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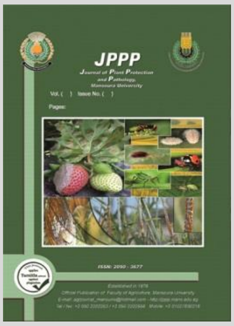
Quantitative Analysis of Some Insecticide Residues Using Quechers Methodology on Pepper (*Capsicum annuum*) Fruits Under Greenhouse Conditions

Rehab E. Khalil*; F. A. Shaheen ; A. A. Abd-El Hady and A. A. Saleh

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



ABSTRACT

The residual levels and degradation behavior of some insecticides (imidacloprid, acetamiprid, clothianidin, pymetrozine, pyriproxyfen, azadirachtin, and spinetoram) in pepper *(Capsicum annuum*) fruits under greenhouse conditions were determined. The high performance-liquid chromatography with photodiode-array detector "HPLC/ DAD" was used and QuEChERS methodology was followed. The tested insecticides were applied to pepper at the recommended rates. The pepper samples were taken at zero time (1 hour) and after 1, 3, 5, 7, 10, 15, and 21 days post-application. The dissipation half-life time (RL_{50}) of imidacloprid, acetamiprid, clothianidin, pymetrozine, pyriproxyfen, azadirachtin, and spinetoram residues in pepper fruits were 0.239, 1.994, 3.277, 0.151, 7.0233, 2.0285 and 1.251 days, respectively. According to, the maximum residue limit "MRL", the pre-harvest intervals "PHIs" were 3, 5, 7, 1, 10, one hour and 1 day after the application for imidacloprid, acetamiprid, clothianidin, pymetrozine, pyriproxyfen, azadirachtin, and spinetoram, respectively. Results of this study suggest that the dissipation data showed that the, usage of peppers treated with the tested insecticides was safe to consume and prevented health problems from consumers after these intervals.

***Keywords**:* insecticides, pepper, dissipation, HPLC, PHI, RL_{50}.

INTRODUCTION

Vegetables are frequently utilized as a source of fiber and vitamins to meet the requirements of a balanced diet (Bempah and Donkor 2011).

Pepper is a significant commercial crop due to its gastronomic, industrial, and medicinal properties (Diao *et al*., 2017). Due to their nutritional value, pepper fruits are an important element of many diets worldwide. Furthermore, it contains a high concentration of minerals and vitamins, such as potassium and vitamins (A and C) (Kim *et al*., 2007). Pepper fruits contain high levels of phytochemicals and antioxidants (Sanatombi and Rajkumari 2020), which are related to several health benefits, like maintaining healthy skin and eyesight (Dreher and Davenport 2013), boosting the immune system (Park *et al*., 2011). Consuming pepper decreases the risks of chronic diseases, such as; cardiovascular as well as cancer diseases (Park *et al*., 2014), and managing blood sugar levels (Dreher and Davenport 2013).

Insecticides are extensively employed on fruits and vegetables, especially under greenhouses to, protect agricultural products against harmful pests and diseases, increase their yields and improve their quality, and fulfill the consumer's needs. Therefore, insecticide residues in raw foods can be unsafe for consumers, particularly when consumed freshly (El-Lakwah *et al*., 1995). The widespread usage of insecticides for this purpose has ultimately resulted in several issues. Among the most common issues are the residues of highly stable insecticides in vegetables and fruits, (Abdella *et al*., 2015).

Usage of pesticides in high doses and farmers' lack of devotion to the preharvest intervals (PHIs) lead to the accumulation of insecticide residues on and in foods. Fruits are most suitable for insecticide residues because they are eaten fresh, followed by fresh vegetables, followed by cooked vegetables, and cooked grains. Monitoring the chemical insecticides in field crops grown in greenhouses is useful for identify the dangers of intensive insecticide use and raising awareness of the need to adhere to the dangers of insecticide residues in pepper plants, (Jawad and Hermize 2020).

It was found that excessive usage of chemical pesticides in pest management caused several environmental and health problems as demonstrated by research on the majority of vegetable crops that were controlled using different insecticides.

QuEChERS (quick, easy, cheap, effective, rugged, and safe) represents a novel method of sample preparation developed between 2000 and 2002 for the analysis of pesticide multi-residue (Anastassiades *et al*., (2003).

The QuEChERS approach covers a wide range of analytes, including high acidity and basic insecticides and extremely polar pesticides. Pre-harvest intervals (PHIs) are required by the maximum residue limits (MRL) rules to make sure that pesticides dissipate below the intended MRLs during harvest time (Karmakar, and Kulhestha 2009). Thus, degradation investigations on pesticide persistence in foodstuffs and the behavior of pesticide residues in agricultural regions are needed to ensure the safety of food and protect the environment. (Abdella *et al*., 2015).

The QuEChERS method has the advantages of excellent capacities for recovery, extraction, and enrichment of the analyte of interest in comparison with traditional methods. (Zainudin and Salleh 2017; Shahrbabki *et al*., 2018).

Neonicotinoid insecticides such as acetamiprid, imidacloprid, and clothianidin are the most extensively used insecticides worldwide, because they are characterized by the advantages of systemic activity, flexible use and favorable toxicological properties. They are used to control thrips, whiteflies, and aphids in numerous crops (Abdel-Gawad *et al*., 2008).

Pymetrozine, is a new pesticide with selective efficacy against homopteran insects, which has been recommended for controlling aphids in vegetables in Egypt. (Liang *et al*., (2012). On the other hand, pyriproxyfen, is an insect growth regulator with juvenile hormone analog

* **Corresponding author.**
E-mail address: rehab158@mans.edu.eg
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capabilities against a spectrum of arthropods, it has also been used since its debut onto the agrochemical market in the early 1990s, (Sihuincha *et al*., 2005).

Azadiractin is a ctetranoritepeniod (limonoids) extractable from the azadirchta plant species. More than 20 compounds are found in neem, that are responsible for characterizing small crushed, neem oils and seeds. Due to this selectivity and its quick dissipation. Azadirachtin is regarded as less harmful to the environment than chemical pesticides and poses a lower risk to non-target organisms, such as people, through food residues, groundwater, contamination of the surface, or exposure by accident, (Koul *et al*., 1990; Quarles 1994).

Spinetoram is a semi-synthetic insecticide derivative of the biologically active sub-stances spinosyns produced by the soil actinomycetes; *Saccharopolyspora spinosa* (Mertz and Yao, 1990) (Actinomycetales: *Pseudono cardiaceae*) (Galm and Sparks 2016), (Zhang and Li 2019). Spinetoram is distinguished by relatively extended persistence and a high safety profile, (Yee et al., 2007).

