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RESIDUES OF THIAMETHOXAM AND CHLORPYRIFOS ON OKRA IN RELATION TO THEIR EFFECTS ON SOME INTERNAL QUALITY PARAMETERS AND ELEMENTS IN FRUITS.

Shalaby A. Aly
Plant Protection Department, Faculty of Agriculture, Zagazig University, Egypt

ABSTRACT

The present work was conducted to study the residues of two insecticides on okra plant. Thiamethoxam (Actara 25% WG) and chlorpyrifos (Dursban 48% EC) were sprayed at mature stage. Fruits and leaves samples were collected at 2 hrs to 15 days after application. QuEChERS method was used for extraction and clean-up and analyzed using HPLC and GC for thiamethoxam and chlorpyrifos, respectively. Results revealed that, okra leaves remained higher initial amounts than fruits by about 382.52% and 893.48% of thiamethoxam and chlorpyrifos, respectively. Loss percentages of initial deposits were higher in okra fruits than leaves. The half-life ($t_{½}$) values of thiamethoxam and chlorpyrifos were 2.09, 3.16 and 1.59, 2.57 in okra fruits and leaves, respectively. Data indicated that okra fruits could be consumed safely after 15 days of treatment with thiamethoxam, washing or boiling of okra fruits (2 min) during the first 6 days after spraying did not alter the PHI value, while in case of chlorpyrifos washed and unwashed okra fruits could be used safely after 6 days and no safety interval was needed after boiling okra fruits for 2 min. The removal percentages of thiamethoxam and chlorpyrifos residues by washing ranged between 9.39 - 46.23%; 5.88 – 21.40%, while the corresponding values due to boiled the okra fruits 2 min ranged from 74.77 to 89.09%; 84.63 - 87.51%. Residues of thiamethoxam and chlorpyrifos significantly decreased total soluble sugar%, glucose mg/100g, acidity %, total soluble solids %, ascorbic acid mg/100g, protein content%, β-carotene%, protein% and dry matter % of fresh treated okra fruits comparing with the control during the tested period. Concerning the trace / nutrients elements thiamethoxam significantly reduced the mean values of N%, P%, K%, Mn% and Ca% and increased the mean amounts of Fe% and Zn in treated okra fruits.

Chlorpyrifos significantly reduced the mean levels of N%, P%, K%, Fe% and Ca% and increased the mean amounts of Mn% and Zn in okra fruits. These effects were more pronounced in thiamethoxam treatment. Therefore, attention must be given to the use of thiamethoxam especially during the mature stage.

***Conclusively**, okra fruits treated with the neonicotonoied insecticide thiamethoxam needed a long interval to reach the maximum residue limits. Also, obtained data revealed that its residues were more effective in some quality attributes as well as some trace and nutrient elements than that the organphosphorus chlorpyrifos. Therefore, special care must be given to the use of this insecticide especially at the mature stage of okra plants.*

Key words: Thiamethoxam, chlorpyrifos, QuEChERS, okra, residues, quality parameters.

INTRODUCTION

In the ancient time, Egyptian farmers cultivated other plants such as okra, squash and onion either between or adjacent of the main crops (cotton fields). Such vegetable crops are exposed directly or indirectly to drifts of pesticides recommended against pests infesting the main crop. This intercropping system results in undesired residues onto the Non-target crops, *i.e,* the vegetable ones which had deleterious effects on consumes.

Nowadays, farmers cultivated okra plants separately in vast areas due to economical return. In Egypt, Okra is one of the most popular vegetable summer crops. It has been used for its young green pods as fresh, canned, frozen and dry states. Okra fruit has high nutritional value. It contains vitamin A, B and C as well as fat, carbohydrate, fiber, iron, iodine and is a protein source in nearly all developing countries. Its fruits contain a small amount of Ca, P, Mg and K. (Grubben and Denton, 2004). Okra plants are liable to be infested with different insect pests (jassid, aphids, whiteflies, cotton leaf worm and spider mite) causing serious injury and reducing the green okra fruits (Mahal *et al.,* 1994; Sattler *et al.,* 2007 and Amro *et al* , 2013). So pest control is necessary and played a significant role in adequate production. Many agricultural pests were controlled with insecticides in extensively way. Insecticides were used especially at fruiting stage with non safe waiting period therefore, leads to accumulation of pesticide residues in consumable vegetables. (Kumari *et al.*, 2002).

