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RESIDUAL BEHAVIOR OF FENARIMOL FUNGICIDE ON CUCUMBER AND PEPPER FRUITS GROWN UNDER GREENHOUSE CONDITIONS

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ABSTRACT

The degradation rates and residue levels of fenarimol fungicide, used to control powdery mildews, were studied in greenhouse grown cucumber and pepper fruits. The role of some household processes in removal of detected residues from treated vegetables was also investigated. The results demonstrated that the initial deposits of fenarimol in cucumber and pepper fruits were 0.38 and 0.61 ppm, respectively. These residues decreased steadily by time until reached to non-detectable level and 0.07 ppm after 15 days from treatment, respectively. The calculated half-life values proved the rapid decline of fenarimol residues in cucumber fruits as compared with pepper fruits (25.92 and 89.84 hours, respectively). Preharvest interval (PHI) of 1.6 and 3.6 days from spraying must be followed before human consumption of fenarimol-treated cucumber and pepper fruits, respectively. Concerning the effect of some household processes in removal of detected residues, the obtained data revealed that peeling was the most effective process; since it removed 92.10 and 75% of the detected fenarimol residues from cucumber fruits after one and 24 hour post treatment, respectively while washing and soaking exhibited great efficiency in decontamination of fenarimol residues from pepper fruits (75.41 and 79.66%) by washing process and (73.77 and 88.14%) by soaking process after the aforementioned intervals, respectively.

Key words: Fenarimol residues - Household processes – Vegetables.

INTRODUCTION

Greenhouse environments provide a variety of benefits for plant production; however, many greenhouses favor pest development as well. The warm, humid conditions and abundant food are ideal for pest build up. For these reasons, pest problems particularly fungal invasion often develop more rapidly and severely in enclosed systems. Pesticides are important tool in managing greenhouse pests. Fenarimol is a systemic fungicide with protective, curative, and eradicant action for control of powdery mildew of commercial greenhouse roses (The Pesticide Manual, 1998). However, some growers used to harvest the treated vegetable crops at random periods, regardless of the safety period that should be elapsed after the last pesticide application and before consumption. As a result, considerable amounts of harmful pesticide residues often remain in the harvested vegetables, which may ultimately reach the consumer and slowly cause healthy hazards. The normal methods used in preparing foods (e.g. washing, trimming, blanching and cooking) go a long way towards reducing pesticide residues on raw commodities (WHO, 1989). Several researchers have investigated the persistence and decontamination ways of fungicide residues on vegetable crops (Heise *et al.,* 2000; Blasco *et al.,* 2002; Paradjikovic *et al.,* 2004 and Li *et al.,* 2006) umber and sweet pepper fruits under greenhouse conditions to determine their dissipation rates, half-life values, preharvest intervals (PHI) and the role of some household processes (i.e. washing, soaking, peeling and pickling) in decontamination of detected fungicide residues after

The main aim of this study is to investigate the residual behavior of fenarimol on two of the common vegetable crops in Egypt i.e. cuc one and 24 hours post treatment.

MATERIALS AND METHODS

Pesticides used:

Fenarimol: (±)-2,4-dichloro-*α*-(pyrimidin-5-yl) benzhydryl alcohol. It is a systemic fungicide known commercially as Rubigan which used to control powdery mildews in cucurbits and peppers according to Pest Control Program, Ministry of Agriculture and Land Reclamation, Egypt (2001).

Field experiments and sampling:

Sweet pepper (*Capsicum annum* var. Khairat) and cucumber (*Cucumis sativus* var. Kareem) seedlings were transplanted into their greenhouses, each of 540 m^2 on September 3rd, 2005 and February 16th, 2006, respectively at Sakha Agricultural Research Station, Kafr El-Sheikh Governorate, Egypt. The greenhouse area of each crop was divided into 4 plots each of 135m^2, three plots were treated at fruiting stage with Rubigan 12% E.C. at a rate of 25 cm^3/100 liter water using a knapsack sprayer on May 4th, 2006 . The fourth plot was left untreated in each crop as a control check and for recovery purposes. The plots received all the normal agricultural practices throughout the experimental period.

