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TETRACONAZOLE AND INDOXACARB PESTICIDES RESIDUES IN AND ON TOMATO FRUITS AND EFFECT OF SOME ENVIRONMENTAL FACTORS.

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ABSTRACT

The residual behaviour of tetraconazole and indoxacarb pesticides on and in tomato fruits was studied under the environmental condition of Egypt.

Residue analysis showed that the initial deposits of tetraconazole and indoxacarb in unwashed tomato fruits were 12.664 and 9.52 ppm, respectively .These figures decreased to 0.98 and0.02 ppm after 28 and 21 days after treatment of tetraconazole and indoxacarb, respectively. Also results showed that the washing process by tap water of initial time dissipated 54.14 and 45.86 % of tetraconazole and indoxacarb,respectively from tomato fruits.

On the other hand, the effect of temperatures, UV-rays and direct sunlight on tetraconazole and indoxacarb degradation were studied.

The data showed that sunlight more effective than UV-rays in degradation of tetraconazole and indoxacarb. Tetraconazole and indoxacarb were reduced after 24 hours of exposure to direct sunlight by 89.74 and 88.7%, respectively. While 24 hours exposure to UV-rays reduced 45.38 and 57.7% for tetraconazole and indoxacarb, respectively.

Also results obtained that tetraconazole and indoxacarb showed a high degradaticn rate when exposure to high degrees of temperature 45-50°C within the period of experiment.

INTRODUCTION

Tomato, *Lycopersicum esculentum* is one of the main important vegetable crops in Egypt and usually attacked with various insects and fungi throughout its growing season.

In Egypt, tetraconazole (Domark 10%EC) is a broad-spectrum systemic fungicide with protective, curative and eradicant properties. Absorbed by the roots, stem and leaves, with translocation a cropetally to all parts of the plant, including subsequent growth. Uses control of powdery mildew and rust on vegetables. (Tomlin , 1997).

On the other hand, indoxacarb(Avaunt 15% SC) is an insecticide, active by contact and ingestion. Affected insects cease feeding, with poor co-ordination, puraysis and ultimately death. Uses for broad-spectrum control of Lepidoptera in cotton, vegetables and fruits. (Tomlin , 1997).

The present study was carried out to investigate the residual behaviuor of tetraconazole and indoxacarb in tomato fruits under field condition and the effect of some environmental factors such as temperature, direct sunlight and UV-rays, on the elimination of fungicide and insecticide residues.

MATERIAL AND METHODS

Pesticides used: -

1- Tetraconazole (Domark 10% EC); (RS)-2-(2,4,dichlorophenyl)-3-(1H-1, 2,4- triazol-1-yl) propyl 1,1,2,2-tetrafluorethylether.

Tetraconazol was used at the rate of 50 ml/100 liters of water on tomato.

2- Indoxacarb (Avaunt 15% SC): Methyl 7-chloro- 2,3,4a, 5- tetrahydro-2-[methoxy carbonyl(4-trifluro=methoxy phenyl) curbamoyl] indeno [1,2e] [1,3,4] oxadiazine-4a-carboxylate.

Indoxacarb was used at the rate of 26.3 ml/100 liters of water on tomato.

Field experiments: -

The experiments were carried out at Kafer Shoker El-Kalyoubia Governorate, to determine the residues of tetraconazole and indoxacarb in and on unwashed and washed tomato fruits. The experimental area was divided into plots of 175 m2 (1/24 Fed). The tested pesticides were applied on May 2 th 2005. Each pesticide was applied once using a knapsack hand sprayer fitted with one nozzle boom. Untreated plots were left as control check.

Sampling: -

Three replicate samples of treated and untreated tomato fruits were randomly picked up one hour after pesticides treatment and then 1,3,5,7,14,21,28 and 35 days for residues estimation. They were divided into two parts. In one part of them, the tomato fruits were washed thoroughly by tap water on the samples collected one hour, 1 and three days after treatment only to study the effect of washing on the percentage loss of pesticide residues of both pesticides. The whole samples of washed, unwashed and control checks were kept in polyethylene bags at –20°C until time of residue quantitation.