Thiamethoxam is systemic neonicotinoied insecticide for soil and foliar application, used to control a variety of pests such as aphids, whiteflies, trips, beetles, leafhopper, bugs and borers in fruiting, corn, tubers, vegetable and cotton (Antunes-kenyon and Kennedy, 2001). Many studies have reported excellent efficacy of thiamethoxam against sucking insect pests such as aphids, trips or leafhopper via contact and ingestion at low rates (Manson *et al.* 2000, Bethke *et al.*, 2001).

Chlorpyrifos was used to control of Coleoptera, Diptera, Homoptera and Lepidoptera in soil or on foliage in over 100 crops, including some vegetables and field crops. Chlorpyrifos was non-systemic insecticide with contact, stomach, and respiratory action (MacBean, 2012).

Therefore, the main objective of this study was to evaluate the residues of thiamethoxam and chlorpyrifos in okra fruits and leaves, and their effects on some chemical constituents and quality attributes. Effects of washing with tap water and boiling to removal their residues from treated okra fruits were also studied.

MATRIALS AND METHODS

1- Pesticide selected for this study:

In this work, pesticides used and their rates per feddan (1 feddan= 4.200 m^2) were thiamethoxam, (Actara 25% WG) at 80 g /feddan and chlorpyrifos, (Dursban 48% EC) at 1 L /feddan. Rates of pesticideal application were chosen on the basis of recommended rates on other related crops.

2- Field experiment and sampling

The research was conducted in summer season of 2016 at private field of okra (*Abelmoschus esculentus* L. ver baladey) located at El-Tahra village, Zagazig district, Sharkia governorate.

The experiments were planned in a randomized complete block design. For each tested insecticide, three plots were done (6×7 m each) and plot to plot distance 2 m. A knapsack-sprayer with one nozzle was used to deliver 200 liters water/ feddan. Mature plants were sprayed (June 15, 2016) with thiamethoxam and chlorpyrifos once at the rate of 20 g a.i. / feddan, 480 g a.i. / feddan, respectively. The control plots were left unsprayed. Samples (fruits and leaves) were taken after 2 hrs, 1, 3, 6, 9, 12 and 15 days. Also, fruit Samples, 2 hrs, 1, 3 and 6 days, were subjected to study the effect of washing and boiling on pesticide residues. In this set treated okra fruits were divided in two subsamples, the first was washed with tap water and the second was boiled for 2 minute then left to cold at room temperature.

3- Residues determination

Okra samples were extracted and cleaned up using QuEChERS methodology (Anastassiades *et al.*, 2003). A homogenized okra fruit and leaves samples (10 g) was taken in to a centrifuge tube (50-mL). Fifteen milliliters of acetonitrile containing 1.0% acetic acid was transferred to the centrifuge tube and vigorously shaken for 1 min. Then, 4 g magnesium sulfate anhydrous, 1 g sodium acetate was added, and then the mixture was shaken vigorously for 5 min. The mixture was centrifuged at 3000 rpm for 5 min. One milliliter of the supernatant was transferred to centrifuge tube (1 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 thiamethoxam was taken for analysis by HPLC with an Agilent 1260 HPLC system (USA), with quaternary pump, auto sampler injector, thermostat compartment for the column, and photodiode array detector. The chromatographic column was Zorbax C_{18} XDB (250 × 4.6 mm, 5 mm). The column was kept at room temperature. Flow rate of mobile phase (acetonitrile / water, 90:10, v/v) was 1 ml min^{-1}, and injection volume was 20 µL.

The supernatant of chlorpyrifos was taken for analysis by Agilent Technologies 7890A gas chromatograph equipped with flame photometric detector (FPD) operated in the phosphorus mode (526 nm filter) was used for the determination of chlorpyrifos residues. The column was HP-5 (30 m×0.32 mm×0.25 µm film thickness) 5% diphenyl and 95% dimethylpolysiloxane. Injector temperature was 250 °C. Detector temperature was 250 °C. Column temperature was 220 °C for chlorpyrifos. Gases flow rates were 60, 30 and 30 ml/min. for nitrogen, hydrogen and air, respectively (Hegazy *et al.*, 2006). These conditions resulted in good separations and high sensitivity was obtained with retention time 3 min and 2.2 min for thiamethoxam and chlorpyrifos, respectively.

