Journal of Plant Protection and Pathology

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

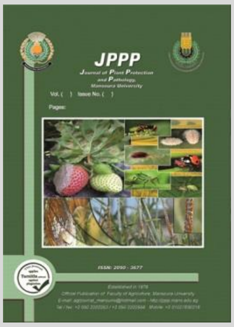
Study of Imidacloprid, Azoxystrobin and Difenoconazole Residues and their Biochemical effects on Cucumber

Shalaby, A. A.[1*] ; T. A. Abd-El Rahman[2] and M. A. Shalaby[2]

[1] Plant Protection Department, Faculty of Agriculture, Zagazig University - Egypt

[2] Pesticides Residues & Environmental Pollution Dept, Central Agricultural Pesticides Laboratory, Agricultural Research Center, Dokki, Giza, Egypt

Cross Mark



ABSTRACT

Cucumber plants at the fruiting stage were sprayed on June 2021 in a private field at El-Tahra village, Zagazig-district, Sharkia-Governorate, Egypt with imidacloprid Avenue 70% WG and azoxystrobin 20%+difenoconazole 12.5% mixture in commercial formulation Decent 32.5% SC to determine their persistence in cucumber-leaves and fruits, also to estimate their biochemical effects on cucumber-fruits. QuEChERS method was used for extraction and clean-up and analyzed using HPLC. Results revealed that, initial amounts of each-pesticide in leaves were much higher-than cucumber fruits. Loss percentages in residues were higher in cucumber fruits than leaves. The t½ values for investigated pesticides in cucumber-fruits (peel and whole-fruits) and leaves, were (1.88, 2.02, 2.47), (1.72, 1.81, 3.2) and (1.77, 2.10, 2.45 days) for imidacloprid, azoxystrobin and difenoconazole, respectively. Residue amounts of tested-pesticides were more greatly detected in the peel than that pulp. Cucumber fruits could be used safely for human-consumption at any time after spraying to the end of the experimental-period (12-days) after peeling. The pickling process removed in great amounts from initial deposits of investigated pesticides. Levels of total soluble sugar%, glucose mg/kg, acidity%, total soluble solids (T.S.S.), % ascorbic-acid mg/kg, β-carotene%, dry matter% and protein% as well as elements N%, P%, K%, Fe mg/kg, Mn mg/kg, Ca%, Zn mg/kg, on treated cucumber-fruits were significantly reduced during tested-periods (3 and 6-days after application). Data revealed that reduction of each quality attributes and elements was more pronounced with Decent than imidacloprid. This finding may be due-to presence of two-fungicide mixture in decent formulation (azoxystrobin+difenoconazole).

***Keywords**:* imidaclopride, azoxystrobin, difenoconazole, cucumber, pickling

INTRODUCTION

Cucumber fruits are worldwide interest in terms of consumer preferences among vegetables that could be cultivated in numerous climatic conditions and a significant part of the Mediterranean diet, being a source of vitamins and minerals, and is consumed mostly raw. Cucumber plants are liable to be infested with different pests causing serious injury and reducing the final yield. (Malhat*et al* 2022).

The low productivity in agriculture due to damage caused by pests has led to the application of pesticides to control pest infestation. Residues of pesticides applied to vegetables are often found in the food which can cause a chronic effect on the health of humans who consume such products. Food consumption is one of the most common routes of pesticide exposure in consumers (Shokrzadeh, *et al* 2008).

Imidacloprid is a systemic insecticide with translaminar activity and with contact and stomach action. Readily taken up by the plant and further distributed acropetally, with good root-systemic action. Imidacloprid control sucking insects, including rice-, leaf- and Plant hoppers, Aphids, Thrips, and Whitefly. Also effective against soil insects, Termites and some species of biting insects, such as Rice water weevil and Colorado beetle.

Plant protection products PPP (more commonly known as pesticides) are widely used in planting and storage phases to increase yield, fight pests, improve quality and extend the life of food crops (Abd-El Rahman 2020). Pesticide residue is a decisive and influencing factor to allow shipments of agricultural products to enter importing countries, especially European Union countries. Vegetable plants are susceptible to infestation with various pests severe damage. Therefore, chemical control represents the major method in this respect and hence pesticides have played a significant role in increasing crops in both quantity and quality. Although such pesticides used as recommended, small amounts may be found on or in treated crops at harvest (Ministry of Agriculture 2021), (Abd-El Rahman *et al.*, 2016).

Azoxystrobin is a fungicide with protectant, curative, eradicant, translaminar, and systemic properties. Inhibits spore germination and mycelia growth, and also shows antisporulant activity. Azoxystrobin is used to control the following pathogens *Pseudoperonospora cubens*is on Cucurbitaceae; *Phytophthora infestans* and *Alternaria solani* on potato and tomato. Difenoconazole is a systemic fungicide with preventive and curative action. Absorbed by the leaves, with acropetal and strong translaminar translocation. Difenoconazole is used to control systemic fungicide with a novel broad-range activity protecting the yield and crop quality by foliar application or seed

*** Corresponding author.**
E-mail address: Shalabey3001@yahoo.com
DOI: 10.21608/jppp.2022.148665.1085

treatment. Provides long-lasting preventive and curative activity against *Ascomycetes, Basidiomycetes, and Deuteromycetes, including Alternaria, Ascochyta, Cercospora, Cercosporidium, Colletotrichum, Guignardia, Mycosphaerella, Phoma, Ramularia, Rhizoctonia, Septoria, Erysiphe and Venturia* spp., Erysiphaceae, Uredinales and several seed-borne pathogens. Used against disease complexes in various vegetable crops. (MacBean, 2012).