Representative and random samples of each treated crop were collected in polyethylene bags one hour after application (Initial deposit) and then after 1, 3, 6, 9, 12 and 15 days. The harvested samples were chopped well and thoroughly mixed before taking a subsampling portion of 100g in triplicates in polyethylene bags, labeled and kept at -18°C until residue analysis.

Household processing operations:

After application of fenarimol fungicide with the recommended rate, three replicates of unbiased and representative samples were collected from each treated crop for conducting some household processes after one hour and one day from application as follows:

Washing:

Samples of cucumber and pepper fruits were rinsed for two minutes with running tap water, then drained on a clean paper for one hour at room temperature until drying, and a potion of 50g in triplicates from washed samples were kept in polyethylene bags and stored at -18°C in a deep freezer until time of residue analysis.

Soaking:

Samples of the two vegetables were soaked in water and 1% acetic acid solution without washing, then drained and a potion of 50g in triplicates were kept and stored as previously mentioned until time of residue analysis.

Peeling:

Cucumber samples were peeled manually by a sharp knife, then a potion of 50g in triplicates from peeled samples were kept and stored as previously mentioned until time of residue analysis.

Pickling:

Cucumber samples were packed into half liter glass jars contained 100ml of 20% sodium chloride solution plus 100 ml of 1% acetic acid solution for two weeks under room conditions, then a potion of 50g in triplicates from the pickled samples were kept and stored as previously mentioned until time of residue analysis.

Analytical procedures:

Extraction procedures for all samples were done according to Luke *et al.* (1981). Frozen samples were left until reach room temperature then three replicates of chopped cucumber and pepper subsamples (100 gm) were each blended with 200 ml acetone in a blender jar for 3 min. at high speed and then filtered through a funnel with a dry pad of cotton into a graduated cylinder. Eighty ml of the sample filtrate were transferred into a separatory funnel and partitioned with a mixture of 100 ml petroleum ether and 100 ml dichloromethane. For separation, the upper organic layer was received in a 500 ml flask through a funnel with a dry pad of cotton and anhydrous sodium sulfate, and then 5 g of sodium chloride were added to the aqueous layer, which was further extracted with two (100 ml) volumes of dichloromethane. The combined dichloromethane (organic layer) was dried with anhydrous sodium sulfate and then collected in the same flask and evaporated to dryness at 40°C under reduced pressure using rotary vacuum evaporator and then the sample became ready for gas liquid chromatography determination.

Gas liquid chromatography determination:

A Hewlett-packard, USA serial 6890 gas chromatograph; equipped with electron capture detector (ECD) was used for the determination of fenarimol residues. The columns and operating conditions used were as follows:

a. Columns:

- HP PAS-5, (ECD tested Ultra 2 Silicone), 25 m length x 0.32 mm (i.d.) x 0.52 µm film thickness.
- HP PAS-1701, (ECD Tested 1701 Silicone), 25 m length x 0.32 mm (i.d.) x 0.52 µm film thickness.

b. Operating conditions:

- Injector temperature: 225°C.
- Detector temperature: 300°C.
- Nitrogen carrier gas flow: 2 ml/min., 60 ml/min. (Carrier + make up).
- Oven program:
  - Initial temperature: 90 °C
  - Initial time: 2 min

Rate (°C / min)	Temp (°C)	Time (min)
Level (1) 20	150	0
Level (2) 6	270	15

Confirmation of the presence of fenarimol residues in all samples was done depending on the use of chromatographic columns of different polarity. Retention time for fenarimol under these conditions was 20.61 minutes. The average recovery values for fenarimol were 94 and 90% in cucumber and pepper fruits, respectively. These figures were used to correct all obtained values and to examine the reliability of the analytical procedures.