4- Effect of thiamethoxam and chlorpyrifos residues on some quality parameters and trace elements

To study the effect of thiamethoxam and chlorpyrifos residues on some quality parameters and some trace and nutrient elements, samples of treated and untreated tomato fruits were taken at 9, 12 and 15 days after application. Quality parameters included total soluble sugars, glucose, acidity, total soluble solid, ascorbic acid, β-carotene, protein and dry matter. While 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 adsorption spectroscopy (Jackson, 1967). Total soluble sugars and glucose were determined colorimetrically using the picric acid method as described by Dubois *et al.*, (1956). Total soluble solid were estimated using a refractometer. Acidity, ascorbic acid, protein and dry matter were determined according to the Methods of Association of Official Analytical Chemists (AOAC) (1984). β-carotene was determined by the method of Ben-Amotza and Avron (1983).

5. Recovery samples and statistical analysis

To estimate the recovery percentages, known quantities of thiamethoxam and chlorpyrifos were added to control samples of okra fruits and leaves at levels of 0.1 and 1 mg/kg extract and clean-up were carried out as described above. The recovery rates in fruits and leaves for the two tested insecticides were 90.18% and 88.15% in leaves and fruit for thiamethoxam, respectively and the respective values for chlorpyrifos were 94.82 and 85.73%. The all results obtained were corrected according to their recovery percentages.

Statistical significance of the data was determined by using the analysis of variance with L.S.D method at the probability of 0.05 Steel and Torrie (1980). The rate of degradation (K) and Half-life (t½) periods of each insecticide were calculated according to (Gomaa and Belal, 1975).

RESULTS AND DISCUSSION

1- Residues of thiamethoxam in and on okra fruits and leaves

Residues and loss percentages of thiamethoxam in and on okra fruits and leaves were illustrated in Table (1) and Figure (1). The initial deposits,

Table 1: Residues of thiamethoxam detected in okra fruits and leaves**.**

Days after treatment	Fruits residues (mg/kg)	Dissipation %	Persistence	Leaves residues (mg/kg)	Dissipation %	Persistence
Initial (2 hrs)	0.532	—	100.00	2.035	—	100.00
1	0.393	26.13	73.87	1.665	18.18	81.82
3	0.218	59.02	40.98	1.072	47.32	52.68
6	0.130	66.92	33.08	0.864	57.54	42.46
9	0.034	91.35	8.65	0.392	80.74	19.26
12	0.014	96.43	3.57	0.115	93.09	6.91
15	0.003	99.41	0.56	0.082	95.07	4.93
K	0.331632			0.218785		
t½	2.09			3.16		

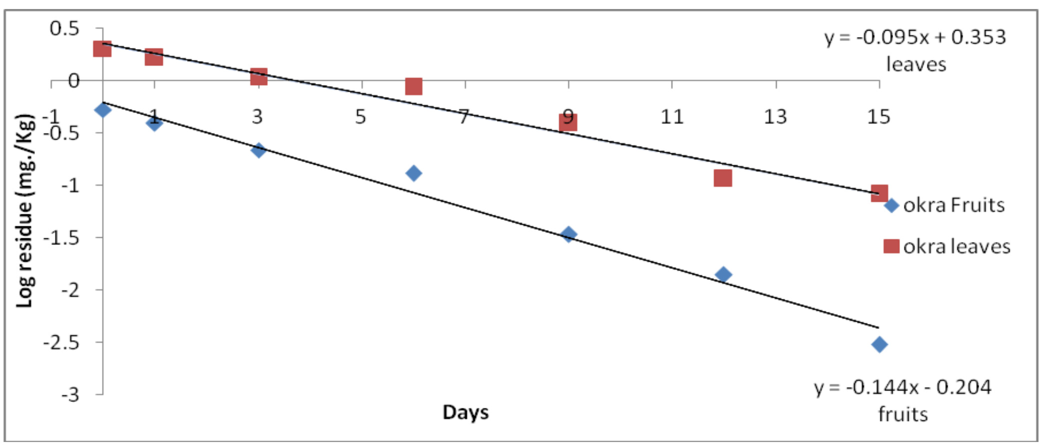

Figure 1: Log. residue – day regression line of thiamethoxam in okra fruits and leaves.

which remained on okra fruits and leaves two hours after treatment were 0.532 mg/kg and 2.035 mg/kg, these amounts dropped to 0.393 mg/kg and 1.665 mg /kg one day after the application indicating a dissipation rate of 26.15% and 18.18%, respectively. Residues of thiamethoxam in and on okra fruits and leaves were gradually decreased to 0.218, 1.072; 0.130, 0.864; 0.034, 0.392;

0.014, 0.105 and 0.003, 0.022 mg/kg indicated loss rates of 59.02, 47.32; 66.92, 57.54; 91.35, 80.74; 96.43, 94.85 and 99.44, 98.92%, respectively after 3, 6, 9, 12 and 15 days of spraying. The $t_{½}$ values were 2.09 and 3.16 days from the treatment with degradation rates of 0.331632 and 0.218785 for the okra fruits and leaves, respectively. These figures indicated that the insecticide thiamethoxam was degraded higher in fruits than that leaves.

