RESIDUES AND HALF-LIVES OF CERTAIN INSECTICIDES ON AND IN SOME VEGETABLES UNDER FIELD CONDITIONS

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Abstract

The present study was carried out to determine the residual behaviour of fenitrothion, profenofos and pyrazofos pesticides on and in tomato and cucumber fruits.The initial residues were 1.92, 2.45 and 0.54 ppm for fenitrothion, profenofos and pyrazofos on and in tomato fruits, respectively. While the initial deposits of profenofos and pyrazofos were 2.40 and 0.68 ppm on and in cucumber fruits. The analytical data showed a gradual decrease of tested pesticide residues with time.

Results revealed that the residue half-lives for fenitrothion, profenofos and pyrazofos in tomato fruits were 29, 23 and 20 hours, respectively, also results revealed that the residue half-lives were 18 and 22 hours for profenofos and pyrazofos on and in cucumber fruits.

INTRODUCTION

Pesticide residues in food may be hazardous to human health. Chemical control is one of the procedures used to achieve this purpose. If an insecticide is to be accepted for the control of insect pests on vegetables, it must be effective against the pest, with low persistence to avoid problems in harvested crop, in addition to its low mammalian toxicity. Tomato (*Lycopersicon esculentum*) and cucumber (*cucumis setivs)* are important vegetable crops in Egypt and usually attacked with various insects and fungi throughout its growing season.

The present study was carried out to investigate the residual behaviour of fenitrothion, profenofos and pyrazofos in tomato and cucumber fruits under field conditions to determine the pre-harvest intervals (PHI). The persistence of some organophosphours insecticides has been studied on different crops by several researchers; Abdalla *et al.* (1993) Al-Khalaf *et al.* (1995) and El-Bakary *et al.* (1999).

MATERIALS AND METHODS

Pesticides Used

1. Fenitrothion (Sumithion 50% EC) O,O-dimethyl-O- 4-nitro-m-toyl phos-phorodithioate It is used against a wide range of chewing and sucking pests. Fenitrothion was used at the rate of 250 ml/100 liters of water (i.e 125 g a.i./ 100 L).

2. Profenofos (Selecron 72% EC) O - (4-bromo-2- chlorophenyl) O-ethyl-s-propyl phosphorothioate. It is non-systemic broad spectrum insecticide used against insect pests. Profenofos was used at the rate of 200ml/100 liters of water (i.e. 144 g a.i/100 liter water).

3. Pyrazofos (Afugan 30% EC) O-6-ethoxy carbonyl-5- methylpyrazdo {1.5,a} pyrimidin-2-yl O,O diethyl phosphorothioate. It is a systemic fungicide controlling powdery mildews on a wide range of crops. Pyrazofos was used at the rate of 100 ml/100 liters of water (i.e 30-g a.i./100 liters of water).

Field experiments

a. Tomatoes (*Lycopersicon esculentum var.*) were planted on March 15th 2002 under the normal field conditions and agricultural practices at El-Khanka, Kalubia Governorate. Four plots were planted in areas of 1/100 per feddan. Three plots were treated at the rates of application recommended dose of the formulated, tomatoes plants were treated on June 3rd 2002; 78 days after planting and the formulation was diluted at the rate of 400 liters water per feddan. One plot was left untreated as control A hand operated knapsack sprayer with one nozzle was used.

b. Profenofos and pyrazofos were separately applied to cucumber plants cultivated in Shanesa village-Dakahlia Governorate, during the 2002 season. The spray was on June 3rd. (60 days age). The rates of use were 200 and 100 ml/100 liters water for Profenofos and pyrazofos, respectively. Plants were sprayed during fruiting at which the majority of the fruits were mature. A complete randomized block design was adopted with three replicates. Each single plot was 1/ 100 of fed and a knapsack sprayer equipped with one nozzle was used.

Sampling

A sample consisted of three replicated, 500-1000 grams of tomato and cucumber fruits. The samples for initial deposit were collected one hour after application. Subsequant samples were taken 1, 3, 7, 10 and 15 days after application. Clean polyethylene bags were used for preservation of the collected samples. All samples were stored at - 20 °C in a deepfreezer until time of analysis.

