RESIDUES OF FENITROTHION AND PAYRAZOPHOS ON 
AND IN SQUASH FRUITS

M.E.A. HEGAZY, M. ABDEL RAZIK, M.F. EL-HADIDI 
S.A. SHOKR AND Y.S. IBRAHIM

Central Agricultural Pesticide Laboratory, Agricultural Research Centre, Dokki, 
Egypt.

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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 (Afulgan 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 (Afulgan) 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*: 0.0 - 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-diethoxyphosphinothioyl-5-methylpyrazolo [1,5-a] pyrimidinem-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 Molhoff (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 Unicum 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 0.069 ppm 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.

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

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.

<table>
<thead>
<tr>
<th>Intervals after treatment</th>
<th>Peel Residues (ppm)</th>
<th>Peel Residues (%)</th>
<th>Unpeeled whole fruits Residues (ppm)</th>
<th>Unpeeled whole fruits Residues (%)</th>
<th>Peeled fruit (pulp) Residues (ppm)</th>
<th>Peeled fruit (pulp) Residues (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial (1 hour)</td>
<td>3.012</td>
<td>-</td>
<td>0.527</td>
<td>-</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>2 days</td>
<td>0.239</td>
<td>92.0</td>
<td>0.042</td>
<td>92.0</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>4 days</td>
<td>0.031</td>
<td>98.9</td>
<td>0.003</td>
<td>99.9</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>7 days</td>
<td>0.041</td>
<td>98.6</td>
<td>0.004</td>
<td>99.9</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>10 days</td>
<td>ND</td>
<td>100.0</td>
<td>ND</td>
<td>100.0</td>
<td>ND</td>
<td>--</td>
</tr>
</tbody>
</table>

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 Kargcogier (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>
<thead>
<tr>
<th>Treatment</th>
<th>Initial Concentration (ppm)</th>
<th>Residue Concentration (ppm)</th>
<th>RSD %</th>
<th>Percent Dissipation</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 days</td>
<td>0.50</td>
<td>0.00</td>
<td>100</td>
<td>95</td>
</tr>
<tr>
<td>21 days</td>
<td>0.20</td>
<td>0.00</td>
<td>100</td>
<td>97</td>
</tr>
<tr>
<td>28 days</td>
<td>0.05</td>
<td>0.00</td>
<td>100</td>
<td>99</td>
</tr>
</tbody>
</table>

The data in the table indicate that the fenitrothion residues were effectively removed by peeling the squash fruits.
REFERENCES


متبقيات مبيدات الفينتريثيون والبيراizophوس على شحار الكوسا

محمد السعيد علي حجازي، محمد عبد الرازيق السيد، محمد فوزي الحديدي.
شكر عبد السلام شكر، يحيى سيد إبراهيم

المعمل المركزي للمبيدات - مركز البحوث الزراعية - الدقي - الجيزة.

أجريت دراسة لتشبيت متبقيات المبيد الأيضي الحضاري الفوسفوري فينتريثيون والذي استخدم في صورة سوميثيون 20٪ مركز قابل للاستحلاب بعمل 500 جم مادة فعالة / حبوب هندي النم، والمبيد النفيضي الفوسفوري بيجازوزوس ومستخدم في صورة 20٪ مركز قابل للاستحلاب بعمل 60 جم مادة فعالة / حبوب هندي الأيض الدقيق وذلك على في شثار الكوسا المعمولة بهذين المبيدلين. وقد أوضح النتائج أن المبيدتين سريعاً التعطح حيث كانت نسبة تصف الحضاري المتبقيات المبيدتين في 2% 14 ساعة للميثروثيون والبيراizophوس على الترتيب. وقد انخفضت متبقيات كلا المبيدتين إلى مستويات متدنية جداً أقل بكثير من الحدود القصوى المسموح بها لكل منهما والizada بواسطة استمر متبقيات المبيدات في الأملاك (كوبيركس) وذلك بعد يومين فقط من المعلولة بوصف كلي. وصل إلى أكثر من 90٪ من متبقيات كل من المبيدتين المقدرة بعد المعلولة بساعة واحدة. وذلك تكون شثار الكوسا المعمولة بناء من المبيدتين آمنة للاستهلاك اليومي بدون يومين من المعلولة.

كما تشير النتائج إلى أن عملية تقشير شثار الكوسا المعمولة بهذين المبيدتين قد أزالت حوالي 90٪ من متبقيات الفينتريثيون وأزالت تقريباً كل متبقيات البيراizophوس (كانت المتبقيات أقل من الصد الأدنى الممكن تقديراً) وذلك لجميع الفترات بما فيها ميتان المثمر الجمعية بعد ساعة واحدة من المعلولة مما يؤكد أن معظم متبقيات هذين المبيدتين تتركز في قشرة شثار الكوسا وتصبح الثمار المفتوحة آمنة وقابلة للاستهلاك حتى لو تم جمعها في يوم الرش نفسه.