Data in the same table indicated that despite of the low $t_{½}$ for thiamethoxam in fruits (2.09 days) okra fruits were consumed safely after 15 days of treatment, concerning health aspects, the maximum residue limit (MRL) of thiamethoxam residues in and on okra according of EU Pesticides database - European Commission was 0.01 mg/kg. This may be due to the dangers effect of thiamethoxam for mammalian.

2- Residues of chlorpyrifos in and on okra fruits and leaves

Residues and loss percentages of chlorpyrifos in and on okra fruits and leaves were shown in Table (2) and Figure (2). The initial deposits determined on fruits and leaves two hours after application were 3.163 and 28.261 mg/kg, respectively. These amounts were decreased to 1.854 and 21.443 mg/kg one day after treatment recording loss rates of 41.39% and 24.13%. Chlorpyrifos residues in and on okra fruits and leaves were decreased gradually to reach 0.829, 13.670; 0.430, 9.532; 0.085, 4.180; 0.011, 1.053 an 0.006, 0.462 mg/kg indicating loss percentages of 73.79, 51.63; 86.41, 66.27; 97.31, 85.21; 99.65, 96.27 and 99.81, 98.37% after 3, 6, 9, 12 and 15 days of spraying, respectively. The $t_{½}$ values were 1.58 and 2.57 days from the treatment with degradation rates of 0.43661 and 0.269451 for the okra fruits and leaves, respectively. These figures indicated that the insecticide chlorpyrifos was degraded higher in fruits than that leaves.

Results in the Tables (1 and 2) revealed that okra leaves remained higher initial amounts than fruits by about 382.52% and 893.48% of thiamethoxam and chlorpyrifos, respectively. This finding may be due to insecticide chemical structure and the effect of nature of the recipient surface (i.e., morphological and chemical aspects) on retention of residues, also leaves have a large surface per weight unit in comparison to fruits.

Table 2: Residues of chlorpyrifos detected in okra fruits and leaves.

Days after treatment	Fruits residues (mg/kg)	Dissipation %	Persistence	Leaves residues (mg/kg)	Dissipation %	Persistence
Initial (2 hrs)	3.163	—	100.00	28.261	—	100.00
1	1.854	41.39	58.61	21.443	24.13	75.87
3	0.829	73.79	26.21	13.670	51.63	48.37
6	0.430	86.41	13.59	9.532	66.27	33.73
9	0.085	97.31	2.69	4.180	85.21	14.79
12	0.011	99.65	0.35	1.053	96.27	3.73
15	0.006	99.81	0.19	0.462	98.37	1.63
K	0.43661			0.26945 1		
t½	1.59			2.57		

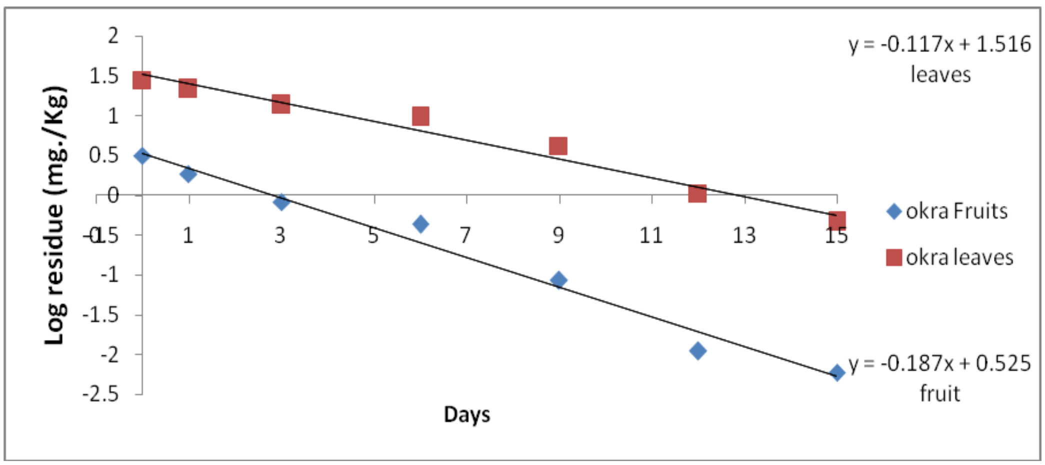

Figure (2): Log. residue – day regression line of chlorpyrifos in okra fruits and leaves.