Extraction

Fenitrothion and profenofos: The freeze samples were left to reach room temperature. then macerated using warning blender. Hundred grams of the macerated sample were placed in the blender and constant amount of methanol (2ml/gram plant material) was added to the blender and mixed for 3 min., then filtered through a dry pad of cotton into a graduated cylinder. Extracts were shaken in separatory funnel successively with 40ml. sodium chloride solution (20%) and extracted three times with a 50 ml. redistill methylenechloride. The methylene chloride phase was passed through cotton and anhydrous sodium sulfate, concentrated to dryness under vacum at 40°C and the residues were ready for clean up. (Mollhoff, 1975)

Pyrazofos: Hundred grams of the sample were placed into the blender cup with 50 grams anhydrous sodium sulfate and 200 ml. ethyl acetate, then blended for 3 min. The liquid was decanted through a funnel with a plug of cotton into a graduated cylinder. then evaporated just to dryness using a rotary evaporator at 40°C.

Clean up

The florisil column clean up procedure of Mills *et al.* (1972) was employed in cleaning - up the sample extract for the analysis on GLC. A 20 mm (I.d.) glass column was prepared by adding successively. a plug of glass wool and 5 grams of activated florisil (60-100 mesh) and compact thoroughly. The column was pre washed using 40-ml n- Hexane and drained the level of the solvent down to the top of florisil. Residue extract was transferred to the florisil columns, already saturated with hexane. The column was eluted with 200 ml eluant (50% methylene chloride-48.5% hexane- 1.5% acetonitrile) at a rate of 5 ml/min. The collected eluate was concentrated on rotary evaporator and dissolved in a know volume of ethylacetate for residue analysis employing GLC equipped with flame photometric detector.

Gas chromatography

Fenitrothion and profenofos were detected and determined using a PYE-Unicum 4500 gas chromatograph equipped with FPD operated in the phosphorous mode (529 nm) and a Pyrex glass column (1.5m x 4 mm i.d) packed with 4% SE 30 + 6% ov-210 on gas chromosorb Q (80 -100 mesh) was used under the following conditions: Detector temp. 250°C Injector temp.245°C oven temp. 240°C. Carrier gas (N_2) flow rates 30 ml/min. Hydrogen flow rate 30 ml/min and air flow rate 30 ml/min. Retention time for fenitrothion and profenofos under these conditions was 2.8 and 2.9 min., respectively. Pyrazofos determined by using HP 6890 serial gas chromatograph equipped with FPD, (phosphorous mode and 529 nm). Capillary column PAS-1701 (23 m x 0.32 mm (i.d) x 0.52 um). Under the following condition: Detector temp. 250°C Injector temp. 250°C, oven temp. 230°C Nitrogen was used as a carrier gas flow rate 3 ml/min, Hydrogen flow rate 75 ml/min and Air flow rate 100/min. The retention time was 13.1 min.

The reliability of the analytical methods was examined by fortifying untreated samples with known quantities (1 ppm) of tested insecticides and fungicides, followed by the same procedure of extraction, clean up and analysis. The rates of recovery of the tested pesticides in tomato fruits were 100, 100 and 97% for fenitrothion, profenofos and pyrazofos, respectively and for cucumber fruits were 100 and 98% for profenofos and pyrazofos, respectively.

RESULTS AND DISCUSSION

Residues on and in tomato fruits: Data presented in Table 1 show the initial deposits as well as the residual behaviour of fenitrothion, profenofos and pyrazofos on and in Tomato fruits. Profenofos showed the highest levels of residues on and in tomato fruits at all intervals, whereas pyrazofos recorded the lowest of residue deposits. On the other hand, fenitrothion showed intermediate residue levels. The initial deposits of profenofos residues an hour after treatment on and in tomato fruits was 2.45 ppm compared with 1.92 and 0.54 ppm for fenitrothion and pyrazofos at the same interval, respectively. The extreme amounts of the pesticide residues as well as the great variation between their deposits could be attributed to the differences in their applied recommended rate. The concentrations of spraying solutions were 125, 144 and 30 grams active ingredients for fenitrothion, profenofos and pyrazofos, respectively. El-Sayed *et al.* (1976) stated that the amounts of deposits depended on the rate of application, the nature of the treated surface and the relation between the surface treated and its weight. The rate of residue decrease as a function of time at 10 day post treatment was 0.06, 0.51 and 0.001 ppm for fenitrothion, profenofos and pyrazofos, respectively.