The present study were conducted to determine the residues and dissipation dynamics of imidacloprid, azoxystrobin and difenoconazole in cucumber fruits and leaves, and determine effect of the investigated pesticide residues on some biochemical constituents of cucumber fruits.

MATERIALS AND METHODS

I- Pesticide selected:

Avenue70% WG (imidacloprid) andDecent32.5% SC, (azoxystrobin 20% +difenoconazole12.5%), were obtained from Central Agricultural Pesticides Laboratory, Agricultural Research Center, Dokki – Giza, Egypt.

2- Field experiment and sampling:

This research was conducted at the private field of cucumber (*Cucumis sativus* ver sahim f1) located at El-Tahra village, Zagazig district, Sharkia governorate, Egypt. A field trial was conducted with three replicates, plot dimensions were 6×7 m^2each and arranged in randomized blocks design. At the fruiting time plants were sprayed with Avenue 70% WG (imidacloprid) and Decent 32.5% SC, (azoxystrobin 20% +difenoconazole 12.5%) at 50 g/100 L water and 200 cm/feddan, respectively on June, 2021 one time using knapsack-sprayer fitted with one nozzle to deliver 200 liters water/ feddan. Representative samples of cucumber leaves and fruits were taken randomly from the experimental plots at 2 hr and after one day then each 3 days up to 12 days posttreatment to determine the residues of imidacloprid, azoxystrobin and difenoconazole. Subsamples of 200 g each of treated cucumber fruits were peeled off to get the peel and pulp separately, and then each component was weighted to determine the effect of peeling on the residues of the tested pesticides. As well as subsamples off 25 g each of green leaves were taken.

To study the effect of pickling for removal imidacloprid, azoxystrobin and difenoconazole residues from the treated fruits, one kg from the first sample of each treatment (2 hours after spraying) was taken and soaked in a jar filled with water (1liter), salt (100g) and vinegar (100ml) for each kilogram (close carefully using glass jar) according to Ryad and Mahmoud (2016), then analyzed after 3 and 6 days after pickling.

To estimate the residue effects of imidacloprid, azoxystrobin+difenoconazole in Decent formulation on some quality parameters and some trace and nutrient elements, samples (3 and9 days after application) were taken to determine some quality parameters including total soluble sugars, glucose, acidity, total soluble solids, ascorbic acid, β-carotene, protein, and dry matter. Total soluble sugars and glucose were determined colorimetrically using the picric acid method as described by Dubois *et al*., (1956). β-carotene was determined by the method of Ben-Amotza and Avron (1983). Acidity, ascorbic acid, protein, and dry matter were determined according to the methods of the Association of Official Analytical Chemists (AOAC) (1984). Total soluble solids (T.S.S.) were estimated using a refractometer. The elements N, P, K, Fe, Mn, Ca, and Zn were also determined; nitrogen, potassium, and phosphorus were determined by the method of Evenhuis*et al.,* (1980). Calcium, manganese, iron, and zinc were determined by atomic absorption spectroscopy (Jackson, 1967).

3- Extraction, clean up procedures and residues determination:

Cucumber samples were extracted and cleaned up using the QuEChERS method (**Anastassiades*et al*., 2003**). A homogenized cucumber fruits and leaves samples of 10 g fruits (peel, pulp, pickled fruits) and leaves were taken into a centrifuge tube (50-mL). Fifteen milliliters of acetonitrile containing 1.0% acetic acid were transferred to the centrifuge tube and vigorously shaken for 1 min. Then, 4 g magnesium sulfate anhydrous and 1 g sodium acetate were added, and then the mixture was shaken vigorously for 5 min. The mixture was centrifuged at 3000 rpm for 5 min. Five milliliters of the supernatant were transferred to a centrifuge tube (15 ml) and shaken with 50 mg primary secondary amine (PSA), 10 mg graphitized carbon black, and 150 mg magnesium sulfate. Thereafter, the tube was centrifuged for 10 min at 6000 rpm. The supernatant of imidacloprid, azoxystrobin+difenoconazole was taken for analysis by HPLC with an Agilent 1260 HPLC system (USA), with a quaternary pump, autosampler injector, thermostat compartment for the column, and photodiode array detector. The chromatographic column was Zorbax C18 XDB (250 × 4.6 mm, 5 mm). The column was kept at room temperature. Mobile phase (acetonitrile/water) and wavelength were 80:20, 260 nm; 50:50, 220 nm, and 90:10, 218 nm for imidacloprid, azoxystrobin, and difenoconazole, respectively. The flow rate of the mobile phase was 1 ml min-1, and the injection volume was 20 µl. Under these conditions, good separations and high sensitivity were obtained with retention times of 2.647, 3.163, and (3.538 and 5.196) min for imidacloprid, azoxystrobin, and difenoconazole (1 and 2), respectively.