3- Effect of washing and parboil on thiamethoxam and chlorpyrifos residues

Data in Table (3) clearly showed the effect of home processing like washing with tap water and boiling on the reduction of thiamethoxam and chlorpyrifos residues in okra fruits. Results indicated that during the first four

Table 3: Effect of washing and boiling on thiamethoxam and chlorpyrifos residues contaminated okra fruits.

Days after treatment	Thiamethoxam			Chlorpyrifos		
	Unwashed fruits	Washed fruits	Boiling	Unwashed fruits	Washed fruits	Boiling
Initial (2 hrs)	0.532	0.286 (46.24)	0.058 (89.09)	3.163	2.486 (21.40)	0.395 (87.51)
1	0.393	0.309 (21.37)	0.083 (78.88)	1.854	1.508 (18.66)	0.258 (84.63)
3	0.218	0.176 (19.49)	0.055 (74.77)	0.829	0.732 (11.70)	0.124 (85.04)
6	0.130	0.118 (9.23)	0.029 (77.69)	0.430	0.396 (7.91)	0.058 (86.51)

Number between brackets indicate the % Dissipation

samples (2 hrs, 1, 3 and 6 days after spraying); the removal percentages of thiamethoxam residues by washing ranged between 9.39 and 46.23%. While the removal percentages due to boiled treated okra fruits for 2 min ranged from 74.77 to 89.09% while, the removal percentages ranged between 5.88 – 21.40 and 84.63 - 87.51% by washing and boiling for 2 minutes, respectively in case of chlorpyrifos

Curiously enough to note that in case of the insecticide thiamethoxam the highest removal percentage by washing with tap water was recorded after 2 hours of application (46.24%) then dropped to be 21.37% after one day. This phenomenon is due to the high solubility in water and the systemic action of thiamethoxam that rapidly taken up into the plant and transported acropetally in the xylem. (MacBean, 2012).

Data in Tables (2 and 3) reveled that unwashed and washed okra fruits treated with chlorpyrifos could be used safely for human consumption after 6 days of treatment which comparing the residues at 6 days with the maximum residues limits (0.5 mg/kg) recorded by EU Pesticides database - European

Commission, while no safety interval was needed for okra fruits if the fruits were boiled for 2 minutes. While in case of thiamethoxam the boiled of treated fruits did not alter the PHI values (Tables, 1 and 3).

The finding results concerning with the residues of thiamethoxam and chlorpyrifos in and on okra fruits are in harmony with those obtained by Randhawa *et al*. (2007) found that the decreased of chlorpyrifos residues ranged for 12% to 48% during boiling of different vegetables with water. Kumari (2008) reported that washing of brinjal, cauliflower and okra reduced the residues of OP insecticides by 77% in brinjal, followed by 74% in cauliflower and 50% in okra. The same treated was observed by boiling process where maximum (100%) reduction of insecticides in brinjal followed by 92% in cauliflower and 75% in okra.

The half-life of thiamethoxam was 2.3 days in spinach treated by 25% thiamethoxam suspension concentration applied at 180 g/ha solution and the residues in spinach was 0.55 mg/kg after 3 days (Bin *et al*, 2009). Ahmed (2010) found that the removal percentages of pirimiphos-methyl on okra fruits ranged between 84.81 – 100.00% resulting of blenching the treated okra fruits. Sheikh *et al*. (2012) reported that blanching of okra fruits was more effective in eliminating pesticide residues as compared to tap water washing. Lozowicka and Jankowska (2014) stated that washing broccoli plants with tap water reduced chlorpyrifos residues by 42.4%. The blanching step decreased chlorpyrifos by 52% and the cooking resulted in decreased of chlorpyrifos residues up to 61.6%. Vemuri *et al.* (2014) found that running tap water washing reduced the residues of OP insecticides in tomato (Dimethoate, Methylparathion, Quinolphos, Endosulfan and Profenophos) by 47.07% to 53.00%. Andrade *et al*. (2015) stated that the most imported mechanism that may be lead to the possible residue alteration during household washing processes is the dissolution, which is related the water solubility of the pesticide residues. Also, the penetration is a dynamic process that may control the fate of a pesticide residue during washing.