RESULTS AND DISCUSSION

1. Residues disappearance after field treatment:

The estimated amounts of the tested fungicide residues in treated vegetable fruits at different intervals post treatment are shown in Table (1). The initial deposits of fenarimol on and in cucumber and pepper fruits were 0.38 and 0.61 ppm which decreased till reached 0.2 and 0.59 ppm, respectively, after 24 hours after treatment. These figures decreased gradually until reached [0.06, 0.025, 0.020, 0.011 & below detection limit (0.001mg/kg)] and [035, 0.22, 0.14, 0.10 & 0.07 ppm] after 3, 6, 9, 12 and 15 days post treatment, consecutively in cucumber and pepper fruits. The loss percentages of fenarimol residues in cucumber fruits were enhanced by time elapse recording 47.37, 84.21, 93.42, 94.73, 97.11 and 10.00% loss of initial deposit after 1, 3, 6, 9, 12 and 15 days, respectively. The corresponding loss percentages from pepper fruits were 3.28, 42.62, 63.93, 77.05, 83.61 and 88.52%, respectively, at the aforementioned intervals.

Table (1): Residues of fenarimol fungicide on and in treated vegetable fruits cultivated under greenhouse conditions.

Time after application (Days)	Cucumber		Pepper	
	Fenarimol residues (ppm)	% Loss	Fenarimol residues (ppm)	% Loss
Initial*	0.380	00.00	0.61	00.00
1	0.200	47.37	0.59	3.28
3	0.060	84.21	0.35	42.62
6	0.025	93.42	0.22	63.93
9	0.020	94.73	0.14	77.05
12	0.011	97.11	0.10	83.61
15	BDL⌂	100.0	0.07	88.52
RL_{50} (hour)	25.92		89.84	
MRLs#(mg/kg)	0.05		0.5	
PHI¤(day)	3.6		1.6	

* One hour after application
# Maximum Residue Limits according to Codex Alimentarius Commission, 2005
¤ Preharvest Intervals
⌂ Below detection limit (0.001mg/kg)

Residues dissipation could be attributed to high temperature inside the greenhouse which reported to be the major factor in reducing the pesticide residues from plant surface (Zweig 1963; Awad *et al*., 1967; Lichtenstein, 1972). Besides plant growth, particularly for fruits, is also responsible to a great extent of decreasing pesticide residue concentration due to growth dilution effects, as the fruits become larger, the chemical residue concentrations will decrease (Walgenbach *et al*., 1991). Furthermore, Fong *et al.* (1999) reported that such noticeable reductions of the pesticide residues could be due to firstly, volatilization to the atmosphere (influenced by the insecticide volatility or vapor pressure, temperature and wind movement); secondly, to the chemical degradation (influenced by the molecular make up of the pesticide and by such factors as sunlight, moisture, and temperature).

The calculated half-life values proved the rapid decline of fenarimol residues in cucumber fruits as compared with pepper fruits, i.e. 25.92 and 89.84 hours, respectively.

Maximum residue limits (MRLs) of fenarimol on cucumber and pepper fruits were determined as 0.05 and 0.5 mg/kg, respectively according to Codex Alimentarius Commission (2005), which indicate that preharvest interval (PHI) of 3.6 and 1.6days from spraying must be followed before human consumption of fenarimol-treated cucumber and pepper fruits, respectively.

These results are quite comparable with those reported by many investigators regardless of experiments carried out under different climate conditions, geographical locations, time of application, application technique, concentrations, type of formulation and plant species. Garcia *et al.* (1993) showed that the half-life periods of Chlorothalonil fungicide were 5.3 days for cucumber and 7.3 days for peppers grown in commercial greenhouses. Knio *et al.* (2000) revealed that the total residues of Zeneb and Meneb fungicides decreased from 0.082 and 0.11mg/kg at zero day to 0.023 and 0.05 mg/kg at 20 days, respectively on greenhouse-sprayed tomatoes fruits. Nasr and Hegazy (2003) found that the residue half life value of Pyrazophos fungicide was 22 hours on and in cucumber fruits. Paradjikovic *et al.* (2004) indicated that Vinclozlin and Procymidone fungicides should be used on greenhouse-cucumber with a time lapse of 14 days, only with cucumber intended for salad consumption. Li *et al.* (2006) revealed that Kresoxim-methyl fungicide residues in a greenhouse-cucumber were below the maximum residue limit (0.05 mg/kg, fixed by Europe Union) after 7 days for both recommended and double the recommended dosage treatments.