4- Recovery rates and statistical analysis:

To determine the recovery percentages, known amounts of active ingredients of the tested pesticides were added to uncontaminated cucumber fruits (peel, pulp and pickled fruits) and leaves at levels of 4, 2 and 1 mg/kg, extraction and clean-up were carried out as described above. The recovery rates for the three investigated pesticides in different subsequent cucumber fruits and leaves are given in Table 1, the all results obtained were corrected according to their recovery percentages. Statistical significances of the results obtained were estimated using the analysis of variance with L.S.D. method at the probability of 0.05 (Steel and Torrie, 1980). The rates of degradation (k) and half-life (t½) periods of each pesticide were calculated according to Gomaa and Belal (1975).The residues of the tested pesticides in the whole cucumber fruits were calculated by the following equation (Shalaby, 1992).

$$\text{Mg/kg in whole cucumber fruits} = A\,\frac{w1}{w1+w2} + B\,\frac{w2}{w1+w2}$$

Where:

A= mg/kg in the peel **w1= weight in grams of peel**
B= mg/kg in the pulp **w2= weight in grams of pulp**

Table 1. averages of recovery percentages at different spiked levels.

substrate	Spiked levels mg/kg	Recovery (%) imidacloprid	azoxystrobin	difenoconazole
leaves	1	87.74	91.78	88.87
	2	94.46	92.96	89.64
	4	98.55	92.89	90.83
	means	93.58	92.54	89.78
peel	1	91.44	92.22	86.24
	2	93.62	94.74	88.50
	4	94.32	95.35	88.86
	means	93.13	94.10	87.87
pulp	1	86.86	87.52	87.62
	2	84.94	89.74	87.84
	4	87.95	88.80	86.92
	means	86.58	88.69	87.46

RESULTS AND DISCUSSION

Data summarized in Tables (2-4) represent the amounts of imidacloprid, azoxystrobin and difenoconazole residues detected in cucumber fruits peel and pulp, whole cucumber fruits and leaves after different intervals of spray. It is obvious that the initial deposits of the tested pesticides in cucumber peel as determined 2hrs after spraying were 4.263, 4.332 and 1.963 mg/kg for imidacloprid, azoxystrobin and difenoconazole, respectively. These figures decreased gradually during the experimental period till reached 0.041, 0.045 mg/kg and UND (undetectable amounts) after 12 days of spraying indicating 99.04, 98.96 and 100% loss, respectively. Concerning the residues of the three tested pesticides in cucumber pulp, it was found that undetectable amounts from all tested pesticides were recorded after 2hrs of spraying. One day after treatment the residues detected in cucumber pulp were 0.276, 0.424 and 0.075 mg/kg for imidacloprid, azoxystrobin and difenoconazole, respectively. These amounts were increased to reach 0.507, 0.832 and 0.276 mg/kg at the third day after spraying, and then decreased gradually to reach 0.019, 0.095 and 0.039 mg/kg after 9 days of spraying for imidacloprid, azoxystrobin and difenoconazole, respectively. While after 12 days of spraying no residues (UND) were detected in cucumber pulp for the three pesticides used. The loss percentages of the residues by peeling of the cucumber fruits were ranged between 72.48-100, 2.06-100 and 13.33-100 indicating migration percentages from peel (2 hr after spray) to pulp of 0.00-11.89, 0.00-19.25 and 0.00-14.06 for imidacloprid, azoxystrobin and difenoconazole, respectively. The amounts of pesticides initially in cucumber leaves after 2h of spraying were 9.042, 6.37 and 1.441 mg/kg for imidacloprid, azoxystrobin and difenoconazole, respectively. These amounts were decreased gradually till reached 0.286, 0.407 and UND after 12 days of spraying recording 96.84, 93.61 and 100% loss, respectively.

Table 2. Residues of imidacloprid detected in cucumber fruits and leaves.

Days after treatment	peel mg/kg	pulp mg/kg	%loss by peeling	Migration%	Whole fruits mg/kg	leaves mg/kg
Initial (2 hrs)	4.263	UND	100	0.00	2.133	9.042
1	3.105	0.276	91.11	6.47	1.689 (20.82)	7.324 (19)
3	1.842	0.507	72.48	11.89	1.176 (44.87)	5.178 (42.73)
6	0.681	0.057	91.63	1.34	0.369 (82.70)	2.201 (75.66)
9	0.246	0.019	92.28	0.45	0.123 (94.23)	0.942 (89.59)
12	0.041	UND	100		0.036 (98.31)	0.286 (96.84)
K	0.3684				0.3431	0.2809
t½	1.88				2.02	2.47
MRL(mg/kg)					1	
PHI days					4	

UND = Undetectable Amounts, K = Degradation Rate, t½= Half-life, MRL= Maximum Residue Limit, PHI= Preharvest Interval.
The number between brackets indicates the % loss
Migration %= $\frac{Residual\ amounts\ in\ pulp\ at\ indicated\ days}{Initial\ deposits\ on\ peel} \times 100$

Table 3. Residues of azoxystrobin detected in cucumber fruits and leaves.

