

RESIDUES OF FENITROTHION AND PYRAZOPHOS ON AND IN SQUASH FRUITS

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Abstract

The present study was conducted to follow up the residues of the insecticide fenitrothion (Sumithion 50% EC), recommended for control of aphids, and the fungicide pyrazophos (Afugan 30% EC), recommended for powdery mildew, on and in squash fruits. The results indicated that both O.P. pesticides were extremely degradable when they were applied on fruitful squash plants. The residues half life values on and in squash fruits for fenitrothion and pyrazophos were 24 and 26 hours, respectively. Residues of both pesticides on and in squash fruits reached negligible levels only two days after treatment with total loss of about 98%. Those residue levels were much less than the established maximum residue limits (MRLs) of both chemicals which confirm that two days after treatment is quite enough as a waiting period, i.e. pre-harvest interval (PHI), before marketing or consuming of treated squash fruits.

The results also indicated that the peeling of the fruits removed 96% of fenitrothion residues and almost all the residues of pyrazophos for all intervals including the fruits collected an hour after application. The peeled fruits were almost pyrazophos residue free or had negligible levels much lower than the established MRL for fenitrothion.

INTRODUCTION

Squash (*Cucurbita pepo* L.) is a common vegetable crop in Egypt. This crop is attacked during its growth season by aphids and powdery mildew. The pesticides recommended for controlling these pests are fenitrothion (Sumithion) for aphids and pyrazophos (Afugan) for powdery mildew.

This study was conducted to follow up the residues of both pesticides on and in squash fruits of treated plants under Egyptian field conditions and to determine the pre-harvest intervals (PHI), i.e. the safety period that the growers must wait after application of either chemicals to pick and market their fruits with no or negligible pesticide residues. The effect of fruit peeling on the dissipation of residues of both pesticides was also studied.

MATERIALS AND METHODS

Pesticides Used

Fenitrothion: O,O - dimethyl O-4-nitro-m-tolyl phosphorodithioate, O.P. insecticide, used at the rate of 1 litre in 400 litre of water per feddan; i.e. 500 g a.i./feddan.

Pyrazophos : Ethyl-2-diethoxyphosphinothioxyloxy-5-methylpyrazolo [1,5-a] pyrimidine-6-carboxylate, O.P. fungicide, known commercially as Afugan, used at the rate of 100 ml per 100 litre of water; i.e. 60 g a.i./feddan.

Field experiment and sampling

The field experiment was conducted in the Experimental Farm of Faculty of Agriculture, Cairo University at Giza. Squash seeds were planted in three plots of 1/100 of feddan (42 square meters) on May 4, 1995. The tested pesticides were sprayed at the mentioned recommended rate for each pesticide on mature plants using a Knapsack sprayer on July 15, 1995 (70 days after sowing). Two plots were left untreated to serve as control.

Representative squash fruit samples were picked an hour after pesticide spraying (zero time or initial) and at intervals of 2, 4, 7 and 10 days after treatment. Three replicates of fruit samples were collected for each treatment including control. Samples were put in clean bags and taken to the Central Agricultural Pesticide Laboratory for analysis. Each sample was divided into two equal portions. One portion was peeled by scraping with a sharp knife and the other portion was left without peeling. Samples of peeled and unpeeled fruits were chopped and representative samples of peel, chopped peeled and unpeeled fruits for all treatments were kept in clean polyethylene bags in the deep freezer at - 20°C until time of analysis.

Pesticide residues analysis techniques

Extraction : The method of Mollhoff (1975) was adapted for extraction of fenitrothion and pyrazophos residues in squash fruits. Methanol was used instead of acetone for extraction. Sub-samples of 50g were extracted by blending with 100ml methanol. The extracts were partitioned with chloroform, drained through anhydrous sodium sulfate and evaporated under vacuum on a rotary evaporator at 35°C.

Clean up : Extracts of fenitrothion were cleaned up through activated florisil using elution solvent system of 50% methylene chloride, 48.5% n-hexane and 1.5% acetonitrile. Extracts of pyrazophos residues were cleaned up through deactivated florisil (6% water) using the same solvent system used with fenitrothion extracts.

GC Analysis : Residues of fenitrothion and pyrazophos were detected and determined using a Pye Unicam 4500 gas chromatograph equipped with flame photometric detector (FPD) at the phosphorus mode and a 1.5 m x 4mm i.d. Pyrex glass column packed 4% SE-30 + 6% OV-210 on gas chromosorb Q 80-100 mesh. The established operating conditions for the GC were as follows :

1. Oven (column) temperature 240°C.
2. Injection port temperature 243°C.
3. Detector temperature 245°C.
4. Carrier gas (N₂), hydrogen and air flow rates were 30 ml/min. for all.