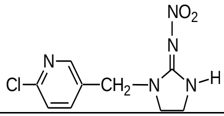
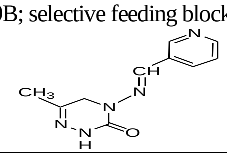
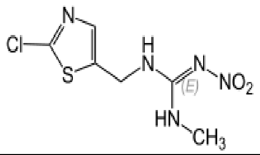
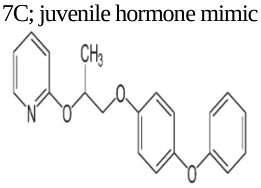
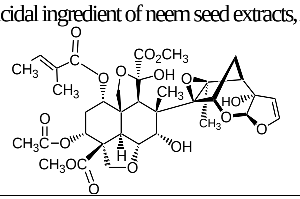
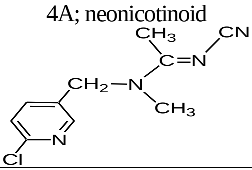
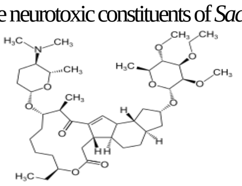
The current investigation aimed to, determine the dissipation behavior and residues of; imidacloprid, pymetrozine, clothianidin, pyriproxyfen, azadirachtin, acetamiprid, and spinetoram in pepper fruits under greenhouse conditions, to guarantee the safety of consumers and prevent health risks.

MATERIALS AND METHOD

Insecticides used: -

The common name, trade name, empirical formula, group of insecticide, and rate of application are displayed in Table (1).

Table 1. The common name, trade name, empirical formula, insecticide group, and rate of application of tested insecticides

Common name	Trade name	Empirical formula	Insecticide group (IRAC)	Field-recommended rates
Imidacloprid	Avenue 70%WG	$C_9H_{10}ClN_5O_2$	Neonicotinoid 	25cm^3/ 100L of water
Pymetrozine	Chess 50% W.G.	$C_{10}H_{11}N_5O$	9B; selective feeding blocker 	25g/100L of water
Clothianidin	Supertox-1 48% sc	$C_6H_8ClN_5O_2S$	Neonicotinoids 	200cm^3/fed.
Pyriproxyfen	Pyrofix 10 % E.C.	$C_{20}H_{19}NO_3$	7C; juvenile hormone mimic 	75cm^3/ 100L of water
Azadirachtin	Save oil 0.03% EC	$C_{35}H_{44}O_{16}$	The principal insecticidal ingredient of neem seed extracts, *Azadirachta indica* 	100cm^3/ 100L of water
Acetamiprid	Tolan 20% S.P.	$C_{10}H_{11}ClN_4$	4A; neonicotinoid 	25g / 100L of water
Spinetoram	Radiant SC 12%	$C_{42}H_{69}NO_{10}$	The mixture of two active neurotoxic constituents of *Saccharopolyspora spinosa* 	100cm^2/ feddan

Reagents and Chemicals

Authenticated reference analytical standards of imidacloprid, acetamiprid, clothianidin, pymetrozine, pyriproxyfen, azadirachtin, and spinetoram were supplied by Dr. Ehrenstorfer (GmbH). "Augsburg, Germany" and were of (purity 99.9%) for all pesticides. The HPLC grade of all the organic solvents utilized (methanol and acetonitrile) was obtained from "Scharlau, Barcelona, Spain," and the solvent's suitability was confirmed by running a reagent blank alongside the actual analysis. Primary-secondary amine "PSA, 40 µm Bondesil" was supplied from Supelco "Bellefonte, Pennsylvania, USA," while; sodium-chloride of analytical grade was obtained from "El-Naser Pharmaceutical Chemicals Co.", "Cairo, Egypt". An-hydrous magnesium sulfate of analytical grade was obtained from Merck "German" and it was activated before use by heating it for four hours at 400°C. in a "muffle furnace" the oven that, stored and cooled in a desiccator.

Preparation of Standard Solutions:

The stock solutions of imidacloprid, acetamiprid, clothianidin, pymetrozine, pyriproxyfen, azadirachtin, and spinetoram were prepared using acetonitrile as a solvent, containing 1,000 µg mL^{-1} of analyte. Serial dilution from the standard solutions was used for fortification of the matrices and instrument calibration purposes, which were stored at 4°C before use. Standard calibration curves for tested insecticides were created by graphing the concentrations of the analyte against the peak area.

Experiment Design

The field experiment was carried out at the Faculty of Agriculture, Mansoura University, Egypt, on pepper plants (*Capsicum annuum*) under greenhouse conditions covered with a net. All agricultural practices were followed as recommended. Eight treatments (measuring 35 m^2) were used for each, including the control (check), in three replicates each), and the distance between each plant in the same line was 50 cm. A hand operated knapsack sprayer (20 L.) was used to apply the treatments. A spray was applied when the size of pepper fruits reached the marketable size during the experimental period on June 26, 2022, with the recommended rate of pesticides.

Analytical Methods

Sampling:

The samples from treated and untreated plots were randomly collected after spraying of examined pesticides, at intervals of one hour, 1, 3, 5, 7, 10, 15, then after 21days, and one kilogram for each treatment. Immediately after collection, the samples of pepper were put in bags of plastic and kept at -20˚C till used for investigation.

Extraction and Clean-up

The QuEChERS method was used for the extraction and clean-up of pepper samples, as reported by (Anastassiades *et al*., 2003) with some modulation. 1 kg of each treatment was chopped into a small cube and then homogenized at high speed in a lab homogenizer for five minutes. 10 gm from each homogenized pepper sample were weighed then put in a (50 ml) Teflon-tube and added to ten ml of acetonitrile acidified with 1.0% acetic acid, and vigorously mixed with a vortex mixer for one min at maximum speed. Afterward, 4 gm of anhydrous magnesium sulfate [$MgSO_4$], 1 gm of sodium chloride [NaCl], 1 gm of sodium citrate dihydrate, and 0.5 gm disodium hydrogen citrate sesquihydrate were added, the mixture was extracted by aggressively shaking on a vortex for one minute and then centrifuged for 5 minutes at 5,000 rpm. Afterward, two milliliters of supernatant were filtered using a 0.2 µm PTFE filter [Millipore, USA] and analyzed using an (Agilent 1100 HPLC/DAD).

Chromatographic Analysis and Determination:

High-performance liquid chromatography (HPLC) analysis using an Agilent 1100 HPLC system (USA) provided with a manual injector (Rheodyne), thermostat compartment for the column, photodiode array-detector, and quaternary pump was used for the determination of imidacloprid, pymetrozine, clothianidin, pyriproxyfen, azadirachtin, acetamiprid, and spinetoram residues under the parameters outlined in Table 2.