Table 1. Residues of fenitrothion, profenofos and pyrazofos on and in tomato fruits.

Time after treatment (days)	Fenitrothion		Profenofos		Pyrazofos	
	ppm	% loss	ppm	% loss	ppm	% loss
Initial*	1.92	0.00	2.45	0.00	0.54	0.00
1	1.13	41.14	1.2	51.02	0.22	59.25
3	0.42	78.12	0.89	63.67	0.12	77.77
7	0.23	88.02	0.56	77.14	0.01	98.14
10	0.06	96.87	0.51	79.18	0.001	99.81
15	0.002	99.89	0.19	92.24	ND**	--
RL50 values (hours)	29		23		20	
MRL	0.5 ppm		0.2 pmm		0.2 ppm	

* One hour after treatment

** ND : below detection limit (.001ppm)

Profenofos was the most persistent in this study. Its residues on and in tomato fruits decreased from 2.45 ppm at zero time to reach 0.19 ppm after 15 days post treatment revealing total loss of 92.24% of the initial deposits. The data further showed that the half-life (RL_{50}) of fenitrothion, profenofos and pyrazofos fungicide were 29, 23 and 20 hours, respectively.

The residue level of fenitrothion and pyrazofos at three days post treatment reached below the maximum permissible limit 0.5 and 0.2 ppm in tomato fruits, (CODEX, 1997).

The maximum permissible residue limit for profenofos was of 0.2 ppm in tomato fruits (CODEX,1997) at 15 days from treatment. The results are in agreement with Ahmed and moursy (1991) who mentioned that profenofos residues persisted in garlic, tomato and strawberries for up to 3 weeks after the second fouler application of profenofos. The results of this study are quite comparable with those reported by (Hegazy *et al*, 1989; Al-Khalaf *et al*, 1992; Shady *et al*, 2000). They found that the safe period for harvesting the vegetables treated with organophosphrous insecticides ranged between 1 and 2 days after treatment.

According to the (CODEX, 1997), the corresponding recommended preharvest intervals (PHI) for tomato fruits were 3, 15 and 3 days for fenitrothion, profenofos and pyrazofos, respectively.

Residues on and in cucumber fruits: Data in Table 2 showed the residues of profenofos and pyrazofos in cucumber fruits. The fungicide pyrazofos revealed the lowest deposit one hour after spraying on cucumber fruits (0.68 ppm), while profenofos showed the relatively higher residues, (2.40-ppm). This was probably due to the lower concentration used with pyrazofos. The residues decreased after 24 hours to 0.78 and 0 31 ppm for profenofos and pyrazofos, respectively. The residues dropped to 0.004 and 0.003 ppm after ten days for profenofos and pyrazofos. respectively. The loss in residues enhanced with time, thus reaching 99.83 and 99.56 % for profenofos and pyrazofos, respectively after ten days from treatment. Residues however undetectable for both chemicals in cucumber fruits after 15 days from treatment.

The calculated half-life values of these pesticides were 18 and 22 hour on cucumber fruits for profenofos and pyrazofos, respectively. Similar results were also reported by several investigators. Khan *et al.* (1985), they found that the halflives for methiathion, phosphamidon and rogodial in cucumber fruits were less than 3 days All residues in cucumber dissipated rapidly during the first 10 days after spray

Table 2. Residues of profenofos and pyrazofos in Cucumber fruits.