Other factors may further affect the pesticide dissolution mechanism, such as the type of formulation applied, temperature and initial concentration of the pesticide residue on commodity, pesticide partition coefficient (Kow), ionic strength and pH of the aqueous media. Sleem (2015) reported that broad bean pods and green bean pods had considerable amounts of thiamethoxam residues (0.495 – 0.002 and 0.872 – 0.01 mg/kg), respectively depending on the time from insecticide application. Also, the same author found that cooking process reduced the residues of thiamethoxam from 0.28 to 0.052 mg/kg (81.43% reduction) and from 0.442 to 0.142 mg/kg (67.87% reduction) in broad bean pods and green bean pods, respectively. Ramadan *et al.* (2016) stated that the half-life in days were 2.5 and 6.3 for chlorpyrifos and thiamethoxam in tomato. The PHI values were 1.5 and 10 days for tomatoes treated with chlorpyrifos and thiamethoxam, respectively.

4- Effect of thiamethoxam and chlorpyrifos residues on some quality attributes

The quality of okra fruits and its validity for edible use by consumer depends on its contamination with pesticide residues. Thus, the possible effects of thiamethoxam and chlorpyrifos residues on okra fruits quality were determined and presented in Tables (4 and 5).

Data in Table (4) showed the residue effects of thiamethoxam and chlorpyrifos on total soluble sugar%, glucose mg/100g, acidity %, total soluble solids %, ascorbic acid mg/100g, β-carotene % and dry matter % of fresh okra fruits. The mean value of total soluble sugar, glucose, acidity, total soluble solids, β-carotene, dry matter and protein content % contents of thiamethoxam and chlorpyrifos treated okra fruits were decreased during the tested period (15 days) comparing with untreated fruits. The corresponding figures were 4.767, 4.301, 4.686; 22.322, 21.735, 21.963; 4.123, 4.421, 4.536; 4.016, 3.643, 3.921; 6.000, 5.645, 5.500; 16.920, 15.996, 16.110 and 9.423, 8.911, 9.413 for the control, thiamethoxam and chlorpyrifos, respectively. In case of ascorbic acid thiamethoxam reduced the mean value (23.11 mg/100g), while chlorpyrifos increased this amount to be 23.726 mg/100g comparing with the control 23.206 mg/100g. Also, data revealed that the reduction of these quality attributes was more pronounced with thiamethoxam than chlorpyrifos. This finding may be due to the ability of thiamethoxam to have a good systemic effect. Although thiamethoxam is well documented as systemic insecticide (**MacBean, 2012)** such systemic effect is result from the higher penetration of thiamethoxam through the okra fruits, where it acts on certain biochemical system.

The decreasing of total soluble sugars, glucose and T.S.S in treated fruits may be due to the decreasing effects of the two tested insecticides thiamethoxam and chlorpyrifos on the carbohydrate hydrolyzing enzymes (invertase, trehase and amylase).

The decreasing effects of thiamethoxam and chlorpyrifos on dry matter in treated okra fruits compared with untreated fruits may be due to the reduction in concentrating the fruit juice because higher remained of water by decreasing the respiration rates resulting lack accumulation of different solutes in cell vacuoles.

Table 4: Effect of thiamethoxam and chlorpyrifos residues on some quality attributes of okra fruits.

Quality parameters	Days after spraying	Untreated fruits	Treated fruits with thiamethoxam	Treated fruits with chlorpyrifos
Total soluble sugar %	6	5.500 a	4.125 c	5.075 b
	9	3.945 b	4.465 a	4.425 a
	15	4.856 a	4.365 b	4.560 b
	Means	**4.767 a**	**4.318 b**	**4.686 a**
Glucose mg/100g	6	23.106 a	21.716 b	21.705 b
	9	21.770 c	21.935 a	21.815 b
	15	22.090 b	21.555 c	22.370 a
	Means	**22.322 a**	**21.735 c**	**21.963 b**
Acidity %	6	3.560 c	4.230 b	4.605 a
	9	4.535 a	4.475 b	4.460 b
	15	4.276 b	4.560 a	4.545 a
	Means	**4.123 c**	**4.421 b**	**4.536 a**
Total soluble solid (T.S.S.) %	6	4.450 a	3.646 b	3.750 b
	9	3.555 c	3.750 b	3.945 a
	15	4.045 b	3.5350 a	4.070 a
	Means	**4.016 a**	**3.643 c**	**3.921 b**
Ascorbic acid mg/100g	6	25.260 a	21.350 c	23.540 b
	9	21.810 c	23.740 b	24.085 a
	15	22.550 c	24.255 a	23.5550 b
	Means	**23.206 b**	**23.115 c**	**23.726 a**
β-carotene%	6	7.160 a	5.860 b	5.458 c
	9	5.665 b	6.040 a	6.095 a
	15	5.175 a	5.035 b	4.955 c
	Means	**6.000 a**	**5.645 b**	**5.500 c**
Dry matter%	6	15.170 c	17.225 a	16.345 b
	9	17.155 b	15.835 c	17.265 a
	15	18.436 a	14.930 b	14.720 c
	Means	**16.920 a**	**15.996 c**	**16.110 b**

