et al.*, 2020). Even if these substances are found at very low concentrations, long-term exposure to combinations of pesticides may have the potential to induce adverse health effects such as hormone disruption, diminished intelligence, immunity suppression, reproductive abnormalities, and cancer (Shalaby *et al.*, 2021). To make sure that the residues are below the tolerance thresholds and the edible parts have become safe for human consumption, it is important to monitor pesticide residues on vegetable and fruit plants after application to establish the waiting period between application and harvest. Tomato (*Solanum lycopersicum* L.) is one of the most essential and common vegetables cultivated in the world (Abdelfatah *et al.*, 2020), the production of tomato in Egypt almost seven million tons of tomato each year (Malhat *et al.*, 2012) and approximately 34% of Egypt's cultivation area were used for tomato

cultivation (Abd-Alrahman and Kotb, 2020). Tomato can be eaten raw, semi-processed or processed as a juice or paste. Production of tomato fruit in greenhouses is a typical agricultural practice. Due to the crops' heightened risk of contracting some illnesses, crops grown in greenhouses must be treated with pesticides. According to the evidence, equivalent covered crops typically have more detectable pesticides than field crops. It's possible that this is brought on by different pesticide use policies and slower pesticide clearance rates in protected systems (Allen *et al.*, 2015). This study aimed to evaluate the kinetics and dissipation of acetamiprid, metalaxyl-M, and fenpyroximate pesticides and assess these pesticides' effects on the ecosystem of tomato under field greenhouses conditions. The development of rules for the lawful application of three pesticides in tomato pest management techniques may be aided by these findings. Additionally, to look into how certain processing affects the removal of pesticide traces from tomato fruits treated with pesticides.

MATERIALS AND METHODS

Chemicals and reagents

Analytical standard (purity $\geq 98\%$ to 99%), and the formulation (Acetamiprid (Mosiplan 20% SP), metalaxyl-M 40 % mancozeb 64 % (Ridomil Gold MZ 68% WG) and fenpyroximate (Ortus super 5% EC)), structure of acetamiprid, metalaxyl-M and fenpyroximate (Tomlin (2009)). HPLC grade organic solvent (acetonitrile, methanol, and analysis grade acetic acid), Magnesium sulfate anhydrous and Sodium chloride were purchased from Merck Millipore Ltd. Milli-Q water purification system for ultrapure water. PSA, 40 μm was purchased from Supelco (Supelco, USA). An Agilent HPLC with a quaternary pump, column thermostat, and photodiode array detector was used.

Field experiment

Field experiment was carried out in the Agricultural Experimental Farm of the Faculty of Agriculture, Sohag University. During season 2019. Tomatoes was cultivated under field and greenhouse condition and sprayed with acetamiprid (Mosiplan 20% SP) at 25 g / 100 L water, metalaxyl-M (Ridomil Gold MZ 68% WG)

at 200 g / 100 L water, and fenpyroximate (Ortus super 5% EC) at 50 ml / 100 L water at 25/11/2019 and 4/3/2019, respectively. In field experiment, the experimental area was divided into plots of 42 m² (1 / 100 Fed.). One plot was left untreated to serve as control. In greenhouse experiment, the applications were conducted in a total area of 425 m² used for the growth of tomato. Each plant was grown in one-meter rows with 0.5 m between plants. The material of greenhouse was polyethylene (180-200 μm). Spray was performed by a specialized operator. Spraying was carried out using a Knapsack- sprayer (Cp-3) provided with one nozzle delivering 200 liters of water per feddan, which has proved to be sufficient to give good coverage on the treated plants. Residue trials were conducted according to the in force and more critical Good Agricultural Practices (GAPs) as to investigate the dissipation rate of the compound on both crops and the terminal residues in the final products. The average temperature in the greenhouse during the experiment period was 30 degrees Celsius, while in the open field it was 37 degrees Celsius.

Sampling

Representative samples were collected from every plot at one hour after pesticides treatments (initial deposits) and 1, 3, 5, 7, 12, 15, and 18 days after the last application. Samples from untreated control plots were also collected in the same way. Clean polyethylene bags were used for preserving the collected samples and transported to the laboratory immediately after picking at room temperature. In all cases, less than 40 min passed between harvest and arrival to the laboratory. Samples are prepared and then stored at - 20 °C in a deep freezer until analysis.

Extraction and clean-up

The extraction and clean -up processes were carried out at the Water and Environment Laboratory in the Regional Center for the Development of Southern Upper Egypt - Quraman Island – Sohag. The samples were prepared with the QuEChERS method according to (Anastassiades *et al.* 2003). Ten grams of homogenized tomatoes sample were weighed into a 50 ml PTFE centrifuge tube, 10 mL of acetonitrile were added, the tube was vigorously hand shaken for 1 min, 4 g of anhydrous MgSO₄ and 1 g of sodium chloride were added, the tube

was hand shaken for 30 s., and the mixture was centrifuged at = 5000 rpm for 5 min. An aliquot of 1.0 mL was transferred into the dSPE tubes containing 25 mg PSA and 150 mg MgSO₄ for clean-up. The tubes were well capped and vortexed for 30 s., then centrifuged for 5 min at = 5000 rpm. The combined elute was filtered through a 0.22-μm nylon syringe filter into an auto sampler vial for HPLC injection.