Retention times were 3.78 min. and 12.48 min. for fenitrothion and pyrazophos, respectively. The minimum detection limits were 0.001 ppm for fenitrothion and 0.003 ppm for pyrazophos. The average recovery percentages using this procedure were 97% for fenitrothion and 91.7% for pyrazophos.

RESULTS AND DISCUSSION

Fenitrothion residues on and in squash fruits

Table 1 shows fenitrothion residues on and in squash fruits at different intervals after the insecticide treatment. The initial deposits (one hour after spraying) of fenitrothion residues were 8.39 ppm in squash peels and 1.834 ppm in the unpeeled whole fruits. Peeling of fruits removed about 96% of fenitrothion residues to reach 0.069ppm in the peeled fruits picked an hour after spraying which was much lower than the Codex Maximum Residue Limits for fenitrothion (0.5 ppm). Considerable decrease in fenitrothion residues was detected on and in squash fruits picked two days after pesticide application, revealing total loss of 98.7% from the peels, 98.0% from the unpeeled whole fruits, and 75.4% from the peeled ones to record 0.109, 0.036, and 0.017 ppm, respectively. It is obviously noticed that those residue levels were much less than the established MRL for this insecticide. Further dissipation in fenitrothion residues were determined in the sample collected four days after application revealing a total loss of more than 99% of the initial deposits. However, fruit samples analyzed 7 or 10 days after application showed undetectable residues

(<0.001 ppm). The estimated half life value of fenitrothion residues in squash fruits was 24 hours.

Table 1. Fenitrothion residues on and in squash fruits at different intervals after pesticide application.

Intervals after treatment	Peel		Unpeeled whole fruits		Peeled fruit (pulp)	
	Residues (ppm)	Loss (%)	Residues (ppm)	Loss (%)	Residues (ppm)	Loss (%)
Initial (1 hour)	8.3900	--	1.834	--	0.069	--
2 days	0.1097	98.7	0.036	98.0	0.017	75.4
4 days	0.0124	99.8	0.011	99.4	0.011	98.8
7 days	ND	100.0	ND	100.0	ND	100.0
10 days	ND	100.0	ND	100.0	ND	100.0

Codex Maximum Residue Limits (MRL): 0.5 ppm

Minimum detection limit : 0.001 ppm

ND : Not detectable

Pyrazophos residues on and in squash fruits

Pyrazophos residues on and in squash fruits at different intervals after application are shown in Table 2. Data indicate that the residues of pyrazophos had the same trend as of fenitrothion residues in and on squash fruits, however, the former showed lower levels of residues due to its lower rate of application (60 g (a.i.) / feddan) compared with 500 g (a.i.) / feddan for the latter. The initial amounts of pyrazophos residues were 3.012 ppm in the peels, and 0.527 ppm in the unpeeled whole fruits. Peeling process reduced all the residues from the fruits to undetectable levels (<0.003 ppm) in the fruit pulp of the samples for all intervals including the initial. Pyrazophos also showed significant decrease in its residues in squash peels as well as in the unpeeled fruits collected 2 and 4 days treatment to reach 0.239 and 0.031 ppm in the peels; and 0.0418 and 0.003 ppm in the unpeeled whole fruits, respectively revealing residue levels in the whole fruits much lower than the Codex MRL (0.1 ppm) for this chemical. The established half life value for pyrazophos residues on squash fruits was 26 hours.

The residue data of this study indicated that the organophosphorus pesticides fenitrothion and pyrazophos were extremely degradable when they were applied on

squash plants with residue half life values of 24 and 26 hours on and in squash fruits, respectively. The residues of both pesticides on and in the fruits reached negligible levels only two days after treatment with total loss of 98%. Those residue levels were much less than the two chemicals which confirm that two days after treatment were quite enough as a waiting period before marketing or consuming the treated squash fruits. The rapid dissipation of originally applied O.P. pesticides are dependent on a variety of environmental factors such as sunlight and temperature (Lichtenstein, 1972). In addition, plant growth, particularly for fruits is also responsible to a great extent for decreasing the pesticide residue concentrations due to growth dilution effects (Walgenbach et al., 1991). Our data are also agree with those obtained and reported by Hegazy et al. (1996a) who found that the residues half life of the O.P. insecticide chlorpyrifos-methyl on and in cucumber fruits was 17 hours and about 94% of the initial residues were lost only three days after treatment.

Table 2. Pyrazophos residues on and in squash fruits at different intervals after pesticide application.