Days after treatment	peel mg/kg	Pulp mg/kg	%loss by peeling	Migration %	Whole fruits mg/kg	leaves mg/kg
Initial (2 hrs)	4.322	UND	100	0.00	2.763	6.37
1	3.412	0.424	87.57	9.81	1.984 (28.19)	4.715 (25.98)
3	1.657	0.832	49.79	19.25	1.083 (60.80)	2.693 (57.72)
6	0.392	0.328	16.33	7.59	0.530 (80.82)	1.854 (70.89)
9	0.097	0.095	2.06	2.19	0.167 (93.96)	0. 931 (85.38)
12	0.045	UND	100		0.020 (99.28)	0.407 (93.61)
K	0.4030				0.3822	0.2164
t½	1.72				1.81	3.2
MRL(mg/kg)					1	
PHIdays					4	

UND = Undetectable Amounts, K = Degradation Rate, t½= Half-life, MRL= Maximum Residue Limit, PHI= Preharvest Interval,
The number between brackets indicates the % loss
Migration %= $\frac{Residual\ amounts\ in\ pulp\ at\ indicated\ days}{Initial\ deposits\ on\ peel} \times 100$

Table 4. Residues of difenoconazole detected in cucumber fruits and leaves.

Days after treatment	peel mg/kg	pulp mg/kg	%loss by peeling	Migration %	Wholefruits mg/kg	leaves mg/kg
Initial (2 hrs)	1.963	UND	100	0.00	0.982	1.441
1	0.72	0.075	89.58	3.82	0.638 (35.03)	1.104 (23.39)
3	0.372	0.276	25.81	14.06	0.424 (56.82)	0.782 (45.73)
6	0.126	0.101	19.84	5.15	0.143 (85.43)	0.391 (72.87)
9	0.045	0.039	13.33	1.99	0.048 (95.11)	0.098 (93.20)
12	UND	UND			UND (100)	UND (100)
K	0.3915				0.3293	0.2832
t½	1.77				2.10	2.45
MRL(mg/kg)					0.2	
PHIdays					4	

UND = Undetectable Amounts, K = Degradation Rate, t½= Half-life, MRL= Maximum Residue Limit, PHI= Preharvest Interval.
The number between brackets indicates the % loss
Migration %= $\frac{\textit{Residual amounts in pulp at indicated days}}{\textit{Initial deposits on peel}} \times 100$

Regarding the residues of the tested pesticides calculated in the whole cucumber fruits, it is obvious that the initial calculated deposits were 2.133, 2.763 and 0.982 mg/kg for imidacloprid, azoxystrobin and difenoconazole, respectively. These amounts were decreased gradually to reach 0.036, 0.020 and UND after 12 days of spraying indicating 98.31, 99.28 and 100%loss of the initial deposits, respectively.

Comparing the permissible limit of imidacloprid (1 mg/kg), azoxystrobin (1 mg/kg), and difenoconazole (0.7 mg/kg), recorded by the EU Pesticides database - European Commission, with the total residues in Tables 2-4, it is clear that cucumber fruits could be used safely for human consumption at any time after spraying to the end of the experimental period (12 days) after peeling. While in the case of the whole cucumber fruits could be used safely for human consumption after 6 days without peeling for fruits contaminated with imidacloprid or Decent formulation (azoxystrobin+difenoconazole).

The abovementioned results are in harmony with those obtained by different authors working on pesticides imidacloprid, azoxystrobin and difenoconazole and other pesticides on different vegetables, fruits and field crops (Chen *et al.,* 2004, Daraghmeh *et al.,* 2007, Montasser and Mahmoud 2009, Aguilera *et al.,* 2012, Kong *et al.,* 2012, Bagi *et al.,* 2014, Abdelhadi *et al.,* 2015, Hanafi *et al.,* 2018, Maofeng Dong *et al.,* 2019, Salem *et al.,* 2021).

The t½ values for the investigated pesticides in cucumber fruits (peel and whole fruits) and leaves, as could be noticed in Tables (2,3 and 4) were 1.88, 2.02, 2.47; 1.72, 1.81, 3.2 and 1.77, 2.10, 2.45 days for imidacloprid, azoxystrobin and difenoconazole, respectively. The corresponding degradation rates (K) were 0.3684, 0.3431, 0.2809; 0.4030, 0.3822, 0.2164 and 0.3915, 0.3293, 0.2832, respectively. These figures indicated that the rate of dissipation of leaves were much lower than those in fruits, this differences reflect the titer of metabolizing enzymes as well as the effect of growth dilution of the residues in fruits. Also, data in the same tables revealed that the initial deposits were greater in leaves compared to fruits. This finding may be is due to the difference in the nature of the recipient surface (I.e. morphological and chemical aspects) on retention of the residues, also cucumber leaves have a large surface per weight unit in comparison to fruits (Shalaby 1992, Soliman 1998, Shalaby 2016 a, b).