Chromatographic conditions

HPLC was used to determine samples' final results. The HPLC system is an Agilent 1260 series with a photodiode array detector attached to an analytical column with dimensions of 150 mm 4.6 mm id, 5 μm ODS. The mobile phase's flow rate (acetonitrile 80% + water 20%) was 1 ml/min, and the injection volume was 20 μl for fenpyroximate and the detection wavelength was chosen at 260 nm. The mobile phase (acetonitrile 70% + water 30%) flow rate for acetamiprid was 1 ml/min, and the injection volume was 20 μl. A 205 nm detection wavelength was used. While the flow rate of the mobile phase for metalaxyl-m (acetonitrile 40%, methanol 20%, and water 40%) was 1.2 ml/min and the injection volume was 20 μl, A 200 nm detection wavelength was used. Under these conditions the retention time was 3.2, 3.6 and 4.8 min for fenpyroximate, acetamiprid and Metalaxyl-M, respectively.

RESULTS AND DISCUSSION

Method performance

Acetamiprid, metalaxyl-M, and fenpyroximate residue recovery rates for tomato samples were determined (Table 1). Analysis of blank tomato samples was used to test the method's selectivity; there are no interference signals from endogenous matrix components. Recovery assays at concentrations of 0.1, 0.5, and 1.0 mg/kg were conducted. The peak area of the analytes added to and extracted from the matrix was compared to the peak area of the pure standard to determine recovery. In order to create the working solutions for the tomato extraction method, the stock solutions of acetamiprid, metalaxyl-M, and fenpyroximate were diluted in acetonitrile. Before starting to use pesticides, untreated, homogenized tomato samples were analysed. The average recoveries were respectively 87.71 ± 1.33, 92.08 ± 2.35 and 91.77 ± 1.06.

Table (1): Recovery percentages of acetamiprid, metalaxyl-m and fenpyroximate in tomatoes fruits.

Spiking level (mg/kg) (n*=3)	Acetamiprid		Metalaxyl-M		Fenpyroximate	
	Mean recovery ±SD	% RSD	Mean recovery ±SD	%RSD	Mean recovery ±SD	% RSD
0.1	92.58±1.22	1.42	87.90±1.99	3.07	81.34±0.95	3.47
0.5	65.18±1.57	2.55	89.01 ±2.47	2.89	89.27±1.28	3.05
1	105.38±1.20	2.01	99.32±2.58	2.07	104.69±0.94	2.48
Average	87.71± 1.33	1.99	92.08± 2.35	2.68	91.77± 1.06	3.00

*: Number of replicate

The single laboratory validation strategy, European Commission guidelines, and method validation protocols for pesticide residues analyses were followed for performing method validation (SANTE/12682/ (2019) and Thompson *et al.*, 2002). Limits of quantification (LOQ) were adjusted to a signal-to-noise ratio of 10, while the limits of detection (LOD) were set to a signal-to-noise ratio of 3 with reference to background noise obtained from the blank sample. The LOQs were 0.05 µg/g for acetamiprid and fenpyroximate; and 0.1 µg/g for metalaxyle -M, while the LODs were 0.01 µg/g acetamiprid and fenpyroximate; and 0.05 µg/g metalaxyle -M. The limits of quantification were, in every instance, lower than the MRLs set by the EU and Codex Committee. The findings revealed that the first-order rate equation was used to calculate the dissipation kinetics and behavior of tested compounds in tomatofruits: $C_t = C_0 e^{-kt}$, where k is the rate constant per day, C_0 is the initial concentration, and C_t is the pesticide concentration at time t. Pesticide half-life can be used to estimate pesticide persistence in the environment. The half-life ($t_{1/2}$), which measures the amount of time it takes for a pesticide to degrade to half its initial concentration, gives information about how quickly plants and the environment absorb pesticides. The half-life ($t_{1/2}$) was calculated as $t_{1/2} = \ln 2/k$ from the k value for each experiment (Abd-Alrahman *et al.*, 2012 and Moye *et al.*, 1987).