Table 2. High Performance - Liquid- Chromatography (HPLC) conditions for tested insecticides:

Analytical parameter	Technical material						
	Imida	**Aceta**	**Cloth**	**Pymet**	**Pyri**	**Azadi**	**Spine**
UV wavelength	250nm	246 nm	250nm	250nm	260 nm	245 nm	245 nm
Mobile phase	65% acetonitrile + 23% water	60% acetonitrile + 40% water	90% acetonitrile + 10% water	90% acetonitrile + 10% water	90% acetonitrile + 10%water	60% acetonitrile: 30% methanol: 10%water	60% acetonitrile: 30% methanol: 10%water
Flow-rate	1ml/min.	0.8mL/min.	1 mL/ min.	1mL/ min.	1mL/min.	1ml/min	1 ml/min
Absolute retention time	4.15min.	5.98 min.	8.26min.	8.26min.	2.54 min.	6.84 min.	8.31 min.
Column	C18Zorbax XDE (250 mm x 4.6 mm, 5 µm). (The column was preserved at room temperature). For imidacloprid: (An Agilent1100) series equipped with an analytical column (150 mm × 4.6 mm. id, × 5 µm. ODS) For spinetoram: (Nucleosil-C18) (30 × 4.6 mm (i.d.) × 5 um. film thickness) with an automatic sampling valve.						

The residuals were determined by, comparing the peak area of standards to that of unknown or spiked samples performed under the same conditions.
Imida = Imidacloprid **Aceta= Acetamiprid** **Cloth= Clothiandin** **Pymet= Pymetrozine**
Pyri= Pyriproxyfen **Azadi= Azadirachtin** **Spine= Spinetoram**

Recovery studies:

A series of fortified samples were prepared, to estimate the validity of the method, extracted, and cleaned-up according to the tested pesticides. The fortification of samples of pepper fruits was conducted by adding a known amount of each pesticide's standard solution (1.0, 0.1, and 0.01 mg/ kg). The efficiency of the analysis method for fortified samples was evaluated for each insecticide. Table 3 shows the average recovery rates from pepper fruits. The percentages of recovery of tested pesticides were estimated using the following equation.

% R.= ((µg) percentage / (µg) added) x 100).

Table 3 revealed that the average recovery percentage reached from: 94.48 to 100.46 %, 89.68 to 99.46%, 91.70 to 100.28%, 94.23 to 101.82%, 86.15 to 92.33%, 98.09 to 101.26%, and 80.71 to 90.18% for imidacloprid, pymetrozine, clothianidin, pyriproxyfen, azadirachtin, acetamiprid, and spinetoram, respectively.

Table 3. Recovery Percentage of Tested Insecticides at Spiked Levels (1.0, 0.1, and 0.01ppm).

Spiked Level (mg/kg) (n= 6)	Recovery percentage of insecticides						
	Imida	Aceta	Cloth	Pymet	Pyri	Azadi	Spine
0.01	95.29±1.22	98.09±1.04	91.70±0.85	93.84±1.84	95.18±0.62	92.33±1.04	90.18±0.60
0. 1	100.46±1.11	101.26±1.62	100.28±1.22	99.46±1.46	101.82±1.91	86.15±1.62	88.15±1.24
1.0	94.48±1.63	100.68±0.45	98.54±0.98	89.68±1.34	94.23±0.38	89.82±0.45	80.71±0.91
Average	96.74	100.01	96.84	94.33	97.08	89.43	86.35

(n) replicates number. Imida = Imidacloprid Aceta= Acetamiprid Cloth= Clothiandin
Pymet= Pymetrozine Pyri= Pyriproxyfen Azadi= Azadirachtin Spine= Spinetoram

Half-life calculation

The residues of tested insecticides were determined by an equation by Mollhoff (1975). The decomposition rate (K) of each insecticide and the Half Life time (RL_{50}) on/in the samples of pepper were estimated using the equation of, Moye et al., (1987).

$$RL_{50} = \text{"}Ln_2 / K\text{"} = 0.6932 / K.$$
$$K = 1 / t\,x.\ Ln.\ (a/bx)$$

Where :-

K = Rate of decomposition. tx = Time in days.
a = Initial Residue. bx = Residue at x time.

Calculation of the Residues:

The following equation was used to calculate the residues (Mollhoff 1975).

$$ppm = mg/kg$$
$$ppm = \text{"Ps. B.V" / "Pst. G. C"} \times F$$

Where:

Ps = Sample peak area.
B = Amount injected of standard solution (ng).
V = Final volume of sample solution. (ml). Pst. = Standard peak area.
G = Sample weight (gm). C = Amount of sample solution injected (µl).
F = 100 / R (recovery rate). R = average of recovery.

RESULTS AND DISCUSSION

Persistence of imidacloprid, acetamiprid, clothianidin, pymetrozine, pyriproxyfen, azadirachtin and spinetoram used on and in pepper fruits:

Imidacloprid residue:

The preharvest interval (PHI), residues, degradation rate, and Half-Life (RL_{50}) value of imidacloprid on/in peppers are displayed in (Table 4).

Results showed that the initial deposit of imidacloprid in/on fruits of pepper are found to be 1.6115 ppm after one hour of spray, and then after one, three, five and seven days of spray dropped to; 1.1488, 0.1896, 0.0134 and 0.00326 ppm, respectively. For the same intervals mentioned previously, rates of loss were 28.72, 88.23, 99.17 and 99.80%, respectively. Imidacloprid was not detected in the treated plants after ten days post application. Imidacloprid had a degradation rate (K) of 2.8952 day^{-1}, and the half-life (RL_{50}) time was 0.239 days in treated fruits. Results indicated that pepper fruits, could be safe for consumption three days after application under greenhouse conditions, according to the maximum residue levels (MRLs) of imidacloprid in pepper plants (0.5 ppm), (European Union 2023).

These findings align with those of, Sabry, *et al*., (2016) who determined the residues of imidacloprid in fruits of tomato after 3 applications and detected that the, residues of imidacloprid were the maximum after 1 h. (zero time) of spray. Additionally, the residue of imidacloprid was found to be 2.62 mg/kg after the first treatment. The corresponding results were (3.14 and 3.42 mg/kg) after the 2nd and 3rd applications, respectively. Moreover, the data detected that the tested insecticide has a minimal pre harvest interval was 3.8 days.

Similarly, Hassanzadeh *et al*., (2012) determined the content and dissipation rate of imidacloprid on the cucumber fruits under greenhouse conditions, at the recommended dose (30 g ai/ ha^{-1}), and its double (60 g ai/ha^{-1}). The samples were collected at one hour to 21 days post treatment. The initial deposits were 3.65 and 1.93 mg/kg^{-1} at the double and single doses, correspondingly. The results illustrated that the amount of degradation in twenty-one days was 99.18% and 94.48%for the double and single dosages, respectively. Imidacloprid residues degraded below the maximum residual levels (MRLs) of one mg/kg^{-1} after three days. A waiting time of three days is recommended for the safe consumption of cucumbers. Half-life (RL_{50}) for dissipation of imidacloprid was observed to be 2.70 and 3.40 days at the double and single rates in cucumber, respectively.