Residue analysis techniques: -

Extraction and clean up: -

Tetraconazole: - The residues were extracted and clean up from tomato fruits according to the method of Nasr et al (2005) and Johnson (1963), respectively. A fifty gm of samples was homogenized with 150 ml methanol for 3 min. The macerate was filtered through a pad of cotton into graduated cylinder. The filtrate was transferred into a separator funnel for extraction with methylene chloride (3x50 ml) after addition 40 ml sodium chloride solution (20%). The combined methylene chloride phases were dried by filtration through anhydrous sodium sulphate. Then, it was evaporated just to dryness using a rotary evaporator. The residues were dissolved in 5 ml methanol and clean up using coagulation solution (0.5 gm ammonium chloride and 1 ml 85% orthophosphoric acid solution in 400 ml distilled water).

The residue was thoroughly mixed with 10 ml of cooled freshly prepared coagulation solution and the contents were quantitatively transferred and filtered through a chromatographic column of 2.5 cm diameter packed with a 5 cm layer of Hyflo-Super cell. Transfer was repeated three times using 5 ml methanol and 10 ml coagulating solution in each.

The filtrate was then collected together in 250 ml separating funnel and extracted with 3x50 ml chloroform. The extracts were collected in round bottom flask and evaporated under vacuum to dryness. The residues were dissolved in the volume of acetone for GC analysis. Recovery percentages of tetraconazole residues using these procedures were 90% for tomato sampling.

Indoxacarb:- residues were extracted from the collected samples according to the method of Dupont (1995). A fifty gm of samples were homogenized with 150 ml acetone for 3 min, and shake vigorously for 1 hour by shaker. The extract was filtered and then evaporated to 5 ml by a rotary evaporator under vacuum. The concentrated extract was transferred into 300 ml separator funnel for extraction with (3x50 ml) ethyl acetate/ cyclohexane 1:1 (v/v) after addition 50 ml of saturated sodium chloride solution. The ethyl acetate/ cyclohexane phase was dried over anhydrous sodium sulfate and then evaporated at 40 C using a rotary evaporator to dryness. Residues were dissolved in 10 ml of acetone. Extracts were cleaned up through silica gel column using 100 ml (toluene/acetone 95:5v/v). The extract was then evaporated under vacuum to dryness. The residues were redissolved in the proper volume of methanol for HPLC determination. Recovery percentages of indoxacarb residues using these procedures were 88% for tomato samples.

Effect of environmental conditions: -

To study the effect of temperature, UV-rays and sun light on the fate of tetraconazole and indoxacarb, one ml ethylacetate containing 500 μg active ingredint was sepread on the surface of uncovered petri dishes (5cm i.d) and the ethyl acetate solvents was left to dry. The treated petri dishes were exposed at 30,35,45,50 °c for different period of exposure from 0 to 144 hours inside a dark electric oven to study the effect of temperature according to the method of Nasr et al (2003).

The treated petri dishes were exposed to short wave of an ultraviolet lamp (254 nm) for 0,1,3,6,12,24 hours to study the effect of UV –rays Nasr et al (2003).

The other treated petri dishes exposed to direct sun light for 0,1,2,4,8,12,24 and 48 hours. Dominating temperature ranged between 35-42 °C.

Chromatographic techniques: -

Tetraconazole residues were determined by Hewlett- Packard serial 6890 gas chromatograph fitted with flam ionization detector (FID), capillary column 15mx0.53 mm. Temperature programming were used under the following conditions; injection temperature was 250°C column temperature was 200-240 °C and detector temperature was 275°C and the carrier gas was nitrogen at a flow rate of 40 ml/min. Under these conditions, the retention time of tetraconazole was 3.539 minutes.

