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Persistence of Acetamiprid and Dinotefuran in Cucumber and Tomato Fruits

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Abstract: Acetamiprid and dinotefuran are a new generation from neonicotinoid insecticides and highly active to protect the various vegetable crops, by controlling mites and insect pests. The rate of disappearance of acetamiprid and dinotefuran residues from tomato and cucumber fruits at a recommended dose was investigated. Under field conditions, the half-life values of acetamiprid were 1.04 and 1.18 days on/in tomato and cucumber fruits and 1.72 and 3.18 days for dinotefuran, respectively. Determined residues of dinotefuran on/in tomato and cucumber fruits were at level below the maximum residue limits (MRL), one hour after application, so that the tomato and cucumber fruits could be used safely at any time after application. Whereas, the residues of acetamiprid reached to the acceptable maximum residue limits in three days post treatment. Residues of acetamiprid and dinotefuran were undetectable on/in tomato and cucumber fruits 15 days after application. It was also concluded, that the loss rate of both insecticides was varied between tomato and cucumber fruits.

Key words: Acetamiprid · Dinotefuran · Neonicotinoid insecticides · Maximum residue limits · Tomato · Cucumber

INTRODUCTION

Tomatoes and cucumbers are the most widely grown vegetables in the world and also the most important items of the vegetables processing sector, In order to maintain a high production yield, the use of pesticides is a conventional agricultural practice [1]. Management of pests in tomato and cucumber fields has largely depended on the use of conventional, neurotoxic, broad-spectrum, synthetic chemical pesticides, such as organophosphates, carbamates, synthetic pyrethroids and a number of new chemical classes, such as neonicotinoids. Neonicotinoid insecticides represent the fastest growing class of insecticides introduced to the market since the launch of pyrethroids. Neonicotinoid insecticides are active against numerous sucking and biting insects, including aphids, whiteflies, beetles and some lepidoptera species as well [2-4]. Neonicotinoid insecticides are relatively a new group of insecticides with novel modes of action. They act as agonists at the insect nicotinic acetylcholine receptors (nAChRs), which plays an important role in synaptic transmission in the central nervous system [5]. Pesticides are applied to crops throughout the world but they can be toxic and can thus be harmful to human health. The residue of pesticides left after treatment may penetrate plant tissues and appear in fruits and vegetables [6, 7]. The presence of pesticide residues in food is one important concern for consumers, due to their possible adverse health effects. Various international organisations (Environmental Protection Agency (EPA), Codex Alimentarius Commission, World Health Organization (WHO) and Food and Agriculture Organization (FAO) of the United Nations) have regulated the use of pesticides, by fixing maximum residue levels (MRL's) for commercial purposes.

The maximum residue levels (MRLs) are the highest levels of residues expected to be in the food when the pesticide is used according to authorized agricultural practices. Government agencies and international organization limit the amount of pesticides in food establishing maximum residue limits, with the aim of protecting consumers' health [8, 9]. The persistence of acetamiprid and dinotefuran in some crops such as chili, mustard, tea and tomatoes has been reported by Barakat *et al.* [10], Paramanik *et al.* [11], Sanyal *et al.* [12], Gupta and Shanker [13] and EFSA [14].

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The present work was carried out to study the persistence of two neonicotinoid insecticides, acetamiprid and dinotefuran on/in tomato and cucumber fruits under the normal field conditions, in order to protect the consumer, by recommending a waiting period from treatment to harvest.

MATERIALS AND METHODS

Field Trials: The field tests were carried out at the experimental farm of the Faculty of Agriculture, Moshtohor, Qalubia Governorate, Egypt during March to July 2011. Tomato seedling [*Lycoprsicon esculentum* Mill.) cv. Elesa] and cucumber seed (*Cucumis sativus* L.) cv. Alfa beta] were planted on 1st March 2011. The experiments were designed in the following ways: plot area, 7 x 6 m, plot to plot distance, 1.5 m, plant to plant distance, 0.4 m for tomatoes and 0.2 m cucumbers and row to row distance, 1m. Treatment plots were arranged in a randomized complete block design with four replications. Irrigation and fertilization were made according to the crop schedule. The two insecticides, acetamiprid and dinotefuran were applied to tomato and cucumber plants as aqueous solutions of (Mospilan and Oshin trade names) with a knapsack sprayer (20 liters) at the recommended rates (250 g/100 L) and (125 g/100 L), respectively. sprayer using a recommended formulation volume of 200 L/feddan (one feddan =0.42 ha). The spray was done on 20th June 2011.

Sampling: After spray of the two insecticides, samples of tomato and cucumber fruits were taken randomly from each replicate at intervals of zero time (1h after application), 3, 5, 7, 10 and 15 days and stored at-20 °C until using for analysis.