Also, Akbar *et al.* (2010) determined the residue of imidacloprid on the cabbage plant and they suggested that after one day of treatment (MRL 0.5), the cabbage plant is safe to be consumed, also the rate of dissipation was 0.262 and 0.278 day^{-1} in both (head and leaf) of cabbage plant, correspondingly, whereas, the half-life (RL_{50}) (was 2.57 days).

In the same trend, Razik *et al*., (2022) determined the imidacloprid residues in tomato plants (fruits and leaves). The results appeared that the residual level of imidacloprid in fruits was less than the maximum residue limit (MRL) of 1 mg/kg of the Codex Alimentarius Commission, and they also found that the half-lives were 6.48 and 6.99 days for fruits and leaves of seedlings obtained from treated seeds and 4.59 and 5.59 days for untreated seeds, The preharvest interval (PHI) was one day on tomato fruits. Sharma *et al*., (2018) discovered that the, initial deposit of Imidacloprid on tomatoes was 0.643 mg/kg, also the half-life time (RL_{50}) was found to be 2.91 days. The relevant safety interval was calculated to be 0.36 day.

On the other hand, Abdella *et al*., (2015) studied the residual levels and dissipation rates of imidacloprid on and in the fruits of squash grown in an open field by HPLC /DAD with the (QuEChERS) methodology. The half-life value (RL_{50}) was found to be (1.93 days). The PHI was seven days after application for squash fruits, based on MRL, maximum residual level.

Badawy *et al*., (2019) determined imidacloprid residue in tomato fruits under greenhouse conditions in Egypt. The half-life period was 2.07 days. Imidacloprid residue was below the already established European maximum residue limits (EU-MRLs) (0.50 mg/kg), while, the preharvest interval (PHI) was 5days after application. In addition, Atia *et al.*, (2024) found that, the half-life values (RL_{50}) for imidacloprid in/on tomatoes were (2.71days). Levels of residue were above the maximum residue limits (MRLs) up to 3 days after spray. The determined PHI for imidacloprid was 6 days. The residue of imidacloprid in tomato fruits poses low health risks to consumers.

Another study by Jawad and Hermize (2020), determined the imidacloprid residues on the fruits of pepper plants in a greenhouse using HPLC liquid chromatography and (QuEchERS) method. Results indicated that the, highest rate of imidacloprid recovery was 95%, This investigation recommended that the, pepper plant could be safely consumed under greenhouse conditions after eight days of application. While, Reddy *et al*., (2007) reported that sweet pepper and tomato fruits could be safely consumed at 10 days after application. Abdel-Ghany *et al*., (2016) determined the disappearance rate and residual level of imidacloprid on cucumber fruits and soil. They found that the half-lives (Rl_{50}) were 8 days in cucumber fruits and 12 days in soil, while, the PHI was 12 days.

Acetamiprid residues:

Data presented in Table 4 revealed that the initial deposit of acetamiprid was 0.562 ppm after one-hour of spray, then decreased to (0.298, 0.250, 0.159, and 0.109 ppm) in and on pepper fruits after 1, 3, 5 and 7 days, respectively. The rates of loss were 46.98, 55.52, 71.71 and 80.60% after the same periods mentioned before, respectively. Acetamiprid was not detected in peppers at 10 days post-application. The dissipation rate (K) was 0.3475 day^{-1}, and the half-life value (RL_{50}) was 1.994 days. Depending on the maximum residue levels (MRL) of acetamiprid in pepper (0.2 ppm) (Codex 2023), data suggested that the fruits of the pepper might be consumed safely after 5 days of application.

Our results are in coordination with the findings of, Abdel-Ghany *et al*., (2016) who determined the residues and rate of disappearance of acetamiprid on cucumber plants and their half-lives, and they discovered that the preharvest interval (PHI) was 5 days, while the half-life (RL_{50}) in cucumber was 6.56 days.

Also, Abdelfatah *et al*., (2020) estimated the acetamiprid residues in/on tomatoes post-application at the recommended rate. They found that, the dissipation RL_{50} period in tomato fruits was 1.19 days. While, acetamiprid PHI was 1 day after the application which suggested that, the use of tomatoes sprayed with this pesticide would be safe for consumption after this interval. Also, El-Latif, *et al.*, (2022) estimated the residues of acetamiprid in tomatoes cultivated under greenhouse and field conditions. The recovery rate for acetamiprid was 1.33 ± 87.71%, and the half-lives were (1.80, and 1.48 days) in a greenhouse and open field. The PHIs were seven and five days in a greenhouse and an open field, respectively.

On the other hand, a simple-analytical approach was developed for the estimation of residues of acetamiprid in/on zucchini cultivated in greenhouse conditions using HPLC. After seven days of treatment the residues of acetamiprid were not detected. Regarding validation purposes, the recovery tests were conducted at high and low levels and gained rates of recovery ranging from (85.70 to 92.20%). In conclusion, they suggested that, under the recommended dose conditions the tested insecticides are appropriate for use on or in fruits of zucchini plants, Park *et al*., (2011).

The residual levels of acetamiprid were found to be lower than the previously established (European maximum residual levels (EU MRLs) (0.5 mg/kg), with a half-life of 5 days after application, according to, Badawy *et al*., (2019)

Clothianidin residues:

Clothianidin had a half-life (RL_{50}) was 3.277 days, and, the degradation rate (K) was 0.2115 $days^{-1}$. In addition, the initial deposit was 0.1979 ppm after one-hour of spray, then reduced to 0.1634, 0.1009, 0.0796, and 0.03498 ppm, indicating that the rates of loss were 17.43, 49.01, 59.78 and 82.32% on and in pepper fruits at 1, 3, 5, and 7 days post-application of clothianidin, respectively. Clothianidin wasn't detected on or in the fruits of pepper after ten days of application. The results of the current research suggested that, based on the maximum-residue limit (MRL) of clothianidin in pepper plants (0.04 ppm) (EU 2023), fruits of pepper could be consumed safely under greenhouse conditions after 7days of application, as presented in Table 4.

The current outcomes were consistent with many investigations, Abdel-Ghany *et al*., (2016) determined the residues of clothianidin on cucumbers, and they reported that the PHI was 8 days, the half-life was 4.65 days in cucumbers.

Also, Abdallah *et al*., (2019) found that the clothianidin dissipation followed first-order kinetics, with a PHI of 6.18 days suggested for safe consumption and a half-life period (RL_{50}) of 2.07 days

Table 4. Residual levels, rate of degradation, pre-harvest interval (PHI), and the half-life (RL_{50}) value of imidacloprid, acetamiprid, and clothianidin in and on pepper fruits.