Concerning the pickling process of treated cucumber fruits (Table 5), curiously enough to note that the pickling process remove great amounts from the initial deposits of the investigated pesticides ranged between 66.16 to 100% after 3 days of pickling, while after 6 days the removal percentages ranged between 93.58 to 100%. Similar results were obtained by Shiboob *et al.,* 2014, Ryad and Mahmoud 2016 and Shalaby 2017.

Table 5. Effect of pickling process on the residues of the investigated pesticides.

pesticides	Initial deposits mg/kg	Days after pickling			
		3 days		6 days	
		residues	Removal %	residues	Removal %
imidacloprid	2.133	0.301	85.89	0.137	93.58
azoxystrobin	2.763	UND	100	UND	100
difenoconazole	0.982	0.332	66.16	UND	100

Effect of imidacloprid and azoxystrobin+difenoconazole mixture in commercial formulation of Decent on some quality parameter and elements of cucumber fruits.

The quality of cucumber fruits and their validity for edible use by consumers depends on their contamination with pesticide residues. Thus, the possible effects of imidacloprid and Decent formulation (which contain azoxystrobin + difenoconazole mixture) residues on cucumber fruits' quality attributes and elements were determined and presented in tales (6 and 7).

Data in Table 6 show the residue effects of the investigated pesticides on total soluble sugar %, glucose mg/kg, acidity %, total soluble solids (T.S.S.) %, ascorbic acid mg/kg, β-carotene%, dry matter %, and protein % of fresh cucumber fruits. It was found that the levels of these parameters on treated cucumber fruits were significantly reduced during the tested periods (3 and 6 days after application) compared with untreated fruits with the exception that acidity % in cucumber fruits treated with imidacloprid recorded a 4.49% increase.

Based on the means of reduction percentages of the determined quality parameters in treated cucumber fruits, it was noticed that the parameter of total soluble solid (T.S.S.) was the most affected by the two investigated pesticides contrary to the parameter of ascorbic acid which was least affected, whereas the rest of the tested parameters were occupied an intermediate position.

Table 6. Effect of imidacloprid and Decent (azoxystrobin + difenoconazole) residues on some quality attributes of cucumber fruits.

quality parameters	Days after spraying	Untreated fruits	Treated fruits with imidacloprid	Mean redaction %	Treated fruits withDecent (azoxystrobin + difenoconazole)	Mean redaction %
total soluble sugar%	3	9.483^{a}	8.237^{b}		7.937^{c}	
	6	10.11^{a}	9.237^{b}		8.58^{c}	
	Means	9.797^{a}	8.737^{b}	10.82	8.258^{c}	15.70
Glucose mg/100g	3	12.167^{a}	11.237^{b}		10.983^{c}	
	6	13.163^{a}	11.877^{b}		11.753^{b}	
	Means	12.665^{a}	11.557^{b}	11.35	11.368^{b}	10.24
Acidity%	3	5.167^{b}	5.987^{a}		4.337^{c}	
	6	5.389^{a}	5.043^{a}		4.78^{b}	
	Means	5.278^{b}	5.515^{a}	4.49	4.558^{c}	13.63
total soluble solid T.S.S.%	3	6.64^{a}	5.153^{b}		4.983^{c}	
	6	5.937^{a}	5.363^{b}		5.17^{c}	
	Means	6.288^{a}	5.258^{b}	16.38	5.077^{b}	19.27
ascorbic acid mg/100g	3	69.763^{a}	67.187^{b}		66.777^{c}	
	6	70.24^{a}	69.077^{b}		68.167^{c}	
	Means	70.002^{a}	68.132^{b}	2.67	67.472^{c}	3.61
β-carotene %	3	12.37^{a}	11.86^{b}		11.187^{b}	
	6	13.137^{a}	12.793^{b}		12.337^{b}	
	Means	12.754^{a}	12.327^{a}	3.35	11.762^{b}	7.77
dry matter %	3	19.76^{a}	18.623^{b}		18.36^{b}	
	6	20.14^{a}	19.477^{b}		18.823^{c}	
	Means	19.95^{a}	19.05^{b}	4.51	18.592^{c}	6.81
Protein %	3	9.625^{a}	8.541^{b}		8.041^{c}	
	6	10.271^{a}	9.333^{b}		8.583^{c}	
	Means	9.948^{a}	8.937^{b}	10.16	8.312^{c}	16.44

In each raw value followed by the same letter are not significantly different at $P \leq 0.05$

Table 7. Effect of imidacloprid and Decent (azoxystrobin + difenoconazole) residues on some quality attributes of cucumber fruits.