Residues of acetamiprid on and in tomato fruits cultivated in open field and greenhouse and effect of washing, and cooking process in removing on its residues from tomato fruits:

The concentration of the initial deposits of acetamiprid on unwashed tomato fruits growing in open field and greenhouse table (2) were 2.13 and 3.25 µg/g, respectively. The residues decreased to 1.45 and 2.04 µg/g, respectively within the first 24

hours after spraying. The residues of acetamiprid in open field samples dropped to 0.65, 0.13 and 0.04 µg/g after 3,5,7days after treatment and the corresponding values for greenhouse were 0.88, 0.51 and 0.14 µg/g after 3,5,7days, respectively. While the amount of residues reached 0.02 µg/g of acetamiprid after 12 days of treatment in green house samples. Also, results showed that the amount of acetamiprid residues were below the detection limits after 12 and 15 days in open field tomato samples and after 15 days in greenhouse tomato samples. The results indicated the great influence of washing method in removing or elimination of acetamiprid residues from sprayed tomatoes growing in open field and greenhouse. After one day of spraying, the residues of acetamiprid on unwashed tomato fruits were 1.45, and 2.04 µg/g. These reduced from 1.27 and 1.08 µg/g (one hour of treatment) to reach 0.71, and 0.72 µg/g on tomato washed with tap water for open filed and greenhouse sample, respectively. The effect of cooking process upon the amount of acetamiprid residues left in the treated tomato fruits. Data showed that tomato paste was nearly free from any detectable residues of acetamiprid. According to the maximum residues limits (MRLs) of acetamiprid was 0.5 µg/g in tomato fruits, presented in (EU, 2019). Acetamiprid sprayed tomato fruits in open field can be picked up after 5 days and 6 days in greenhouse samples, from spraying. The same conclusion was pointed out by Badawy *et al.*, (2019) found that the PHI values of acetamiprid on tomato fruits residues grown in greenhouse were 3.72 days. Thus, the fruits are safe for consumers after 4 days for acetamiprid. Acetamiprid residues were below the already established European maximum residue limits (codex MRLs) (0.2 mg/kg) days after application. Also, Abdelfatah *et al.*, (2020) found that the half-life time of abamectin, spinosad, and acetamiprid

residues in tomato fruits under field conditions were 3.91, 0.36, 1.19 days, respectively. According to the maximum residue limits (MRL), the pre-harvest interval (PHI) of abamectin, spinosad, and acetamipride were 10, 1, 1 days after the application, respectively. This recommended that the use of tomato fruits treated with these pesticides were safe for consumption after these intervals. El-Sayed, *et al.*, (1977) they reported that waiting periods between application of insecticides and harvesting for marketing were defined for the consumer safety, avoiding health hazards, ranged between one and twelve days according to kinds of

pesticides and vegetables. This finding is in harmony with those of Abd El-Daim and Zidan (1996) found that insecticide residues on tomato completely removed by one of six sequential processes. Tomato paste removed all insecticide residues. Generally, removal of residues by cooking process may be attributed to decomposition of residues by heating in addition to hydrolysis in water. It is finally observed from this study that tomato fruits could be safely consumed after processing steps, because the remove most insecticide residues to below the (MRLs).

Table (2): Residues of acetamiprid on and in tomato fruits cultivated in open field and greenhouse.

Days after spraying	Unwashed		Washed		Tomato paste	
	Residues (mg/kg)	% Loss	Residues (mg/kg)	% Loss	Residues (mg/kg)	% Loss
Tomato fruits cultivated in open field						
0	2.13	0.00	1.27	40.38	ND	---
1	1.45	31.92	0.71	51.03	ND	---
3	0.65	69.48	0.24	63.08	ND	---
5	0.13	93.89	0.05	61.54	ND	---
7	0.04	98.12	ND	---	ND	---
12	ND	---	ND	---	ND	---
15	ND	---	ND	---	ND	---
MRL	0.5 (EU, 2019)					
PHI	5 days					
RL ₅₀	1.80		1.19		---	
Tomato fruits cultivated in greenhouse						
0	3.25	0.00	1.08	66.77	ND	---
1	2.04	37.23	0.72	64.71	ND	---
3	0.88	72.92	0.41	53.41	ND	---
5	0.51	84.31	0.24	52.94	ND	---
7	0.14	95.69	ND	---	ND	---
12	0.02	99.38	ND	---	ND	---
15	ND	---	ND	---	ND	---
PHI	7 days					
RL ₅₀	1.48		1.71		---	

ND = (Not detectable); MRL (Maximum Residue Limits); PHI (pre harvest intervals); RL50 (Residue half-life).