Time after application (days)	Residues					
	Imidacloprid		Acetamiprid		Clothianidin	
	Residues (ppm)**	% loss	Residues (ppm)**	% loss	Residues (ppm)**	% loss
Initial *	1.6115	00. 00	0.562	00 .00	0.1979	00 .00
1	1.1488	28.72	0.298	46.98	0.1634	17.43
3	0.1896	88.23	0.250	55.52	0.1009	49.01
5	0.0134	99.17	0.159	71.71	0.0796	59.78
7	0.00326	99.80	0. 109	80.60	0.03498	82.32
10	N.D.	>99.9	N.D.	>99.9	N.D.	>99.9
15	N.D.	>99.9	N.D.	>99.9	N.D.	>99.9
21	N.D.	100	N.D.	100	N.D.	100
K	2.8952		0.3475		0.2115	
RL_{50} (days)	0.239		1.994		3.277	
MRL (ppm)	0.5 (EU2023)		0.2 (Codex 2023)		0.04 (EU 2023)	
PHI days	3		5		7	

: Samples were collected after one hour (zero time) of treatment.** *: Average of three replicates.**
N.D. = Not detectable. **K= Rate of degradation.**

On the other hand, Rabie *et al*., (2018) studied the residual levels of some pesticides belonging to the chemical group (dinotefuran and thiamethoxam) in peppers. Samples were randomly collected at zero time (one hour), one, three, five, seven, ten, fifteen, and twenty-one days post application by using the QuEChERS method, and HPLC/DAD was used for the determination. The recovery levels were 78-112% and 77-80% for thiamethoxam and dinotefuran, respectively, at the spike levels [0.01- 1 mg/kg] in pepper fruits. The initial residue was 1.38 mg/kg for thiamethoxam and 6.59 mg/kg for dinotefuran in fruits of pepper. The half-lives (RL_{50}) values were 3.11 and 2 days for thiamethoxam and dinotefuran, respectively. According to the maximum residue limit (MRL) (0.7 mg/ kg for thiamethoxam and 0.01 mg/kg for dinotefuran, and the PHI was four and eleven days, respectively.

Pymetrozine residues:

Residues half-life time (RL_{50}), rate of degradation (K), and preharvest interval (PHI) of pymetrozine in pepper fruits were displayed in Table 5.

Initial deposits of pymetrozine on and in fruits of pepper was 1.967 ppm after 1 h. of spray and were reduced to, 0.019 ppm after one day of treatment, indicating that the rates of loss were 99.38 and 100 after 1 and 3 days of application, respectively. After three days of application, pymetrozine was not found in fruits of pepper. The RL_{50} value was 0.151 days, and a rate of degradation was 4.590 day^{-1}. The data demonstrated that the fruits of pepper could be safely consumed after one day of spray. Depending on the maximum residue limit (MRL) of pymetrozine on pepper (0.2 ppm) (EPA Tolerance 2023).

The current results are in agreement with those achieved by, Abd-Alrahman and Kotb (2020), who analyzed the residual behavior of pymetrozine in tomatoes by QuEChERS method and (HPLC/DAD). Also, it was reported that the average recovery of pymetrozine was 90.75% (88.5–93%) in tomatoes, the residue half-life (RL_{50}) was 1.31days, and the PHI was 3 days.

On the other hand, Halawa., (2020) illustrated that the level of pymetrozine residue in pea fruits was less than the maximum residue limit (MRL) of 0.02 mg/kg, as recommended by the (Codex Alimentation Commission). Data showed that the half-life (RL_{50}) value was 2.5 days, whereas, the pre-harvest interval was 8 days post-application for pea fruits. These variations may be due to the type and growth rate of crops, environmental conditions, and application doses.

3.5. Pyriproxyfen residues:

The results in Table5 showed that the initial deposits of pyriproxyfen in and on pepper fruits were (2.514 ppm) after one-hour post application, subsequently reduced to; 2.206, 1.771, 1.528, 1.032, 0.767, and 0.353 ppm, after (1, 3, 5, 7, 10, and 15 days) post application, respectively. Also, the rates of loss were 12.25, 29.55, 39.22, 58.95, 69.49 and 85.96 % after the same intervals mentioned before, respectively. After 21 days of application, pyriproxyfen was not found in pepper fruits. The degradation rate (K) was 0.0987 day^{-1}, and the half-life (RL_{50}) value was 7.0233 days. The obtained results revealed that pepper fruits might be safe to consume after 10 days of treatment, based on the, Maximum Residual Limits (MRLs) for pyriproxyfen on pepper (1 ppm), (European Union 2023).

As for the dissipation of pyriproxyfen in peppers grown in the greenhouse Fenoll *et al*., (2009), found the PHI was 3 days. While, the half-life times of pyriproxyfen were 21.47, and 18.57 days after the first and second applications, respectively. While, Dong *et al*., (2018) suggested that 14 days was the PHI of pyriproxyfen in citrus, and the half-life was 13.3 days.

In contrast, Sulaiman *et al*., (2008) calculated the degradation of pyriproxyfen on green peppers and tomatoes grown in greenhouses. Data showed that the initial residues of the tested insecticide were 6.71 and 2.89 mg/kg on green pepper and tomato fruits, correspondingly. Over time, the percentage of disappearance reached, 88.08% in peppers and 84.14% in tomatoes after 14 days of spray. The RL_{50} value was 5.41 days on both (pepper and tomato fruits).

Azadirachtin residues:

The data in Table 5 demonstrated that the initial deposits of azadirachtin in and on pepper fruits was 0.95 ppm after one-hour post-application and gradually decreased to (0.79, 0.4, and 0.06 ppm), after one, three, and five days from spray, respectively. Also, a rate of loss were 16.84, 57.89 and 93.68 % after the same intervals mentioned before, respectively. respectively. After 7 days of application, azadirachtin was dissipated in pepper fruits. Azadirachtin had a half-life (RL_{50}) of 2.0285 days and a degradation rate (K) of 0.3417 day^{-1}, this study suggested that fruits of pepper could be collected safely after one hour of application based on the maximum residual levels (MRLs) in pepper (1ppm), (European Union 2023).

Our data obtained in the current study agree with Akbar *et al*,. (2010); they found that, azadirachtin was observed at levels of (0.446 and 0.232 ppm) in the leaf and head of cabbage at one h /zero-day, correspondingly, whereas after seven days azadirachtin was not found. The rate of degradation was 0.484 and 0.364 day^{-1} in cabbage leaf and head, correspondingly also, the half-life was 1.43 days in leaf but cabbage head was 1.90 days, and they recommended that, Azadirachtin can be sprayed till harvest (PHI = 0 day).

Also, Akbar, et al., (2020) they mentioned that the neem product (azadirachtin) was not discovered at the recommended dose used in field experiments, so they conducted separate field experiments using 10 times the recommended dose (d=158g a.i./ha^{-1}), and found that, the initial residues of neem product were 0.413 mg/kg^{-1} in cauliflower leaves, while it was 0.178mg/kg^{-1} in cauliflower curd. Azadirachtin was not found in the cauliflower curd and leaves after 7 days of treatment. The half-life value of azadirachtin for cauliflower curd was 1.87 days, whereas, in cauliflower leaves, cauliflower was 1.75 days, which was the lowest period among the tested pesticides. In conclusion, it was recommended that crops treated with bioinsecticides appeared to be safe for humans to consume within a few hours post application in comparison with (EU and Codex MRL).