quality parameters	Days after spraying	Untreated fruits	Treated fruits with imidacloprid	Mean redaction %	Treated fruits with decent (azoxystrobin + difenoconazole)	Mean redaction %
N %	3	1.54^{a}	1.367^{b}		1.287^{c}	
	6	1.643^{a}	1.493^{b}		1.373^{c}	
	Means	1.592^{a}	1.430^{b}	10.16	1.330^{c}	16.44
P %	3	0.834^{a}	0.815^{b}		0.794^{c}	
	6	0.863^{b}	0.879^{a}		0.852^{c}	
	Means	0.849^{a}	0.847^{a}	0.15	0.823^{b}	3.01
K %	3	2.487^{a}	2.29^{b}		2.16^{c}	
	6	2.683^{a}	2.543^{b}		2.483^{c}	
	Means	2.585^{a}	2.417^{b}	6.51	2.322^{c}	10.19
Fe mg/kg	3	71.58^{a}	69.137^{b}		68.47^{c}	
	6	72.843^{a}	71.487^{b}		70.14^{c}	
	Means	72.212^{a}	70.312^{b}	2.63	69.305^{c}	4.02
Mn mg/kg	3	21.543^{a}	18.473^{b}		17.583^{c}	
	6	22.76^{a}	19.913^{b}		18.887^{c}	
	Means	22.152^{a}	19.193^{b}	13.36	18.235^{c}	17.68
Ca %	3	1.875^{a}	1.686^{b}		1.573^{c}	
	6	1.938^{a}	1.709^{b}		1.684^{c}	
	Means	1.906^{a}	1.698^{b}	10.95	1.628^{c}	14.59
Zn mg/kg	3	42.76^{a}	41.12^{b}		40.327^{c}	
	6	43.853^{a}	72.4^{b}		41.783^{c}	
	Means	43.307^{a}	41.76^{b}	3.57	41.055^{b}	5.19

In each raw value followed by the same letter are not significantly different at $P \leq 0.05$

The reduction of total soluble sugars, glucose, and T.S.S. levels on treated fruits may be due to the decreasing effects of the tested pesticides on the carbohydrate hydrolyzing enzymes (trehase, amylase, and invertase). The decreasing effects on the dry matter in treated fruits compared with untreated ones may be due to a reduction in concentrating the fruits juice because higher remained of water by decreasing the respiration rates resulting luck accumulation of different solutes in cell vacuoles. The loss in ascorbic acid level may be attributed to the rapid conversion of L-ascorbic acid into dihydro ascorbic acid in the presence of L-ascorbic acid oxidase (Hussien*et al.*, 1998 and Gad 2008). The decrease in protein level was related with the correlation between nitrogen (N) and potassium (K), it is well known that potassium element enhanced the conversion of amino acids to protein.

Regarding the effect of the tested pesticides on the trace and nutrient elements, data in Table 7 showed that the tested pesticides significantly reduced the mean values of N %, P %, K %, Fe mg/kg, Mn mg/kg, Ca % and Zn mg/kg in treated cucumber fruits comparing with untreated fruits. Also, in the same table data revealed that the investigated pesticides treatments gave a higher reduction effect in the levels ofMn% recording 13.36 and 17.68% reduction for imidacloprid and the commercial formulation Decent which contain two fungicides as a mixture (azoxystrobin + difenoconazole), respectively. While the lower effect was recorded in the levels of P% indicating a 0.15 and 3.01% reduction for the above-mentioned two tested pesticides, respectively. The decrease in the tested elements may be due to the reduction effects of the used pesticides on the ability of cucumber plants to absorb the elements from the soil.

Also, data in tables 6 and 7 revealed that the reduction of each quality attribute and element was more pronounced with Decent than imidacloprid. This finding may be due to the presence of two fungicides mixture in the decent formulation (azoxystrobin + difenoconazole).

The tested pesticides are well documented as systemic pesticides (Bac Bean, 2012), such systemic effect is result from the higher penetration through the cucumber fruits, where they act on a certain biochemical system. These results are in harmony with those obtained by Habiba *et al*., 1992, Shalaby and Eisa 1992, Ismail *et al.*, 1993, Habiba and Ismail 1998, Shalabey 2016 (a and c), Shalaby 2017, working with different pesticides in some vegetables and field crops.

REFERENCES

Abd-El Rahman, T.A ,Fayza A. S, and Amany R. M .(2016) Dietary Intake of Pesticides Based on Import Animal LiverConsumption: A Case Study, Cairo, Egypt. International Journal of Innovation and Applied Studies 2016.Vol. 17No. , pp. 424-431.

Abd-El Rahman, T.A.(2020)A survey study of the level of pesticide residues in Egyptian exports of vegetables for the period 2015-2019, based on the RASFF database. GSC Advanced Research and Reviews, 2020, 05(01), 015-029.

Abdelhadi A.I.; M.B.A. Ashour; M.R.A. Tohamy and D. A. Ragheb (2015).Azoxystrobin residues on tomato leaves and fruits.Zagazig J. Agric. Res., 42 (6):1547-1547.

Aguilera, A.; A. Valverde; F. Camacho; M. Boulaid and L. G.Fuentes (2012).Effect of household processing and unit to unit variability of azoxystrobin, acrinathrin and kresoxim methyl residues in zucchini. Food Control 25: 594-600.