Intervals after treatment	Peel		Unpeeled whole fruits		Peeled fruit (pulp)	
	Residues (ppm)	Loss (%)	Residues (ppm)	Loss (%)	Residues (ppm)	Loss (%)
Initial (1 hour)	3.012	--	0.527	--	ND	--
2 days	0.239	92.0	0.042	92.0	ND	--
4 days	0.031	98.9	0.003	99.9	ND	--
7 days	0.041	98.6	0.004	99.9	ND	--
10 days	ND	100.0	ND	100.0	ND	--

Codex Maximum Residue Limits (MRL): 0.1 ppm

Minimum detection limit : 0.003 ppm

ND : Not detectable

The present data also indicated that the residues of both pesticides mainly located on the fruit surfaces (in the peels). Peeling of treated squash fruits removed about 96% of fenitrothion residues and almost removed all the residues of pyrazophos. The peeled fruits were almost residues free (undetectable levels) for pyrazophos and the detected residues were much lower than the established MRL for fenitrothion in all intervals including the fruits picked an hour after treatment which can

be safely consumed immediately after spraying if they are peeled. This trend of residue distribution could be attributed to the ability of wax in squash peels to absorb most of the residues deposited on fruits since these chemicals are fat soluble. Similar results were obtained and reported by Kargorgier (1979) who found that peeling of fruits resulted in complete disappearance of pesticides. Hegazy *et al.* (1996a, b) also support our results, they found that peeling of cucumber fruits removed about 97% of the total residues of chlorpyrifos-methyl previously detected on and in unpeeled fruits. They also reported that peeling process removed about 99% of fenitrothion residues that were detected on and in the unpeeled potato tubers which indicated poor penetration of organophosphorus pesticides in potato pulp.

Table 5. Organophosphorus residues on and in squash fruits at different intervals after application.

Interval after treatment (days)	Peeled fruit (ppm)		Unpeeled whole fruits (ppm)	
	Residue loss (%)	Residue (ppm)	Residue loss (%)	Residue (ppm)
10 days	ND	ND	ND	100.0
7 days	ND	ND	0.04	99.8
4 days	ND	ND	0.008	99.9
2 days	ND	ND	0.045	99.0
Before 2 days	ND	ND	0.527	99.5

Lower Residue (ppm) = 0.1 ppm
 Minimum detectable level = 0.100 ppm
 ND = not detectable

The present data also indicated that the residues of both pesticides were removed from the fruit surfaces in the water. Peeling of treated squash fruits removed about 99% of fenitrothion residues and almost removed all the residues of pyrethroids. The present data were almost similar to those reported by Kargorgier (1979) who found that peeling of fruits resulted in complete disappearance of pesticides. The present data also indicated that the residues of both pesticides were removed from the fruit surfaces in the water. Peeling of treated squash fruits removed about 99% of fenitrothion residues and almost removed all the residues of pyrethroids. The present data were almost similar to those reported by Kargorgier (1979) who found that peeling of fruits resulted in complete disappearance of pesticides.

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متبقيات مبيدئ الفينثروثيون والبيرانوفوس على وفي ثمار الكوسة

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المعمل المركزى للمبيدات - مركز البحوث الزراعية - الدقى - الجيزة.

أجريت دراسة لتتبع متبقيات المبيد الحشرى الفوسفورى فينثروثيون والذى استخدم فى صورة سوميثيون ٥٠٪ مركز قابل للاستحلاب بمعدل ٥٠٠ جم مادة فعالة /فدان ضد المن ، والمبيد الفطرى الفوسفورى بيرانوفوس والمستخدم فى صورة ٢٠٪ مركز قابل للاستحلاب بمعدل ٦٠ جم مادة فعالة /فدان ضد البياض الدقيقى وذلك على وفي ثمار الكوسة المعاملة بهذين المبيدين. وقد أوضحت الدراسة أن المبيدين سريعى التحطم حيث كانت قيم فترة نصف العمر لمتبقيات المبيدين هى ٢٤ ، ٢٦ ساعة للفينثروثيون والبيرانوفوس على الترتيب. وقد انخفضت متبقيات كلا المبيدين الى مستويات متدنية جدا أقل بكثير من الحدود القصوى المسموحة لكل منهما والمحددة بواسطة دستور متبقيات المبيدات فى الأغذية (كودكس) وذلك بعد يومين فقط من المعاملة وبنسبة فقد كلى وصلت الى اكثر من ٩٠٪ من متبقيات كل من المبيدين المقدره بعد المعاملة بساعة واحدة. وبذلك تكون ثمار الكوسة المعاملة بأى من المبيدين آمنة للاستهلاك الأدمى بعد يومين من المعاملة.

كما تشير النتائج الى أن عملية تقشير ثمار الكوسة المعاملة بهذين المبيدين قد أزالته حوالى ٩٦٪ من متبقيات الفينثروثيون وأزالته تقريبا كل متبقيات البيرانوفوس (كانت المتبقيات أقل من الحد الأدنى الممكن تقديره) وذلك لجميع الفترات بما فيها عينات الثمار المجموعه بعد ساعة واحدة من المعاملة مما يؤكد أن معظم متبقيات هذين المبيدين تتركز فى قشرة ثمار الكوسة ولتصبح الثمار المقشورة آمنة وصالحة للاستهلاك حتى لو تم جمعها فى يوم الرش نفسه.