Takla *et al*., (2021) determined the residues of azadirachtin using GC – Ms -Mass in eggplant fruits and they found that residues of azadirachtin were discovered in all eggplant samples taken (12, 24 days) after application, it seems that no (effective substance remnant) was detected. In addition, Caboni *et al*., (2009) investigated the dissipation of main azadirachtioids in tomato fruits grown in greenhouses at concentrations of 1 and 5 times the manufacturer's recommendation. Azadirachtin-A (AZA/ A) deposition was lower than the MRL in all studies. The (RL_{50}) was 1.2 days, whereas, the (PHI) was 3days.

Spinetoram Residues:

The results in Table 5, revealed that the degradation rate (K) was 00.5539 day^{-1}, and the half-life (RL_{50}) of spinetoram was 1.251 days in pepper fruits. The initial residue of spinetoram in and on pepper fruits was 00.79 ppm after 1h post application, after that reduced to; 00.41, 00.03, and 00.01ppm, indicating that the rates of loss were; 48.10, 96.20, 98.73 and >99.9% after one, three, five and seven days of spray, respectively. After seven days of application spinetoram was not detected in pepper fruits. Depending on the maximum residue level (MRL) of spinetoram on pepper (0.5 ppm), (EU 2023) the fruits of pepper could be consumed safely after one day of spray.

Malhat (2013) evaluated a sensitive and simple approach for analyzing residues of spinetoram and their dissipation in tomatoes. The extract was cleaned up using the QuEChERS technique and analyzed with (HPLC/DAD). The results demonstrated that the spinetoram deposits in tomato fruits were below the codex maximum residue level (0.06 mg/kg^{-1}) after ten days of treatment. The dissipation pattern followed first-order kinetics, with a 2.6-days half-life. This study demonstrates that spinetoram is safe for application on tomatoes at the authorized doses.

Additionally, spinosad was discovered at 0.614 ppm in cabbage leaf and 0.414 ppm in cabbage head after 1 hour (zero-day), but after seven days it was 0.143 in cabbage leaf and 0.110 in cabbage head. Furthermore, the rate of dissipation and half-life (RL_{50}) time values in the leaf and head were 0.201 and 0.198 day^{-1}, and 3.45 and 3.50 days, correspondingly, Akbar *et al.*, (2010).

Table 5. Insecticide residues, preharvest intervals, half-life values (RL_{50}) and degradation rates of pymetrozine, pyriproxyfen azadirachtin and spinetoram on and in pepper fruits.

Time after application (days)	Residues							
	Pymetrozine		Pyriproxyfen		Azadirachtin		Spinetoram	
	Residue (ppm) **	% loss	Residues (ppm)**	% loss	Residues (ppm)**	% loss	Residues (ppm)**	% loss
Initial *	1.967	00 .00	2.514	00 .00	0.95	00 .00	0.79	00 .00
1	0.019	99.38	2.206	12.25	0.79	16.84	0.41	48.10
3	N D.	>99.9	1.771	29.55	0.40	57.89	0.03	96.20
5	N D.	>99.9	1.528	39.22	0.06	93.68	0.01	98.73
7	N D.	>99.9	1.032	58.95	N D.	>99.9	N D.	>99.9
10	N D.	>99.9	0.767	69.49	N D.	>99.9	N D.	>99.9
15	N D	>99.9	0.353	85.96	N D.	>99.9	N D.	>99.9
21	N D	100	N D.	100	N D.	100	N D.	100
K	4.590		0.0987		0.3417		0.5539	
RL_{50}(days)	0.151		7.0233		2.0285		1.251	
MRL(ppm)	0.2 (EPA Tolerance 2023)		1 (EU 2023)0.8(EPA Tolerance)		1(EU 2023)		0.5 (EU 2023)	
PHI (days)	1		10		1		1	

: Samples were collected after 1hour of treatment.** *: Average of three replicates.**
N.D. = Not detectable. **K= Rate of degradation.**

The degradation of spinetoram residues in pepper and cabbage was investigated using the QuEChERS technique and LC/MS -MS, to trace the recovery and the residues by Ali *et al.* (2018) and they found that spinetoram dissipated quickly from (0.62 to 0.36 mg/kg) and from (0.33 to 0.12 mg/kg) in pepper and cabbage respectively. The loss percentages were 41.9% and 63.6% on the first day after application in pepper and cabbage, respectively, which was below the MRL of EU regulation (0.5 mg/kg) for pepper and MRL of codex (0.3 mg/kg) for cabbage plant. Spinetoram disappeared after seven days for cabbage and ten days for pepper. Half-lives were 1.29 and 1.95 for cabbage and pepper, respectively. The pre-harvest period was a day for both.

While, Akbar, et al., (2020) found that the average half-life (RL_{50}) time for spinosad was 3.87days, moreover, the initial residues of spinosad in cauliflower curd were 2.540 mg/kg^{-1}, but in leaves were 3.222 mg/kg^{-1}. Also, Šunjka *et al*., (2021) determined spinetoram residue in pear fruits and found that spinetoram deposits were lower than the (MRL) (0.2mg/kg) after 3days of treatment.

The RL_{50} value was 2.17 days. In conclusion, the researchers proposed that, the tested insecticide might be safely used on pear plants.

Spinosad residues on green peppers and tomatoes were determined to be 0.23 and 0.52 mg/kg, respectively. Gradually, over time, the disappearance rate increased until it reached 84.14% on tomatoes and 88.08% on peppers at 14 days after treatment, and the RL_{50} value was 5.41 days for each of the tomato and pepper fruits, as reported by Sulaiman *et al*., (2008).

It may be concluded that, the differences in results could be due to the formulation and dose. Also, our results suggested that the variations in the relative distribution of insecticides between the current investigation and previous studies could be due to a variety of factors such as; differences in crop species, plant cultivation methods or physical and chemical properties of the insecticides.

In conclusion, this study could be used as a guide for the safe use of imidacloprid, acetamiprid, clothianidin, pymetrozine, pyriproxyfen, azadirachtin, and spinetoram in pepper plants grown under greenhouses.

REFERENCES

Abdallah, O. I., Abd El-Hamid, R. M., and Abdel Raheem, E. H. (2019). Clothianidin residues in green bean, pepper and watermelon crops and dietary exposure evaluation based on dispersive liquid-liquid microextraction and LC–MS/MS. *Journal of Consumer Protection and Food Safety*, *14*, 293-300.

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.

Abdelfatah, R. M., Saleh, A. A., Elgohary Laila, R. A., & Negm, S. E. (2020). Dissipation of some pesticide residues in tomato (*Lucopersicon esculentum* L.) fruits using QuEChERS methodology under the Egyptian field conditions. *journal of plant Protection and Pathology*, *11*(7), 327-332.