Anastassiades, M.; S. J. Lehotay; D. Stajnbaher and F. Schenck (2003).Fast and easy multiresidue method employing acetonitrile extraction/partitioning and ‘‘dispersive solid-phase extraction’’ for the determination of pesticide residues in produce. *J. AOAC. Int*., 86: 412–431.

AOAC (1984).*Association of Official Analytical Chemists.*Official Methods Of Analysis, 19th ed., Washington, D.C. (APC)Agricultural Pesticide Committee2021.http://www.apc.gov.eg/en/default.aspx

Bagi, F. F.; D. B. Budakov; V. P. Bursić; V. B. Stojšin; S. D. Lazić and S. M. Vuković (2014). Efficacy of azoxystrobin for the control of cucumber downy mildew (*Pseudoperonosporacubensis*) and fungicide residue analysis.Crop Protection, 61: 74-78.

Ben-Amotz, A. B. and M. Avron (1983).On the factors which determine massive β-carotene accumulation in the halo tolerant algeDunaliellabardawil. *Plant. Physiol*., 72: 593-597.

Chen, M.F.; H.P. Chien; S.S. Wong and G.C.Li (2004) Dissipation of the fungicide azoxystrobin in Brassica vegetables*. Plant Prot. Bull*,46: 123 – 130.

Daraghmeh, A.; A.Shraim; S.Abulhaj; R.Sansourand J. C. Ng (2007).Imidacloprid residues in fruits, vegetables and water samples from Palestine. Environ Geochem Health, 29:45–50.

Dong,M.; L. Ma; X. Zhan; J. Chen; L. Huang; W. Wang and L. Zhao (2019). Dissipation rates and residue levels of diflubenzuron and difenoconazole on peaches and dietary risk assessment.Regulatory Toxicology and Pharmacology, 108: 104447

Dubois, M., K. A. Giles; J. K. Hamilton; P. A. Robers and F. Smith (1956).Colorimetric method for determination of sugar and related substance.*Analytical Chemistry*, 28: 350-356.

Evenhuis, B. and P. W. Waard (1980).Principle and practices in plant analysis F.A.O. *Soils Bell.*, 38 (1) 152-163.

Gad, M.M. (2008).Effect of some postharvest treatments on storage and shelf life of guava fruits.M.Sc. thesis. Fac. Agric., Zagazig University, Egypt.

Gomaa, E.A.A. and M.H. Belal (1975).Determination of dimethoate residues in some vegetables and cotton plant.*Zagazig Journal of Agric. Res*., 2: 215–219.

Habiba, R.A. and M.M. Ismail (1998).Biochemical effects of Dicofol in strawberries. *Egypt. J. Appl. Sci*., 13 (7):257-273.

Habiba, R.A.; H.M. Ali and S. M. M. Ismail (1992). Biochemical effects of profenofos residues in potatoes. J. Agric. Food Chem. 40: 1852-1855.

Hanafi,A.; M. Dasenaki;A. Bletsou and N. S. Thomaidis (2018).Dissipation rate study and pre-harvest intervals calculation of imidacloprid and oxamyl in exported Egyptian green beans and chili peppers after pestigation treatment.Food Chemistry, 240: 1047-1054.

Hussien, A.M.; M.B. El-Sabrout and A.E. Zaghloul (1998).Postharvest physical and biochemical changes of common and late types of seedy guava fruits during storage. Alex. J. Agric. Res. 43 (3): 187-204.

Ismail, S. M.; H. M. Ali and R. A. Habiba (1993).GC-ECD and GC-M Sanalysis of profenofos residues and biochemical effects in tomatoes and tomato products. J. Agri. Food. Chem. 41:610-615.

Jackson, M. L. (1967). *Soil Chemical Analysis Prentice*.Hall Inc. Englewood cliffs N.J. Library of congress, USA.

Kong, Z.;F. Dong; J. Xu;X. Liu;C. Zhang;J. Li;Y. Li;X. Chen;W. Shanc and Y. Zheng (2012). Determination of difenoconazole residue in tomato during home canning by UPLC-MS/MS. Food Control, 23 (2): 542-546

MacBean, C. (2012). The Pesticide.Manual version 5.2, fifteenth Ed. imidacloprid (485), azoxystrobin (52) and difenoconazole (266).

Malhat, F.; C.h. Anagnostopoulos; S. El-Sayed and S. AbdelsalamShokr (2022).Dissipation of spiroxamine residues in open fi eld cucumber and dietary risk assessment. Hellenic Plant Protection Journal, 15: 40-48.

Montasser, M. R. and H. A. Mahmoud (2009).Chromatographic determination of azoxystrobin, fenhexamid and lufenuron residues in grapevine.*Alex. Sci. Excha. J.,* 30 (1), 37-44.

Ryad, L. M. and A. A. Mahmoud (2016).Study the Effect of Household Processing on some Pesticide Residues in Olive Fruits. *Middle East Journal of Applied Sciences,* 6 (3): 588-593.

Salem, R. E. M. (2011). Sid effects of certain pesticides on the relationship between plant and soil. Ph. D. Thesis. Fac. of Agric., Zagazig Univ.