Indoxacarb residues were determined using Agilent 1100 serious HPLC fitted with quartry pump. G1311A, UV detector, and stainless stell column (2.6/250mm) packed with c18 with following conditions: wave length 254 nm, flow rate 0.9 ml/min., and mobile phase 50:50 MeoH/ACN. At these conditions, the retention time of indoxacarb was 3.459 minutes.

RESULTS AND DISCUSSION

Residues on and in tomato fruits: -

Results in Table (1) showed that the concentration of the initial deposits of tetraconazole and indoxacarb in unwashed tomato fruits were 12.664 and 9.52 ppm respectively.

Tetraconazole showed the highest levels of residues on and in tomato fruits at all intervals.Generally the extreme amounts of the pesticide residues as well as the great variation between their deposits could be attributed to the chemical structure of the used pesticide, their rate of application; also mode of action.

The initial deposit of indoxacarb was 9.52 ppm, and then gradually decreased to 7.25 ppm one day of application revealing 23.84% loss. This value declined to 4.95, 3.53, 1.55, 0.49 and 0.02 ppm recording the rate of loss 48.0, 62.92, 83.71, 94.85 and 99.78% at 3,5,7,14,21 days after treatment, respectively.

Results also showed that the initial deposits for tetraconazole was 12.664,11.332,8.966,8.243,7.12,3.817,2.242 and 0.98 ppm reduced by 10.5,29.9,34.9, 43.77, 69.85, 82.26 and 92.26% at 1,3.5,7,14,21 and 28 days after treatment, respectively.

Generaly, decreasing the pesticide residue concentration due to growth dilution effect (Walgenbach et al., 1991). Also could be due to a variety of environmental factor such as sunlight and temperature Liechtentein, (1972). These results in agreement with those obtained by Hegazy et al. (1999), Nasr and Hegazy (2003) and Nasr and Shereen (2005).

The effect of washing with tap water on residue levels of tetraconazole and indoxacarb on tomato fruits grown in field condition is shown in Table (1). Washing removed 54.14 and 45.86% of the initial residues of tetraconazole and indoxacarb, respectively compared with unwashed tomato fruits. Washing after one and three days was removed 59.69 and 63.033% for tetraconazole and 43.03 and 44.85% for indoxacarb.

Washing process is very important to eliminate most of the surface residues of parent compounds. So, washing of tomatoes with tap water removed high percent of initial deposits of used pesticides, therefore we advised that tomato must be washed very well by tap water before its consuming.

The obtained results are inagreement with Nasr and Shereen (2005) reported that washing process removed residues from 38.33 % to 80.00% for fenarimol on tomato fruits. El-Bouze et al (2004) found that washing process of treated egg- plant fruits with tap water reduced pirimiphos- methyl residues by 33.57 –78.43% through the experimental periods. Also the obtained results are in agreement with those findings of Attalla (2005) and Shereen (2006).

Removal of pesticides residues by washing depends on several factors: character of the surface of the plant food (smooth or youth, waxy or non-waxy) surface to volume ratio on washing is effective for bigger fruits; reference point of residue levels (higher levels easier to remove); chemical and physical properties of the applied pesticides; the length of time that the pesticide has been in contact with the plant foods; rate and number of application and penetrability of pesticide into fruit tissues El-Kins (1989), and Tag El-Din(1993).

Table (1): Tetraconazole and indoxacarb residues (ppm) in unwashed and washed tomato fruits under field condition at different time intervals.

Time after application (days)	Tomato fruits							
	Tetraconazole				Indoxacarb			
	Unwashed		Washed		Unwashed		Washed	
	ppm	% loss	ppm	% loss	ppm	% loss	ppm	% loss
Initial*	12.664	0.00	5.807	54.14	9.52	0.00	5.154	45.86
1	11.332	10.50	4.567	59.69	7.25	23.84	2.77	43.03
3	8.966	29.90	3.314	63.033	4.95	48.00	1.946	44.85
5	8.243	34.90			3.53	62.71		
7	7.12	43.77			1.55	83.71		
14	3.817	69.85			0.49	94.85		
21	2.242	82.26			0.02	99.78		
28	0.96	92.26			ND**			
35	ND**				ND**			

*One hour post field treatment.
ND** Non detected

Effect of direct sunlight: -

[illegible] in Table (2) show that photodecomposition of tested pesticide tetraconazole and indoxacarb is positively correlated with exposure period.