Reagents, Chemicals and Insecticides: All reagents and solvents used were analytical-reagent grade (Algomhuria Company for Trading Chemicals and Medical Appliances-Egypt). Analytical standard of acetamiprid [N-[(6-chloro-3-pyridyl) methyl]-N'-cyano-N-methyl-acetamidine] (98.89%) was supplied by Syngenta and dinotefuran [N-methyle-N-nitro-N-[(tetrahydro-3-furanyl) methyl)] guanidine] (99.99%) was supplied by Sumitomo Chemical Co. Ltd. and the formulated products of acetamiprid, (Mospilan 20 % SP) and of dinotefuran (Oshin 20 % SG) were supplied by Shoura Chemicals and Sumitomo Chemical Co., respectively.

Extraction and Clean-Up

Acetamiprid: Residues were extracted according to the method of Masanori and Gomyo [15]. Sub-samples of 20 g were homogenized with 100ml methanol, the homogenate was filtered. The filtrate was shaken with 10ml saturated sodium chloride solution and 100 ml hexane, the hexane layer was discarded. The aqueous methanol was extracted with 100 ml dichloromethane. The dichloromethane layer was dried over anhydrous sodium sulfate. The extract was concentrated to near dryness under reduced pressure. The extract was cleaned up by column chromatography using florisil activated 60-100 mesh (10g). The column was first eluted with 150 ml of mixed solvent of acetone and hexane (20:80) and it was discarded. Then it was eluted with 150ml of mixture of acetone and hexane (50:50). The eluted was collected and concentrated to dryness by rotary evaporator at 40 °C [16]. The residues of acetamiprid were estimated by HPLC.

Dinotefuran: Sub-samples of 50g blended with 150ml acetonitrile for 5 min. The extracted sample was filtered through anhydrous sodium sulfate, then evaporated just dryness using a rotary evaporator at 30°C [10]. Dinotefuran residues were kept in the freezer for 24 hours then re-dissolved with 5 ml cold acetone (three times). The combined acetone extract (15 ml) was evaporated using a rotary evaporator, the residues were re-dissolved with 1ml Methanol and determined by HPLC.

HPLC Analysis: High Performance Liquid Chromatography Agilent 1100 series. The U.V. Diod array detector set at 260 nm and the analytical column Nucleosil-C18, 5um (4 x 250 mm) was used. The mobile phase was acetonitrile: water (65: 35 v/v) at flow rate 0.8 ml/min.

RESULTS AND DISCUSSION

Recovery studies of the tested insecticides were performed at 50 and 100 µg (a.i.) /100 g (fruit sample) (Table 1). The tested insecticides were not detected when blank determination on tomato and cucumber fruits was done. The purpose of pesticide residues monitoring is to ensure that in fruits and vegetables do not exceed maximum residues levels (MRLs), no misuse of pesticides that could result in unexpected residues in food and that good agricultural practices are maintained or due to the demands by international trade.

Table 1: Recoveries of acetamiprid and dinotefuran insecticides and limits of determination (LOD)

Fruit Samples	Insecticides	Insecticide Level (ppm)	Recovery % mean ± SE	Average (%)	LOD (ppm)
Tomatoes	Acetamiprid	1	99.6 ± 0.08	99.2	0.003
		0.5	98.8 ± 0.01		
	Dinotefuran	1	98.0 ± 0.025	97.5	
		0.5	97.1 ± 0.022		
Cucumbers	Acetamiprid	1	99.0 ± 0.012	98.5	
		0.5	98.0 ± 0.016		
	Dinotefuran	1	97.5 ± 0.42	96.4	
		0.5	95.3 ± 0.018		

Table 2: Residues of acetamiprid on and in tomato and cucumber fruits (the values were corrected according to the recoveries percent).

	Persistence of acetamiprid					
	Tomatoes			Cucumbers		
Time interval (days)	Residues (ppm)	Loss (%)	persistence (%)	Residues (ppm)	Loss (%)	persistence (%)
Initial	0.98± 0.005	0.00	100	1.26 ± 0.004	0.00	100
1	0.51± 0.011	47.96	52.04	0.73 ± 0.006	42.06	57.94
3	0.08 ± 0.005	91.84	8.16	0.07 ± 0.006	94.44	5.56
7	0.02 ± 0.007	97.96	2.04	0.02 ± 0.005	98.41	1.59
10	0.01± 0.006	98.98	1.02	0.012±0.005	99.05	0.95
15	ND	100	0	ND	100	0
$T_{½}$ (Days)		1.04			1.18	
MRL (ppm)		0.15			0.3	

(Initial) samples were taken one hour after application, (ND) not detectable, (% loss) = [(initial residue-residues found at different time) / initial residue] x 100, (% persistence) =100-% loss, (T½) Half-life, MRL=the maximum residue limits according to EU [17].