Residues of metalaxyl-M on and in tomato fruits cultivated in open field and greenhouse and effect of washing, and cooking process in removing on its residues from tomato fruits:

The concentration of the initial deposits of metalaxyl-M Table (3) on unwashed tomato fruits growing in open field and greenhouse were 2.75 and 2.39 µg/g, respectively. The amount of residues decreased to 1.16 and 1.76 µg/g, respectively within the first 24 hours after spraying. The residues of metalaxyl-M dropped to 0.74, 0.22, 0.08 µg/g, and undetectable after 3, 5, 7, and

12 days, respectively. The corresponding values for greenhouse were 0.43, 0.23, 0.12, and 0.02 µg/g, respectively. Residues of metalaxyl-M became below the detection limits after 15 and 18 days of treatments in both open field and greenhouse samples. The great influence of washing method in removing or elimination of metalaxyl-M residues from sprayed tomatoes growing in open field and greenhouse. After one hour of spraying, the residues of metalaxyl-M on washed tomato fruits were 1.19, and 1.20 µg/g. These residues reduced to 0.48 and 0.65 µg/g on tomato washed with tap

water. Washing process removed residues from 56.73 to 81.08 and 49.79 to 86.96 % for metalaxyl-M on tomato fruits cultivated in open field and greenhouse, respectively. As a general trend, washing process caused considerable removal of metalaxyl-M residues. The effect of cooking process upon the amount of metalaxyl-M residues left in the treated tomato fruits. The tomato sauce was nearly free from any detectable residues of metalaxyl-M. The half-life periods of metalaxyl-M residues in unwashed tomato fruits cultivated in open field and greenhouse were 1.51 and 1.91 days, respectively. According to the EU (2017) codex, maximum residues limits (MRLs) for metalaxyl-M, was 0.3 µg/g in tomato fruits; so, metalaxyl-M treated tomato fruits in open field and greenhouse can be picked up after 5 days, from spraying. The same conclusion was pointed out by Malhat, (2017), who found that residues of metalaxyl dissipated below the maximum residue limit (MRL) of 0.5 µg/g in 7 days. Half-life ($t_{1/2}$) for degradation of metalaxyl on tomato fruit was observed to be 1.81 days. A waiting period of 7 days is suggested for safe consumption of tomato. While Abd Al-Rahman *et al.*, (2012) they found

that the half-life of metalaxyl-M, metalaxyl fungicides were found to be 1.98, and 4.88 days, respectively. Pre harvest intervals (PHI) for metalaxyl-M, metalaxyl fungicides were 3 and 9 days, respectively. Lixu *et al.*, (2009) stated that metalaxyl-M degrades rapidly from tomato pulp after application to tomato plants, and its half-life was 1.74 day. The rapid degradation/dissipation of fungicide in subsequent sampling after spraying may be due to dilution of the toxicant due to plant growth coupled with favorable climatic conditions, i.e., clear sunshine, temperature, and relative humidity prevailing during the application. This finding is in harmony with those of Abd El-Daim and Zidan (1996) found that insecticide residues on tomato completely removed by one of six sequential processes. Tomato paste removed all insecticide residues. Generally, removal of residues by cooking process may be attributed to decomposition of residues by heating in addition to hydrolysis in water. It is finally observed from this study that tomato fruits could be safely consumed after processing steps, because the remove most insecticide residues to below the (MRLs).

Table 3. Residues of metalaxyl -M on and in tomato fruits cultivated in open field and greenhouse.

Days after spraying	Unwashed		Washed		Tomato paste	
	Residues (mg/kg)	% Loss	Residues (mg/kg)	% Loss	Residues (mg/kg)	%
Tomato fruits cultivated in open field						
0	2.75	0.00	1.19	56.73	ND	---
1	1.16	57.81	0.48	58.62	ND	---
3	0.74	73.09	0.14	81.08	ND	---
5	0.22	92.00	0.07	68.18	ND	---
7	0.08	97.09	ND	---	ND	---
12	ND	---	ND	---	ND	---
15	ND	---	ND	---	ND	---
18	ND	---	ND	---	ND	---
MRL	0.3 (EU, 2017)					
PHI	5 days					
RL ₅₀	0.80		0.76		---	
Tomato fruits cultivated in greenhouse						
0	2.39	0.00	1.20	49.79	ND	---
1	1.76	26.35	0.65	63.07	ND	---
3	0.43	82.00	0.12	72.09	ND	---
5	0.23	90.37	0.03	86.96	ND	---
7	0.12	94.97	ND	---	ND	---
12	0.02	99.16	ND	---	ND	---
15	ND	---	ND	---	ND	---
18	ND	---	ND	---	ND	---
PHI	5 days					
RL ₅₀	2.27		1.13		---	

ND= (Not detectable); MRL = (Maximum Residue Limits); PHI =(pre harvest intervals); RL50 =(Residue half-life)

Residues of fenpyroximate on and in tomato fruits cultivated in open field and greenhouse and effect of washing, and cooking process in removing on its residues from tomato fruits:

The initial deposits of fenpyroximate (Table 4) on unwashed tomato fruits growing in open field and greenhouse were 3.49 and 4.28 µg/g, respectively. The amount of residues decreased to 2.35 and 2.57 µg/g, respectively within the first 24 hours after spraying. The residues of fenpyroximate dropped to 1.02, 0.52, 0.21, 0.05 µg/g and undetectable after 3, 5, 7, 12 and 15 days, respectively. The corresponding values for greenhouse were 1.55, 0.35, 0.13, 0.01 and undetectable µg/g after 3, 5, 7, 12 and 15 days, respectively. The great influence of washing method in removing or elimination of fenpyroximate residues from sprayed tomatoes growing in open field and greenhouse. After one day of spraying, the residues of fenpyroximate on unwashed tomato fruits were 2.35, and 2.57 ppm. These reduced to 1.14, and 0.96 ppm on tomato washed with tap water. Washing process removed residues from 21.49 to 52.38 and 53.74 to 77.42 % for fenpyroximate on tomato fruits cultivated in open field and greenhouse, respectively. As a general trend, washing process caused considerable removal of fenpyroximate residues. The effect of cooking process upon the amount of fenpyroximate

residues left in the treated tomato fruits. Data showed that tomato paste was nearly free from any detectable residues of fenpyroximate. The washing and cooking procedures lead to the decrease of pesticide residues in tomato growing in greenhouse and open field. Among them, the cooking procedure has the greatest impact on residual reduction. Therefore, these procedures can be used as simple and effective processing techniques for reducing and removing pesticides from greenhouse products before their consumption. The half-life periods of fenpyroximate residues in unwashed tomato fruits cultivated in open and greenhouse were 2.14 and 1.77 days, respectively. According to the EU (2019) codex the maximum residues limits (MRLs) for fenpyroximate was 0.3 ppm in tomato fruits. Fenpyroximate –sprayed tomato fruits in open field and greenhouse can be picked up after 7 days, from spraying. A few papers have been published to describe the pre-harvest interval of fenpyroximate residues after treatment on vegetables, Alakhdar, *et al.*, (2021); Taklaet *al.*, (2020) and Mahmoud (2004). Alakhdaret *al.*, (2021) found that the pre-harvest interval (PHI) period was (10 and 4 days), (10 and 10 days) and (6-7 and 6 days) for tomatoes and cucumbers treated by abamectin, fenpyroximate, and buprofezin, respectively.

Table (4) Residues of fenpyroximate on and in tomato fruits cultivated in open field and greenhouse

Days after spraying	Unwashed		Washed		Tomato paste	
	Residues (mg/kg)	% Loss	Residues (mg/kg)	% Loss	Residues (mg/kg)	% Loss
tomato cultivated in open field						
0	3.49	0.00	2.74	21.49	ND	---
1	2.35	32.66	1.14	51.49	ND	---
3	1.02	70.77	0.61	40.20	ND	---
5	0.52	85.10	0.33	36.54	ND	---
7	0.21	93.98	0.10	52.38	ND	---
12	0.05	98.56	ND	---	ND	---
15	ND	---	ND	---	ND	---
18	ND	---	ND	---	ND	---
MRL	0.3 (codex 2019)					
PHI	7 days					
RL ₅₀	1.75		0.79		---	
tomato cultivated in greenhouse						
0	4.28	0.00	1.98	53.74	ND	---
1	2.57	39.95	0.96	62.65	ND	---
3	1.55	63.78	0.35	77.42	ND	---
5	0.35	91.82	0.11	68.57	ND	---
7	0.13	96.96	0.04	69.23	ND	---
12	0.01	99.76	ND	---	ND	---
15	ND	---	ND	---	ND	---
18	ND	---	ND	---	ND	---
PHI	7 days					
RL ₅₀	1.36		0.96		---	

ND= (Not detectable); MRL = (Maximum Residue Limits); PHI = (pre harvest intervals); RL50 = (Residue half-life)