The results showed that tetraconazole and indoxacarb were reduced after one houre of exposure to direct sunlight by 48.3% and 11.45%, respectively.

The peresent loss of tetraconazole and indoxacarb after 48 hours reached 94.58 and 95.55%, respectively. The results are in agreement with Nasr et al.(2003) found that the percent loss of penconazole after 48 hours exposure to direct sunlight reached 99.06%.

Table (2) Effect of direct sunlight on tetraconazole and indoxacarb degradation.

Exposure time hrs	Tetraconazole		Indoxacarb	
	ug	%loss	ug	% loss
0	500.00	0.00	500.00	00.00
1	258.50	43.3	442.75	11,45
2	251.20	49.76	384.78	23.04
4	206.33	58.73	335.23	32.95
8	111.82	77.63	222.46	55.51
12	81.250	83.75	109.00	78.20
24	51.264	89.74	56.5	88.70
48	27.090	94.58	22.25	95.55

Effect of ultra-violet rays: -

Data in Table (3) showed that the decomposition percentage of tetraonazole and indoxacarb was influenced when exposed to UV rays as a thin film on a glass surface. The percentage losses of tetraconzole after one hour exposure to UV rays was 6.6% and reached 45.38% loss after 24 hours, while the percentage losses of indoxacarb was 5% loss after one hours exposure to UV rays and reached to 57.7% loss after 24 hours.

The results obtained agreed with the finding of Nasr et al (2003) They reported that the time taken for 50% degradation of penconazole was 18 hours, after exposure to UV- rays, also Peterson et al (1990). They stated that 1 ppm concentration , captan was found to be degraded with half-life of 1.4 min and the half- life of captan increased substantially to 2.9 min when the concentration was elevated to 75 ppm after exposure to UV rays.

From the above results, it can be observed that sunlight is more effective than UV rays in accelerating the photodecomposition of tetraconazole and indoxacarb. This may be due to thermal, evaporation and light intensity consideration.

Table (3) Effect of direct UV rays on tetraconazole and indoxacarb degradation.

Exposure time hrs	Tetraconazole		Indoxacarb	
	ug	%loss	ug	% loss
0	500.00	0.00	500.00	00.00
1	467.00	6.60	475.0	5.00
3	436.97	12.60	384.74	23.05
6	376.20	24.76	311.14	37.77
12	310.50	37.90	261.14	47.70
24	273.09	45.38	211.20	57.70

Effect of temperature: -

The influenced of tetraconazole and indoxacarb by temperature and period of exposure are presented In Table (4 and 5), respectively. The percentage losses of tetraconazole were 0.00, 0.00, 3.54, 41.1 and 49.51 % after six hours of exposure to temperature at 30,35,45 and 50 °c, respectively. Reached to 88.2, 90.61, 94.8 and 95.68% losses after 144 hours of exposure to temperature at 30,35, 45 and 50°C, respectively.

Table (4): - Effect of different degrees of temperature on degradation of tetraconazole.

Exposure time hrs	30 °C		35°C		45°C		50°C	
	ug	%Loss	ug	% Loss	ug	% Loss	ug	% Loss
0	500.00	0.00	500.00	0.00	500.00	0.00	500.00	0.00
6	500.00	0.00	482.34	3.54	294.48	41.10	252.45	49.51
24	388.50	22.3	328.71	34.26	282.08	43.35	125.01	74.90
48	361.70	27.66	204.17	59.30	80.33	83.93	60.50	87.90
96	279.98	44.00	166.89	66.60	38.49	92.30	25.01	94.99
144	59.03	88.20	46.92	90.61	25.88	94.8	21.56	95.68

On the other hand, results in Table (5) indicated that the persistence of indoxacarb was influenced by temperature and period of exposure.