Protein%	6	10.870 a	9.275 c	9.620 a
	9	8.625 c	9.025 b	9.625 a
	15	8.776 a	8.435 a	8.995 b
	Means	**9.423 a**	**8.911 b**	**9.413 a**

5- Effect of thiamethoxam and chlorpyrifos residues on some trace and nutrients elements.

Concerning the trace and nutrients elements, data in Table (5) showed that thiamethoxam significantly reduced the mean values of N%, P%, K%, Mn% and Ca% in treated okra fruits comparing with the untreated fruits. The mean values of Fe% and Zn% were significantly increased in the fruit treated with thiamethoxam comparing with untreated one. While in case of chlorpyrifos it was found that the mean levels of N%, P%, K%, Fe mg/kg, Ca% were significantly reduced in treated fruit when compared to the untreated samples. The mean values of Mn mg/kg and Zn mg/kg were significantly increased in the fruits treated with thiamethoxam comparing with untreated one. Data in the same table revealed that thiamethoxam treatments gave higher reduction effect in the levels of P%, K%, Ca% in okra fruits when compared with fruit treated with chlorpyrifos. The decreasing in the tested elements may be due to reduction effects of the two tested insecticide on the ability of okra plants to absorb the trace nutrient elements from the soil. In this respect, Rouchaud *et al.* (1983) found that the percentage of Birlane, Nexion and Dyeonate generally increased the free sugar concentration of summer carrots. Habiba *et al.* (1992) reported that the organophosphorus insecticide profenofos residues slightly decreased the glucose content in potatoes and ascorbic acid was elevated by 20% in profenofos treated potatoes. Ismail *et al.* (1993) reported the same in tomatoes. Radwan (1995) found that pirimiphos-methyl residues appeared to have significant effects on total soluble sugars, ascorbic acid, Iron and calcium levels of tomato fruits and breoad bean seeds. Significant effects were also noticed on a pH values in bean seeds and manganes content in tomato after treated with chlorpyrifos-methyl and pirimiphos-methyl.

Chlorpyrifos-methyl exhibited a significant increased in crude protein in bean seeds, whereas significant decreased on β-carotene in tomato fruits was noticed. Habiba and Ismail 1998 found that dicofol treated in strawberries decreased the total soluble solids, glucose, ascorbic acid and protein content after 2 weeks of treatment, but the normal value were restored at the third week following application. Salem (2011) reported that the elements N, P, K, Mg, Fe, Mn, Na and Ca were reduced in wheat treated with malathion.

Table 5: Effect of thiamethoxam and chlorpyrifos residues on some trace and elements of okra fruits.

Elements	Days after spraying	Untreated fruits	Treated fruits with thiamethoxam	Treated fruits with chlorpyrifos
N %	6	1.740 a	1.486 b	1.540 c
	9	1.380 c	1.445 b	1.540 a
	15	1.405 b	1.350 c	1.440 a
	Means	**1.508 a**	**1.427 b**	**1.506 a**
P %	6	0.764 a	0.545 c	0.676 b
	9	0.666 a	0.653 b	0.552 c
	15	0.682 a	0.623 c	0.633 b
	Means	**0.704 a**	**0.607 c**	**0.620 b**
K %	6	3.618 a	2.090 b	2.362 b
	9	2.195 a	2.335 a	2.180 a
	15	2.250 a	2.075 c	2.240 b
	Means	**2.687 a**	**2.166 b**	**2.260 b**
Fe mg/kg	6	77.100 b	85.546 a	89.535 a
	9	86.435 b	95.620 a	83.113 b
	15	96.310 b	105.113 c	75.935 a
	Means	**86.615 b**	**95.460 a**	**82.861 c**
Mn mg/kg	6	60.126 c	75.106 b	78.535 a
	9	83.555 a	72.865 c	79.865 b
	15	84.095 b	77.150 a	82.150 c
	Means	**75.925 b**	**75.040 c**	**80.183 a**
Ca ???	6	0.855 a	0.670 c	0.760 b
	9	0.745 b	0.754 a	0.640 c
	15	0.694 b	0.690 b	0.785 a
	Means	**0.765 a**	**0.704 c**	**0.728 b**
Zn mg/kg	6	22.216 c	25.746 b	28.346 a
	9	27.345 b	25.835 c	28.265 a
	15	28.405 a	26.735 b	27.155 b