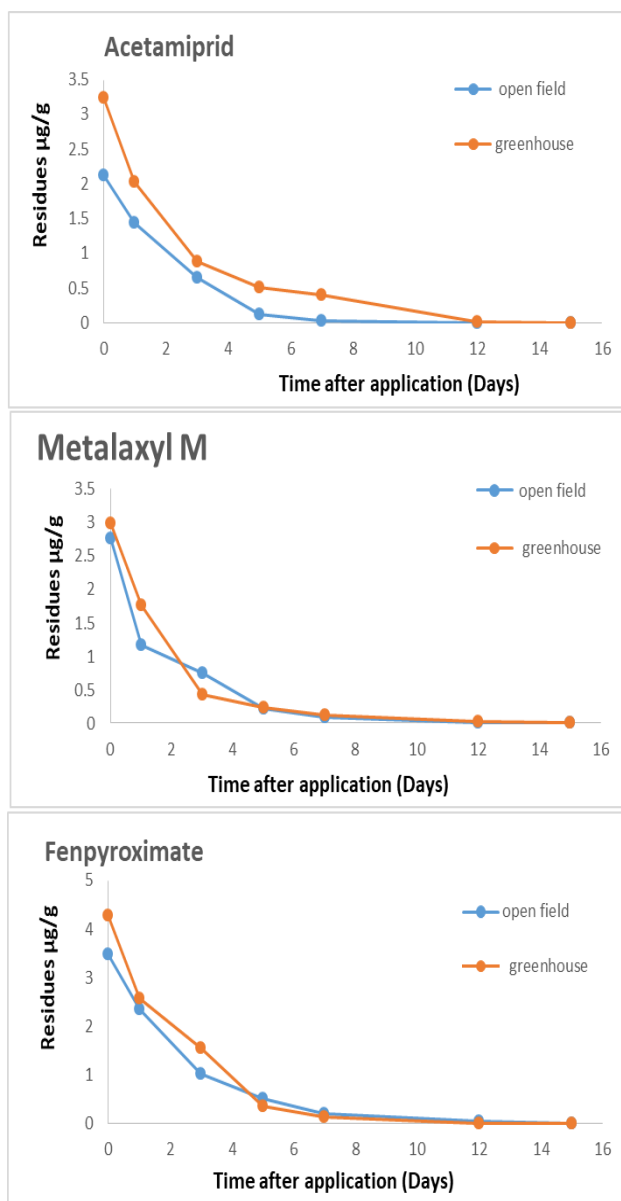


Figure (2): Dissipation of tested pesticides in the field and greenhouse.

The persistence of pesticides is influenced by a variety of factors. These include the pesticide's general stability as a parent ingredient or as metabolites, volatility, solubility, formulation, and method and site of application. (Cabraset *al.*, 1989). Additional environmental factors include temperature, precipitation (and humidity), and air movement. (Gennariet *al.*, 1985), affect the longevity of pesticides. In addition to the correlation between the treated surface's weight and the living state of the plant surface, other factors include the characteristics of the treated surface, the treated surface's species, the nature of

the harvested crop, the cuticle's structure, the stage and rate of growth, and the general health of the plant. (Ambrus,1978; Tewary *et al.*, 2005; Malhat *et al.*, 2014; Malhat, 2017) noted that the rapid degradation/dissipation of the fungicide metalaxyl in tomato fruit sampling after spraying may be caused by dilution of the toxicant due to plant development along with favourable environmental circumstances, i.e., bright daylight, temperature, and relative humidity prevailing.

CONCLUSION

A reliable QuEChERS technology method with (HPLC-DAD) was applied for the determination of acetamiprid, metalaxyl-M, and fenpyroximate in tomato fruits. The method used for extraction, clean-up and estimation of acetamiprid, metalaxyl-M, and fenpyroximate in tomato fruits was found to be satisfactory, qualitatively as well as quantitatively. acetamiprid, metalaxyl-M, and fenpyroximate rapidly degraded in tomato fruits. The initial concentration of acetamiprid, metalaxyl-M, and fenpyroximate in greenhouse (3.25, 2.99 and 4.28 mg/kg) was higher than that in the open field (2.13, 2.75 and 3.49 mg/kg) and the half-lives of acetamiprid, metalaxyl-M, and fenpyroximate in tomato fruits ranged from 1.48, 2.27 and 1.36 (greenhouse) to 1.80, 0.80 and 1.75 (open field) days. The Preharvest intervals (PHI) for these pesticides in greenhouse and field tomato plants ranged from 5 to 7 days. The residue of acetamiprid, metalaxyl-M, and fenpyroximate is affected by factors such as light, temperature, humidity, rainfall, wind speed, and crop growth rate. Results showed that tomato paste was nearly free from any detectable residues of acetamiprid, metalaxyl-M, and fenpyroximate. Generally, removal of residues by cooking process may be attributed to decomposition of residues by heating in addition to hydrolysis in water.

REFERENCES

- Abd Al-Rahman, S. H., H., Almaz, M. M., and Osama, I. A. (2012). Determination of degradation rate of acaricide fenpyroximate in apple, citrus, and grape by HPLC-DAD. *Food Analytical Methods*, 5 (2): 306-311.