Based on the obtained results and earlier discussion it could be concluded that, the period after which the sprayed crops with the same pesticide could be harvested differed greatly depending on the morphological and physiological differences between crop kinds. Furthermore, the recommended preharvest interval (PHI) or safety period must be taken into consideration.

2. Removal of detected residues by some household processes:

Results in Table (2) demonstrated that fenarimol initial deposit and 24 hour residue in cucumber fruits were found to be reduced from 0.38 and 0.20 ppm to (0.17, 0.20, 0.03 & 0.19 ppm) and (0.13, 0.11, 0.05 & 0.09 ppm) representing removal of (55.26, 47.37, 92.10 &50%) and (35.00, 45.00, 75.00 &55%) after washing, soaking, peeling and pickling processes, consecutively for the two abovementioned intervals. The data showed that peeling process contributed much in decontamination of residues in comparing with the other processes indicating the major role of cucumber skin in adsorbing fenarimol residues which may be due to incorporation of pesticide residues into the cuticular layers of the fruit surface, resulting in deposits that are removable only by peeling (Dejonckheere *et al.*, 1996).

On the other hand, fenarimol residues in unprocessed pepper fruits after zero time (initial) and one day after application were 0.61 and 0.59 ppm, respectively. These values decreased (0.15 and 0.12 ppm) by washing process and to (0.16 and 0.07 ppm) by soaking process, respectively, thus recording removal of (75.41 and 79.66%) by washing process and (73.77 and 88.14%) by soaking process, consecutively.

Table (2): Effect of some household processes on removal of fenarimol residues from treated vegetable fruits.

Time after application (hours)	Process	Cucumber		Pepper	
		Fenarimol residues (ppm)	% Removal	Fenarimol residues (ppm)	% Removal
Initial*	Unprocessed	0.38	00.00	0.61	00.00
	Washing	0.17	55.26	0.15	75.41
	Soaking	0.20	47.37	0.16	73.77
	Peeling	0.03	92.10	-	-
	Pickling	0.19	50.00	-	-
24	Unprocessed	0.20	00.00	0.59	00.00
	Washing	0.13	35.00	0.12	79.66
	Soaking	0.11	45.00	0.07	88.14
	Peeling	0.05	75.00	-	-
	Pickling	0.09	55.00	-	-

*One hour after application

The majority of pesticide residue appears to reside on the surface of the produce where it is removed by the mechanical action of rinsing (Krol *et al.*, 2000). The extent to which pesticide residues are removed by commercial processing depends on a variety of factors, such as the chemical properties of the pesticide, the nature of the food commodity, the processing step and the length of time the compound has been in contact with the fruit (Farris *et al.*, 1992; Holland *et al.*, 1994).

The obtained results are in accordance with those reported by many investigators. Hegazy *et al.* (1998) indicated that, the peeling of the squash fruits removed almost all the residues of pyrazophos fungicide for all intervals post treatment including the fruits collected an hour after application. Krol *et al.* (2000) showed that a short rinse in tap water reduces fungicide residues on many types of vegetables and fruits. Gad Alla (2002) demonstrated that peeling after washing cucumber was the most effective process in removing almost all ethylenebisdithiocarbamates fungicide residues. Paradjikovic *et al.* (2004) revealed that peeling eliminated 79-85% of vinclozlin and procymidone fungicide residues from greenhouse-cucumber, while washing eliminated 22-24% from these residues.

The most significant result that could be derived from our data is that major amounts of fenarimol residues on and in treated vegetables are possibly removed by some household processes.

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