Abdel-Gawad, H., Afifi, L. M., Abdel-Hameed, R. M., & Hegazi, B. (2008). Distribution and degradation of 14C-ethyl prothiofos in a potato plant and the effect of processing. *Phosphorus, Sulfur, and Silicon and the Related Elements*, *183*(11), 2734-2751.

Abdel-Ghany, M. F., Hussein, L. A., El Azab, N. F., El-Khatib, A. H., & Linscheid, M. W. (2016). Simultaneous determination of eight neonicotinoid insecticide residues and two primary metabolites in cucumbers and soil by liquid chromatography–tandem mass spectrometry coupled with QuEChERS. *Journal of Chromatography B*, *1031*, 15-28

Abdella, H. M., Halawa, S. M., & El-Hefny, D. E. (2015). Dissipation of penconazole and imidacloprid residues in squash fruits under the Egyptian field conditions. *Alexandria Science Exchange Journal*, *36*(OCTOBER-DECEMBER), 292-296.

Akbar, M. F., Haq, M. A., Ahmad, I., Viliana, V., & Sultan, A. (2020). Biological degradation of some synthetic and bio-pesticides sprayed on cauliflower crop. *Pakistan Journal of Zoology*, *52*(3), 1121.

Akbar, M. F., Haq, M. A., Parveen, F., Yasmin, N., & Sayeed, S. A. (2010). Determination of synthetic and bio-insecticides residues during aphid, *Myzus persicae* (Sulzer) control on cabbage crop through high performance liquid chromatography. *Pak. Entomol*, *32*(2), 155-162.

Ali, A. M., Mohamed, A. M., & Lamia, R. (2018). Dissipation and persistence of spinetoram residue in pepper and cabbage by using LC-MS/MS and QuEChERS method. *Middle East Journal of Applied Sciences*, *8*, 508-514.

Anastassiades, M., Lehotay, S. J., Štajnbaher, D., & 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.

Atia, M. R. M., Darwish, A. A. F., & Mansy, A. S. M. (2024). Efficacy of certain neonicotinoids against cotton whitefly, *Bemisia tabaci* and their residues in fruits and leaves of tomato plants under open field conditions. *Alexandria Science Exchange Journal*, *45*(1), 1-10.

Badawy, M. E., Ismail, A. M., & 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.

Bempah, C. K., & Donkor, A. K. (2011). Pesticide residues in fruits at the market level in Accra Metropolis, Ghana, a preliminary study. *Environmental monitoring and assessment*, *175*, 551-561.

Caboni, P., Sarais, G., Angioni, A., Lai, F., Dedola, F., & Cabras, P. (2009). Fate of azadirachtin A and related azadirachtoids on tomatoes after greenhouse treatment. *Journal of Environmental Science and Health*, *Part B*, *44*(6), 598-605.

Codex Alimentarius Commission for Pesticide Residues (CAC/PR). 2023. List of maximum residue limits for pesticides in food and animal feeds. https://www.fao.org/faowhocodexalimentarius/meetings/archives/en/?y=2023&mf=07

Diao, Y. Z., Zhang, C., Liu, F., Wang, W. Z., Liu, L., Cai, L., & Liu, X. L. (2017). Colletotrichum species causing anthracnose disease of chili in China. *Persoonia-Molecular Phylogeny and Evolution of Fungi*, *38*(1), 20-37.

Dong, M., Wen, G., Tang, H., Wang, T., Zhao, Z., Song, W., ... & Zhao, L. (2018). Dissipation and safety evaluation of novaluron, pyriproxyfen, thiacloprid and tolfenpyrad residues in the citrus-field ecosystem. *Food chemistry*, *269*, 136-141.

Dreher, M. L., & Davenport, A. J. (2013). Hass avocado composition and potential health effects. *Critical reviews in food science and nutrition*, *53*(7), 738-750.

El-Lakwah, F. A., Hamed, M. S., Darwish, A. A., & Shams El-Din, A. M. (1995). Determination of certain organochlorine and organophosphorus pesticide residues in home-produced tomatoes and cucumber used for consumption in two Egyptian governorates.

El-Latif, A., Sallam, A. A., & El-Hefny, D. S. (2022). Dissipation kinetics study of acetamiprid, metalaxyl-M and fenpyroximate in the ecosystem of tomato fruits under field and greenhouses conditions. *Journal of Sohag Agriscience (JSAS)*, *7*(2), 127-137.

EU. (2023). European Commission. Information on pesticides. EU, MRLs. [internet]. Accessed.

Fenoll, J., Ruiz, E., Hellín, P., Lacasa, A., & 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.

Galm, U., & Sparks, T. C. (2016). Natural product derived insecticides: discovery and development of spinetoram. *Journal of Industrial Microbiology and Biotechnology*, *43*(2-3), 185-193.

Halawa, S. M. (2020). Dissipation of pymetrozine and penconazole on and in pea fruits. *Annals of Agricultural Science, Moshtohor*, *58*(4), 1089-1098.

Hassanzadeh, N., Sari, A. E., & Bahramifar, N. (2012). Dissipation of imidacloprid in greenhouse cucumbers at single and double dosages spraying. 557-564.

Jawad, S. A., & Hermize, F. B. (2020). Residue analysis of imidacloprid in fruits of sweet pepper carisma (*capsicum annuum* L.) using QUECHERS HPLC method in greenhouse. *Plant Archives*, *20*(1), 2067-2073.

Karmakar, R., & Kulshrestha, G. (2009). Persistence, metabolism and safety evaluation of thiamethoxam in tomato crop. *Pest Management Science: formerly Pesticide Science*, *65*(8), 931-937.

Kim, I. K., Abd El-Aty, A. M., Shin, H. C., Lee, H. B., Kim, I. S., & Shim, J. H. (2007). Analysis of volatile compounds in fresh healthy and diseased peppers (*Capsicum annuum* L.) using solvent free solid injection coupled with gas chromatography-flame ionization detector and confirmation with mass spectrometry. *Journal of Pharmaceutical and Biomedical Analysis*, *45*(3), 487-494.

Koul, O., Isman, M. B., & Ketkar, C. M. (1990). Properties and uses of neem, *Azadirachta indica*. *Canadian Journal of Botany*, *68*(1), 1-11.

Liang, Y., Wang, W., Shen, Y., Liu, Y., & Liu, X. J. (2012). Effects of home preparation on organophosphorus pesticide residues in raw cucumber. *Food Chemistry*, *133*(3), 636-640

Malhat, F. M. (2013). Simultaneous determination of spinetoram residues in tomato by high performance liquid chromatography combined with QuEChERS method. *Bulletin of environmental contamination and toxicology*, *90*, 222-226.

Mertz, F. P., & Yao, R. C. (1990). *Saccharopolyspora spinosa* sp. nov. isolated from soil collected in a sugar mill rum still. *International Journal of Systematic and Evolutionary Microbiology*, *40*(1), 34-39.