- Abd-El-Daim, Y. A. and Zidan, Z. H. (1996). Removal of profenofos and methomyl insecticide residues from tomatoes and potatoes by processing. *Arab Universities Journal of Agricultural Sciences*, 4 (1&2): 113-123.
- Abdelfatah, R. M., Saleh, A. A., Elgohary, I. R. A., and Negm, S. E. (2020). Dissipation of some Pesticide Residues in Tomato (*Lucopersicon esculentum L.*) Fruits Using QuEACHERS Methodology under the Egyptian Field Conditions. *Journal of Plant Protection and Pathology*, 11 (7): 327-332.
- Alakhdar, H. H., Dar, A. A. R. and Abd-El Rahman, T. A. (2021). Toxicological evaluation and residual analysis of some acaricides against two-spotted spider mite *Tetranychus urticae* by using certain ground spraying equipment on cotton and its intercrops in Egypt. *International Journal of Entomology Research*, 6 (1): 58-67.
- Allen, G., Halsall, C. J., Ukpebor, J., Paul, N. D., Ridall, G. and Wargent, J. J. (2015). Increased occurrence of pesticide residues on crops grown in protected environments compared to crops grown in open field conditions. *Chemosphere*, 119: 1428-1435.
- Al-Rahman, A., Hussein, S., Almaz, M. M., and Ahmed, N. S. (2012). Dissipation of fungicides, insecticides, and acaricide in tomato using HPLC-DAD and QuEACHERS methodology. *Food Analytical Methods*, 5(3): 564-570.
- Abd-Alrahman, S. H. and Kotb, G. (2020). Dissipation kinetics of pymetrozine in tomato field ecosystem. *The Egyptian Journal of Hospital Medicine*, 81(7): 2305-2309.
- Ambrus, A. (1978). The influence of sampling methods and other field techniques on the results of residue analysis. *Advances in pesticide science, Zürich*, part 3 pp., 620-633.
- Anastassiades, M., Lehotay, S. J., Stajnbaher, 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.
- Anonymous, (2019). Codex Alimentarius Commission, Food and Agriculture Organization of the United Nation. Joint FAO/WHO Food Standards Programme Codex Committee on Pesticide Residues, Thiety-fifth session, Rotterdam, The Netherlands, pp. 153 and 191.
- Badawy, M. E., Ismail, A. M. and Ibrahim, A. I. (2019). Quantitative analysis of acetamiprid and imidacloprid residues in tomato fruits under greenhouse conditions. *Journal of Environmental Science and Health, Part B*, 54 (11): 898-905.
- Boobis, A. R., Ossendorp, B. C., Banasiak, U., Hamey, P. Y., Sebestyen, I. and Moretto, A. (2008). Cumulative risk assessment of pesticide residues in food. *Toxicology letters*, 180 (2): 137-150.
- Cabras, P., Gennari, M., Meloni, M., Cabitza, F. and Cubeddu, M. (1989). Pesticide residues in lettuce. 2. Influence of formulations. *Journal of Agricultural and Food Chemistry*, 37 (5): 1405-1407.
- El- Sayed, M. M., Dogheim, S. M., Hindi, S. A., Shahin, A. and M. Abdel- Salam (1977): Persistence of certain organophosphorus insecticides on some vegetables. *Bulletin-Entomological Society of Egypt*, (10): 41- 45.
- EU (2017). [European Union. Maximum residue limits for pesticides. <http://ec.europa.eu/food/plant/pesticides/eupesticidesdatabase/public/?event=download.MRL>.
- EU (2019). [European Union. Maximum residue limits for pesticides. <http://ec.europa.eu/food/plant/pesticides/eupesticidesdatabase/public/?event=download.MRL>.
- Gennari, C., Bernardi, A., Colombo, L. and Scolastico, C. (1985). Enantioselective synthesis of anti-. alpha. -methyl-. beta. -hydroxy esters through titanium tetrachloride-mediated aldol condensation. *Journal of the American Chemical Society*, 107 (20): 5812-5813.
- Lixu, H. B. T. J. P. and Hongsheng, X. D. L. (2009). Residue and degradation of metalaxyl-M in tomato. *Chinese Journal of Tropical Agriculture*. 44(2): 462-476.
- Mahmoud, H. A. (2004). Biochemical studies on the behavior of some pesticides in broad bean crop (Doctoral dissertation, PhD Thesis, Faculty of Agriculture, Cairo University).
- Malhat, F. M. (2012). Determination of chlorantraniliprole residues in grape by high-