The presentage losses of indoxacarb were 5.09, 9.3, 20.64 and 37.76 % after six hours of exposure to temperature at 30, 35, 45 and 50°C, respectively and reached to 91.76, 92.48, 93.98 and 97.72 % after 144 hours exposure to temperature at 30,35,45 and 50 °C, respectively.

Tetraconazole and indoxacarb showed a high degradation rate when exposure to high degrees of temperature (50°C) with the period of experiment. So it is recommended for use in area of dominant low temperature 30-35°C.
The results obtained agreed with the findings of Hong and Pehkonen (1998), Barakat et al (1999) and Barakat et al (2001).

Table (5): **Effect of different degrees of temperature on degradation of Indoxacarb**

Exposure time hrs	30 °C		35°C		45°C		50°C	
	ug	%Loss	ug	% Loss	ug	% Loss	ug	% Loss
0	500.00	0.00	500.00	0.00	500.00	0.00	500.00	0.00
6	474.51	5.09	453.5	9.30	396.76	20.64	311.2	37.76
24	377.6	24.48	326.90	34.62	302.7	39.46	217.3	56.54
48	253.8	49.24	228.7	54.26	211.10	57.78	143.9	71.22
96	113.9	77.22	98.1	80.26	65.60	82.80	57.6	88.48
144	41.2	91.76	37.50	92.48	30.10	93.98	11.4	97.72

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متبقيات التتراكونازول و الاندوكساكارب فى و على ثمار الطماطم و تأثير بعض العوامل البيئيه

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يهدف البحث الى دراسه سلوك متبقيات مبيدى التتراكونازول و الاندوكساكارب على و فى نبات الطماطم تحت الظروف المصرية و قد تم التوصل الى النتائج التالية.

كانت متبقيات التتراكونازول ١٢,٦٦٤ جزء فى المليون بينما كانت متبقيات الاندوكساكارب ٩,٥٢ جزء فى المليون على ثمار الطماطم وذلك بعد ساعة واحدة من الرش وقد تدهور متبقيات كلا من المبيدين ليصلا الى ٠,٩٨ جزء فى المليون للتتراكونازول بعد ٢٨ يوم من المعاملة و ٠,٠٢ جزء فى المليون للاندوكساكارب بعد ٢١ يوم من المعاملة.

ادى غسيل الثمار المعاملة بماء الصنبور بعد ساعة من المعاملة الى فقد ٥٤,١٤ % و٤٥,٨٦ % من متبقيات التتراكونا زول والاندوكساكارب على الترتيب

و من جهة أخرى تم دراسة تاثير درجات الحرارة و التعرض لاشعة الشمس المباشرة و التعرض للاشعة فوق البنفسجيةعلى تدهور كلا من التتراكونازول و الاندوكساكارب و قد وجد ان التعرض لاشعة الشمس المباشرة كان اكثر تاثيرا على تدهور متبقيات كلا المبيدين عن التعرض للاشعة البنفسجيه حيث وجد ان التعرض لاشعة الشمس لمدة ٢٤ ساعة ادى الى حدوث فقد بمقدار٨٩,٧٤ % و٨٨,٧ % لكلا من التتراكونازول والاندوكساكارب على التوالى بينما التعرض للاشعة فوق البنفسجية لمدة ٢٤ ساعة ادى الى حدوث فقد بمقدار ٤٥,٣٨ % و٥٧,٧ % للتتراكونازول والاندوكساكارب على الترتيب ايضا اوضحت النتائج حدوث تدهور كبير لكلا المبيدين عند التعرض لدرجات الحرارة المرتفعة ٤٥-٥٠ م خلال فترة التجربة.