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

Moye, H. A., Malagodi, M. H., Yoh, J., Leibee, G. L., Ku, C. C., & Wislocki, P. G. (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. Y., Choi, J. H., Kim, B. M., Park, J. H., Cho, S. K., Ghafar, M. W., ... & Shim, J. H. (2011). Determination of acetamiprid residues in zucchini grown under greenhouse conditions: application to behavioral dynamics. *Biomedical Chromatography*, *25*(1-2), 136-146.

Park, S. Y., Kim, J. Y., Lee, S. M., Jun, C. H., Cho, S. B., Park, C. H., & Rew, J. S. (2014). Capsaicin induces apoptosis and modulates MAPK signaling in human gastric cancer cells. *Molecular medicine reports*, *9*(2), 499-502.

Quarles, W. (1994). Neem tree pesticides protect ornamental plants. *The IPM practitioner: the newsletter of integrated pest management (USA)*, *16*(10).

Rabie, M., Ibrahim, E. D. S., Elhafny, D., & Bayoumi, M. (2018). Determination of dinotefuran and thiamethoxam residues in pepper fruits under greenhouse conditions using the QuEChERS method and HPLC/DAD. *Egyptian Journal of Chemistry*, *61*(2), 249-257.

Razik, M. A. A., Al Dhafar, Z. M., Alqahtani, A. M., Osman, M. A., & Sweelam, M. E. (2022). Dissipation and residues of imidacloprid and its efficacy against whitefly, *Bemisia tabaci*, in tomato plants under field conditions. *Molecules (Basel, Switzerland)*, *27*(21), 7607.

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

Sabry, A. K. H., Abolmaaty, S. M., Abd-El, T. A. E. A., & Abd-El Rahman, A. (2016). Residue determination of some rational insecticides in tomato fruits and their efficacy on sweet potato whitefly, *Bemisia tabaci*. *IJCSPUB-International Journal of Current Scienc (IJCSPUB), 6(4),* 37-46.

Sanatombi, K., & Rajkumari, S. (2020). Effect of processing on quality of pepper: A review. *Food Reviews International*, *36*(6), 626-643.

Shahrbabki, P. E., Hajimohammadi, B., Shoeibi, S., Elmi, M., Yousefzadeh, A., Conti, G. O., ... & Khaneghah, A. M. (2018). Probabilistic non-carcinogenic and carcinogenic risk assessments (Monte Carlo simulation method) of the measured acrylamide content in Tah-dig using QuEChERS extraction and UHPLC-MS/MS. *Food and chemical toxicology*, *118*, 361-370.

Sharma, P. C., Chandresh, P., & Sharma, S. (2018). Persistence of imidacloprid, indoxacarb and λ-cyhalothrin on tomato (*Solanum lycopersicum* L.) under protected cultivation. *Int. J. Curr. Microbiol. Appl. Sci*, *7*, 2783-2794.

Sihuincha, M., Zamora-Perea, E., Orellana-Rios, W., Stancil, J. D., López-Sifuentes, V., Vidal-Ore, C., & Devine, G. J. (2005). Potential use of pyriproxyfen for control of Aedes aegypti (Diptera: Culicidae) in Iquitos, Peru. *Journal of medical entomology*, *42*(4), 620-630.

Sulaiman, A. A., Kmel, A. & Al-Rajhi, D.H. (2008). Detection and elimination of certain insecticide residues from tomatoes and green peppers fruits. Alexandria Science Exchange Journal, 29(October-December), 223-229.

Šunjka, D., Lazić, S., Vuković, S., Alavanja, A., Nađ, Đ., & Mitrić, S. (2021). Residue and dissipation dynamic of spinetoram insecticide in pear fruits. *Plant Protection Science*, 57(4): 326–332.

Takla, S. S., El-Dars, F. M., Amien, A. S., & Rizk, M. A. (2021). Prospects of Neem essential oil as bio-pesticide and determination of its residues in eggplant plants during crop production cycle. *Egyptian Academic Journal of Biological Sciences, F. Toxicology & Pest Control*, *13*(2), 1-15.

Yee, W. L., Jack, O., & Nash, M. J. (2007). Mortality of *Rhagoletis pomonella* (Diptera: Tephritidae) exposed to field-aged spinetoram, GF-120, and azinphos-methyl in Washington State. *Florida entomologist*, *90*(2), 335-342.

Zainudin, B. H., & Salleh, S. (2017). Method development, optimization and validation of matrix hydration effect on pesticide residues in cocoa beans using modified QuEChERS method and gas chromatography tandem mass spectrometry. *Food analytical methods*, *10*, 3874-3885.

Zhang, K., & Li, J. (2019). A novel semi-synthesis of spinetoram-J based on the selective hydrolysis of 5, 6-dihydro spinosyn A. *Natural Product Research*, *33*(19), 2801-2808.

التحليل الكمي لبعض متبقيات المبيدات الحشريه باستخدام طريقة QUECHERS على ثمار الفلفل الرومي (*Capsicum annuum*) تحت ظروف البيوت المحمية.

رحاب السيد خليل، فؤاد عبدالله شاهين ، علي علي عبدالهادي و عادل عبدالمنعم

قسم المبيدات – كلية الزرراعة – جامعة المنصورة- مصر

الملخص

تم تقدير معدل اختفاء ومستوي متبقيات كل من مبيدات الايميداكلوبريد، الاسيتامبريد، الكلوثيانيدين، البيميتروزين، البيربروكسيفين، الأزاديريكتين والاسبينيتورام في ثمار الفلفل تحت ظروف الصوب الزراعيه، باستخدام جهاز الكروماتوجرافى السائل العالى الاداء باستخدام طريقة QuEChERS. تم رش المبيدات المختبرة على الفلفل بالجرعة الموصى بها وتم جمع عينات الفلفل بعد ساعة واحدة وبعد 1، 3، 5، 7، 10، 15، 21 يوما بعد المعامله. كانت فترة نصف العمر للإيميداكلوبريد ،أسيتامبريد ،كلوثيانيدين ،البيميتروزين ،البيربيروكسيفين ،الأزاديراكتين والاسبينيتورام في ثمار الفلفل هي 0.239، 1.994، 3.277، 0.151، 7.0233، 2.0285 و1.251 يومًا، على التوالي. أشارت النتائج الي أن بيانات التحطم أظهرت أن ثمار الفلفل تكون امنه للاستخدام (فترة ما قبل الحصاد (PHI)) بعد 1 ساعه و1و1 و3 و5و7و 10 أيام لمبيدات الأزاديراكتين ، البيميتروزين ، الاسبينيتورام ، الإيميداكلوبريد ، الأسيتاميبريد ، الكلوثيانيدين و البيربروكسيفين علي التوالي، وذلك وفقًا للحد الأقصى للمتبقي (MRL).