- performance liquid chromatography. *Food Analytical Methods*, 5 (6): 1492-1496.
- Malhat, F. M. (2017). Persistence of metalaxyl residues on tomato fruit using high performance liquid chromatography and QuEChERS methodology. *Arabian journal of chemistry*, 10: 765-768.
- Malhat, F., Badawy, H. M., Barakat, D. A. and Saber, A. N. (2014). Residues, dissipation and safety evaluation of chromafenozide in strawberry under open field conditions. *Food Chemistry*, 152: 18-22.
- Mermer, S., Yalcin, M. and Turgut, C. (2020). The uptake modeling of DDT and its degradation products (o, p' - DDE and p, p' - DDE) from soil. *SN Applied Sciences*, 2 (4): 1-7.
- Moye, H. A., Malagodi, M. H., Yoh, J., Leibee, G. L., Ku, C. C. and Wislocki, P. G. (1987). Residues of avermectin B_{1a} in rotational crops and soils following soil treatment with [¹⁴C] avermectin B_{1a}. *Journal of agricultural and food chemistry*, 35 (6), 859-864.
- Nougadère, A., Sirot, V., Kadar, A., Fastier, A., Truchot, E., Vergnet, C., Vergnet, C., Hommet, F., Baylè, J., Gros, P. and Leblanc, J. C. (2012). Total diet study on pesticide residues in France: levels in food as consumed and chronic dietary risk to consumers. *Environment international*, 45: 135-150.
- Oliva, J., Cermeño, S., Cámara, M. A., Martínez, G. and Barba, A. (2017). Disappearance of six pesticides in fresh and processed zucchini, bioavailability and health risk assessment. *Food chemistry*, 229: 172-177.
- SANTE/12682/2019; Main changes introduced in Document with respect to the previous version (Document N SANTE/11813/2017) AqcGuidance_SANTE_2019_12682.pdf. <https://ec.europa.eu/food/sites>
- Shalaby, S. E. S., Elmetwally, I., Abou-elella, G. and Abdou, G. Y. (2022). Occupational workers understanding of pesticide labels and safety practices in Dakahlia Governorate, Egypt. *Egyptian Journal of Chemistry*, 66 (6): 367 – 380.
- Shalaby, S. E., Abdou, G. Y., El-Metwally, I. M., and Abou-elella, G. (2021). Health risk assessment of pesticide residues in vegetables collected from Dakahlia, Egypt. *Journal of Plant Protection Research*, 61 (3): 254-264.
- Soydan, D.K., Turgut, N., Yalçın, M., Turgut, C. and Karakuş, P.B.K. (2021). Evaluation of pesticide residues in fruits and vegetables from the Aegean region of Turkey and assessment of risk to consumers. *Environmental Science and Pollution Research*, 28: 27511–27519.
- Takla, S. S., El-Dars, F. M., Amien, A. S. and Rizk, M. A. (2020). Analysis of fenpyroximate residues in eggplant, Aubergine (*Solanum melongena L.*) during crop production cycle by HPLC and determination of its biological activity. *Egyptian Academic Journal of Biological Sciences, F. Toxicology and Pest Control*, 12 (1): 163-174.
- Tewary, D. K., Kumar, V., Ravindranath, S. D. and Shanker, A. (2005). Dissipation behavior of bifenthrin residues in tea and its brew. *Food Control*, 16 (3): 231-237.
- Thompson, M., Ellison, S. L. and Wood, R. (2002). Harmonized guidelines for single-laboratory validation of methods of analysis (IUPAC Technical Report). *Pure and applied chemistry*, 74(5) :835-855.
- Tomlin, C. D. (2009). The pesticide manual: a world compendium. British Crop Production Council, Farnham, Surrey, United Kingdom.
- Tudi, M., Daniel Ruan, H., Wang, L., Lyu, J., Sadler, R., Connell, D., Chu, C. and Phung, D. T. (2021). Agriculture development, pesticide application and its impact on the environment. *International journal of environmental research and public health*, 18(3): 1112-1135.
- Zhang, W., Jiang, F. and Ou, J. (2011). Global pesticide consumption and pollution: with China as a focus. *Proceedings of the international academy of ecology and environmental sciences*, 1 (2): 125-144.

الملخص العربي

دراسة حركية اختفاء اسيتامبريد وميتالكسيل-ام وفينبيروكسيميت في النظام البيئي للطماطم المنزوعة في الحقل والبيوت المحمية

جابر¹، س.س؛ الحفنى²، د.س؛ عبداللطيف، أ.ع؛ وسلام، أ.أ.
1- قسم وقاية النبات، كلية الزراعة، جامعة سوهاج
2- قسم متبقيات المبيدات والتلوث البيئي، المعمل المركزي
للمبيدات، مركز البحوث الزراعية

ان الاستخدام المفرط للمبيدات الحشرية يؤثر سلبا علي البيئة وصحة الانسان. في هذه الدراسة تم تقييم معدل اختفاء ثلاثة مبيدات حشرية شائعة الاستخدام في زراعة الطماطم وهي اسيتامبريد، ميتالكسيل -ام وفينبيروكسيميت. تم جمع عينات الطماطم من الحقول والبيوت المحمية خلال اسبوعين من تطبيق المبيدات وتم تقدير متبقيات المبيدات عن طريق استخلاص المبيدات بطريقة QUECHERS واستخدام جهاز التحليل الكروماتوجرافي السائل عالي الأداء. اوضحت النتائج أن معدلات عملية استرجاع مبيدات اسيتامبريد، الميتالكسيل - ام، فينبيروكسيميت عند تركيزات 0.1، 0.5، 1.0 ملجم/كجم هي 87.71، 92.08، 91.77% علي التوالي. تراوحت فترة ما قبل الحصاد (PHI) لهذه المبيدات في البيوت المحمية والحقل من 5 - 7 أيام. فترة عمر النصف لمبيدات اسيتامبريد وميتالكسيل - ام وفينبيروكسيميت هي 1.80، 0.80، 1.75 يوم علي التوالي لعينات الطماطم المأخوذة من الحقل المفتوح بينما كانت القيم المقابلة في البيوت المحمية هي 1.48، 2.27، 1.36 يوم. لوحظ أن متبقيات المبيدات في الطماطم تأثرت بعملية الطهي لذا لم يلاحظ متبقيات في صلصة الطماطم أو قد تكون أقل من حساسية الجهاز.