Table 3: Residues of dinotefuran on and in tomato and cucumber fruits (the values were corrected according to the recoveries percent)

	Persistence of dinotefuran					
	Tomatoes			Cucumbers		
Time interval (days)	Residues (ppm)	Loss (%)	persistence (%)	Residues (ppm)	Loss (%)	persistence (%)
Initial	0.83± 0.006	0.00	100	0.53± 0.03	0.00	100
1	0.54± 0.012	34.94	65.06	0.39 ± 0.01	26.42	73.58
3	0.14 ± 0.006	83.13	16.87	0.28 ± 0.01	47.17	52.83
7	0.02 ± 0.005	97.59	2.41	0.03 ± 0.01	94.34	5.66
10	0.01± 0.003	98.80	1.20	0.008±0.01	98.49	1.51
15	ND	100	0	ND	100	0
$T_{½}$ (Days)		1.72			3.18	
MRL (ppm)		2.00			2.00	

(Initial) samples were taken one hour after application, (ND) not detectable, (% loss) = [(initial residue-residues found at different time) / initial residue] x 100, (% persistence) =100-% loss, (T½) Half-life, MRL=the maximum residue limits according to EU [17].

Data in Table 2 represent the residues of acetamiprid on and in tomato and cucumber fruits. The data showed that the residues in the initial deposit were 0.98 ppm, one hour after application on tomato fruits. The amount of residues decreased to 0.51 ppm, it gave the rate of loss 47.96 % within the first 24 hours after spray. The residues reduced to 0.08, 0.02 and 0.01 ppm after 3, 7 and 10 days from treatment and the corresponding calculated rates of loss were 91.84, 97.96 and 98.98 %, respectively. The samples taken 15 days after treatment contained no detectable amounts of acetamiprid.

In case of cucumber fruits, the initial deposit of acetamiprid was 1.26 ppm. This value was dropped to 0.73 ppm, recorded 42.06 % loss, one day after application. Residues decreased gradually, at the intervals of 3, 7 and 10 days after treatments, the estimated residues were 0.07, 0.02 and 0.012 ppm, respectively. Their rates of loss were 94.44, 98.41 and 99.05 %, respectively. Also, samples of cucumber fruits taken 15 days after treatment were devoid of any detectable amounts of acetamiprid residues according to the sensitivity of determination procedure. The half life value of acetamiprid was 1.04 days on tomato fruits, while it was 1.18 days on cucumber fruits. Because the residues of acetamiprid became under the level of the MRL after three days of spray, the tomatoes and cucumbers could be used safely for consumption. Data in Table 3 indicated that the initial deposit (one hour after treatment) of dinotefuran insecticide on / in tomato fruits was 0.83 ppm, but this value started to decrease at the first day after treatment to 0.54, it recorded 34.94 % loss through this time. Also, the residues of other days after application were gradually decreased to 0.14, 0.02 and 0.01 ppm after 3, 7 and 10 days of application, respectively. While, the rate of loss were 83.13, 97.59 and 98.80 %, respectively. The half life value of dinotefuran was 1.72 days on tomatoes. On the other hand, there were no detectable amounts of dinotefuran showed after 15 days of treatment. In contrast to acetamiprid, the residues of dinotefuran on / in cucumber fruits were less than the tomato fruits through the first 24 h after spray. The initial deposit of dinotefuran was 0.53 ppm, this decreased to 0.39, 0.28, 0.03 and 0.008 ppm after 1, 3, 7 and 10 days of application, respectively, so the calculated rates of loss were 26.42, 47.17, 94.34 and 98.49 %, respectively. The half life value of dinotefuran was 3.18 days on cucumbers. After 15 days of spray, no residue was detected. The present findings may be supported by the crop metabolism stdies of acetamiprid in four different crop groups following foliar applications. Where the metabolic patterns in the different studies were not shown to be similar [14].

Results indicated that the difference in the relative distribution of the pesticides between crops might be due to the influence of various factors such as differences in crop species, plant cultivation methods and physicochemical properties of the pesticides [18]. Sanyal *et al*. [12] reported the half-life values of acetarniprid in chili were in the range of 2.24-4.84 days and a waiting period of 1 day. Paramanik *et al.* [11] stated the half-life value of acetamiprid in mustard plants was 1.02 days; no residue was detected in the 7 day. On the other hand, Gupta and Shanker [13] found the waiting period of 15 days for tea plucking after acetamiprid application at recommended dose. Also, Barakat *et al*. [10] reported the half life value of dinotefuran was 19.48 hours on tomatoes. Although degradation of pesticides is influenced by different environmental processes, Celik *et al*. [19] concluded that under natural field conditions volatilization is the main process that affects pesticides. These researchers applied six pesticides (azinphos-methyl, ethion, diazinon, methidathion, phosalone and pirimicarb) to apples and found that volatilization was the dominant process followed by solar irradiation. Bacterial degradation had the lowest influence except for phosalone. Pirimicarb was highly degraded by solar irradiation.

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