Salem,S. H.; S. Abd-El Fatah; G. N. Abdel-Rahman; A. S. Fouzy and D. Marrez (2021).Screening for pesticide residues in soil and crop samples in Egypt. Egypt. J. Chem. 64 (5): 2525-2532

Shalaby, A. A. (1992). Residues of some insecticides on and in broad bean plants. Egypt. J. Appl. Sci., 7 (11): 531-539.

Shalaby, A. A. (2016 a).Residual behavior of abamectin and cyflufenamid in squash plants.Annals of Agric. Sci., Moshtohor, Vol. 54 (4).

Shalaby, A. A. (2016 b).Residues of thiamethoxam and chlorpyrifos on okra in relation to their effects on some internal quality parameters and elements in fruits. J. Product. & Dev., 21(3): 349-367.

Shalaby, A. A. (2016 c).Residues of Profenofos with Special Reference to Its Removal Trials and Biochemical Effects on Tomato. J. Plant Prot. and Path., Mansoura Univ.,7 (12) ,845–849

Shalaby, A. A. (2017).Residues of lambda-cyhalothrin insecticide and its biochemical effects on sweet pepper fruits. J. Product. & Dev., 22 (1): 65-81.

shalaby, A.A. and E. S. Eisa (1992).Insecticide application on rape in relation to their residues, biochemical constituents in seeds and aphid infestation. Egypt. J. Apple. Sci., 7 (10): 144-158.

Shiboob, M. H.; M. H. Madkour and A. A. Zaitoun(2014). Effect of washing and household processing on removal performance of some organophosphorus insecticides. J. of Food, Agric. & Envir.12 (2): 1255 - 1259.

Shokrzadeh, M.;M. Saberyan and S. SaeediSaravi (2008).Assessment of lead (Pb) and cadmium (Cd) in 10 sam-ples of Iranian and foreign consumed tea leaves and dis-solved beverages. Toxicological and Environmental Chemistry 90(5): 879–883.

Soliman, M.H.A. (1998).Studies on certain pests infesting some cucurbitaceous plants. M. Sc. Thesis. Fac.Of Agric., Zagazig Univ.

Steel, R. C. D. and J. H. Torrie (1980).*Principles and Procedures of Statistics*: A Biomatrical Approach, Second ed. Mc-Graw Hill Kogakusha Ltd., pp. 633.

Sundravadana, S.; D. Alice; R. Samiyappan and S. Kuttalam (2008).Determination of azoxystrobin residue by UV detection high performance liquid chromatography in mango.*J. Braz. Chem. Soc*., 19 (1), 60-63

دراسة متبقيات مبيدات أميداكلوبريد و أزوكسيستروبين و دايفينوكينازول وتأثيراتها البيوكيميائية فى الخيار

على عطا على شلبى[1] ، طارق عبد العليم عبد الرحمن[2] و محمد عطا على شلبى[2]
[1] قسم وقاية النبات ـ كلية الزراعة ـ جامعة الزقازيق ـ مصر.
[2] قسم بحوث متبقيات المبيدات وتلوث البيئة ـ المعمل المركزى للمبيدات ـ مركز البحوث الزراعيه ـ الدقي الجيزه ـ مصر.

الملخص

تم رش نباتات الخيار وقت الاثمار فى يونيه 2021 فى حقل بقرية الطاهرة مركز الزقازيق محافظة الشرقية بمبيدات أميداكلوبريد (Avenue70% WG) والمستحضر التجاري (Decent32.5% SC) والمحتوي على خليط من المبيدين الفطريين ازوكسيستروبين 20% و دايفينوكينازول 12.5% بغرض تقدير متبقيات هذه المبيدات فى كل من ثمار وأوراق الخيار وكذلك تقييم فعالية متبقياتها على بعض المحتويات الكيماوية فى ثمار الخيار المعاملة. وأوضحت النتائج أن كمية المترسب الأولى فى الاوراق أكثر من الثمار. وسرعة تحطم المبيدات كان فى الثمار أعلى من الأوراق. وقدرت كميات من متبقى المبيدات فى قشرة الثمار أكثر كثيرا من اللب. كما يمكن تناول ثمار الخيار بعد تقشيرها فى أي وقت خلال فترة التجربة بعد الرش. وأدى تخليل الخيار إلى إزالة كميات كبيرة من متبقى المبيدات المستخدمة. وقد نتج عن استخدام المبيدات تحت الدراسة إلى انخفاض معنوى فى محتويات ثمار الخيار المعاملة من السكريات الكلية ، الجلوكوز ، الحموضة ، المواد الصلبة الذائبة ، حمض الأسكوربيك ، والبيتا كاروتين ، الوزن الجافوالبروتين وكذلك بعض العناصر مثل النيتروجين ، الفوسفور ، البوتاسيوم ، الحديد ، المنجنيز ، الكالسيوم والزنك وكان التأثير أكثر وضوحا مع المستحضر التجاري Decent لإحتوائه على مخلوط مبيدين فطريين.