Time after treatment (days)	Profenofos		Pyrazofos	
	ppm	% loss	ppm	% loss
Initial*	2.40	0.00	0.68	0.00
1	0.78	67.5	0.31	45.41
3	0.56	76.67	0.14	79.06
7	27.00	88.75	0.02	97.06
10	0.00	99.83	0.003	99.56
15	ND**	100	ND	100.00
RL50 values (hours)	18		22	
MRL	0.1 pmm		0.1 ppm	

* : One hour after treatment

** ND : below detection limit (.001ppm)

On the other hand, the present results differed from those obtained by shoker (1997). who studied the residues of fenitrothion on and in some vegetable crops and found that the half-live values of this insecticide was 8.2 hours on cucumber fruits. These results were generally in agreement with many research workers, e.g., Al-Samariee et al. (1987). Al-Azawi *et al.* (1991), Haggag (1994) Hegazy *et al.* (1997) Hegazy et al.(1999) and Shady *et al.* (2000).

According to (CODEX Alimentarius commission, 1997), the maximum residue limits (MRL's) for profenofos and pyrazofos on cucumber-fruits were 0.1 ppm. This indicates that PHI was 9 days for profenofos and 5 days for pyrazofos, should be considered before consumption of cucumber sprayed with profenofos and pyrazofos.

Generally, the short persistence in tomato and cucumber fruits could be due to a variety of environmental factors such as sunlight and temperature (Lichtenstein, 1972). Growth is also responsible to certain extent for decreasing the pesticide residue concentrations due to growth dilution effect, (Walgenbach *et al.* 1991).

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متبقيات مبيدات الفينتروثيون والبروفينوفوس والبيرازوفوس على وفى بعض ثمار الخضر تحت الظروف الحقلية

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اوضحت النتائج ان كميات المتبقى من مبيد الفينتروثيون على ثمار الطماطم بعد ساعة من المعاملة بلغت ١.٩٢ جزء فى المليون ، ثم تناقصت تدريجياً بعد يوم من المعاملة الى ١.١٣ جزء فى المليون ، ثم اخذت فى التناقص الى ان وصلت الى ٠.٠٦ و ٠.٠٠٢ جزء فى المليون بعد ١٠ ، ١٥ يوماً من المعاملة صفر كانت فترة نصف العمر لمبيد الفينتروثيون على ثمار الطماطم ٢٩ ساعة ، اوضحت النتائج كذلك ان كمية المتبقى من مبيد البروفينوفوس على ثمار الطماطم بعد ساعة من الرش كانت ٢.٤٥ جزء فى المليون ثم تناقصت تدريجيا حتى وصلت الى ٠.١٥ و ٠.١٩ جزء فى المليون بعد ١٠ ، ١٥ يوم من المعاملة ، وكانت فترة نصف العمر مبيد البروفينوفوس ٢٣ ساعة وكانت كمية المتبقى من مبيد البيرازوفوس فى ثمار الطماطم بعد ساعة من الرش ٠.٥٤ جزء فى المليون ثم تناقصت تدريجيا الى آن وصلت ٠.٠٠١ جزء فى المليون بعد ١٠ ايام من المعاملة . وبعد ١٥ يوم لم يكشف عن اى متبقيات (تحت حدود الطريقة المستخدمة ٠.٠٠١ جزء فى المليون) وأمكن تحديد فترة نصف العمر لمبيد البيرازوفوس على ثمار الطماطم بـ ٢٠ ساعة .

اظهرت نتائج مبيدى البيروفينوفوس و البيرازوفوس على ثمار الخيار إختفاء نسبة كبيرة من متبقيات هذه المبيدات خلال اليوم الاول بعد المعاملة قدرت بحوالي ٥٦١ من البروفينوفوس و٥٤.٤١ من مبيد البيرازوفوس ثم توالى تدهور هذه المبيدات بمرور الوقت حتى وصلت الي ٨٣ ٩٩. لمبيد البروفينوفوس و ٥٦ ٩٩ ٪ لمبيد البيرازوفوس بعد مرور عشرة ايام من المعاملة وبعد ١٥ يوم من المعاملة كانت الكميات اقل من حدود الطريقة المستخدمة (٠.٠٠٢ جزء في المليون)

طبقا للحدود المسموح بها يمكن تسويق ثمار الخيار المعاملة بالبروفينوفوس بعد عشرة ايام من المعاملة , كما يمكن استهلاك ثمار الخيار المعاملة بالبيرازوفوس بعد خمسة ايام من المعاملة