	Means	**25.988 c**	**26.105 b**	**27.922 a**

Conclusively, okra fruits treated with the neonicotonoied insecticide thiamethoxam needed a long interval to reach the maximum residue limits. Also, obtained data revealed that its residues were more effective in some quality attributes as well as some trace and nutrient elements than that the organphosphorus chlorpyrifos. Therefore, special care must be given to the use of this insecticide especially at the mature stage of okra plants.

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متبقيات الثياميثوكسام والكلوربيريفوس فى الباميا وعلاقة ذلك بتأثيرهما على بعض خواص الجودة والعناصر فى الثمار

على عطا على شلبى
قسم وقاية النبات – كلية الزراعة – جامعة الزقازيق – الزقازيق - مصر.

أجريت هذه الدراسة لتحديد بقايا اثنين من المبيدات الحشرية على نباتات البامية. حيث تم رش الثيامثوكسام (Actara 25٪ WG) والكلوربيريفوس (Dursban 48٪ EC) على نباتات البامية في مرحلة النضج. تم أخذ عينات من الثمار والاوراق بعد ساعتين إلى ١٥ يوما بعد الرش. وإستخدم طريقة كويتشرز لإستخلاص وتنقية العينات وتم تقدير المتبقى باستخدام HPLC وGC لثيامثوكسام والكلوربيريفوس، على التوالي. وكشفت النتائج أن أوراق البامية إحتفظت بكميات أولية أعلى من الثمار بنحو ٣٨٢,٥٢٪ و ٨٩٣,٤٨٪ من الثيامثوكسام والكلوربيريفوس، على التوالي. كانت نسبة الفقد للمتبقى الأولى أعلى في ثمار البامية عن الأوراق. وكانت قيم التحطم النصفية ($t_{½}$) كالتالى ٢,٠٩ ، ٣,١٦ و ١,٥٩ ، ٢,٥٧ في ثمار البامية وأوراق البامية للثيامثوكسام والكلوربيريفوس، على التوالي.

وأوضحت النتائج أنه يمكن استهلاك ثمار البامية بعد ١٥ يوم من المعاملة بالثيامثوكسام و لم تؤثر عمليات الغسيل والسلق الجزئى على هذه الفترة بينما فى حالة مبيد الكلوربيريفوس. وكذلك أوضحت النتائج ايضا أنه يمكن استهلاك ثمار البامية المغسولة والغير مغسولة بعد ٦ أيام ولا توجد فترة انتظار للاستهلاك الادمى بعد اجراء السلق الجزئى للثمار المعاملة بمبيد الكلوربيريفوس. وكانت نسبة إزالة متبقيات الثيامثوكسام والكلوربيريفوس عن طريق الغسيل تراوحت بين ٩,٣٩ – ٤٦,٢٣% ، ٥,٨٨ – ٢١,٤٠% أما عن طريق غلي ثمار البامية لدقيقتين تراوحت بين ٧٤,٧٧ – ٨٩,٠٩% ، ٨٤,٦٣ – ٨٧,٥١% ، على التوالي.

وكان لمتبقى الثيامثوكسام والكلوربيريفوس تأثير معنوى فى انخفاض السكريات الكلية ، الجلوكوز ، الحموضة ، المواد الصلبة الذائبة ، حمض الأسكوربيك ، والبيتا كاروتين ، الوزن الجاف والبروتين لثمار البامية المعاملة مقارنة مع بالكنترول.

بينما كان لمتبقى الثيامثوكسام تأثير معنوى فى إنخفاض النيتروجين ، الفوسفور ، البوتاسيوم ، المنجنيز والكالسيوم وزيادة فى الحديد والزنك لثمار البامية المعاملة بينما كان لمتبقى الكلوربيريفوس تأثير معنوى فى انخفاض النيتروجين ، الفوسفور ، البوتاسيوم ، الحديد والكالسيوم وزيادة فى المنجنيز والزنك في ثمار البامية. وكانت هذه التأثيرات أكثر وضوحا مع مبيد الثيامثوكسام ولذلك يجب لفت الانتباه الى خطورة إستخدام هذا المبيد وخاصة خلال طور نضج الثمار.

التوصية: