RESIDUES OF PIRIMIPHOS-METHYL AND PROTHIOFOS ON AND IN BROAD BEAN PLANT AND SOIL

SH. A.A. SHOKR, M.ABDEL-RAZIK, M.E.A. HEGAZY, M.M. ABU-ZAHW AND NEVEIN S. AHMED

Central Agricultural Pesticides Laboratory, Agricultural Research Centre, Dokki, Giza, Egypt.

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Abstract

These studies were carried out to determine the residual behaviour of pirimiphos-methyl and prothiofos organophosphorus insecticides on green pods of broad bean plants and the contamination of soil under these plants. The residue half-life values (RLH50) determined on green pods, peels and soil were 15.8, 15.6 and 144 hours for pirimiphos-methyl and 24, 316.8 and 120 hours for prothiofos.

Prothiofos was more persistent in green pods and peels than pirimiphos-methyl, also prothiofos and pirimiphos-methyl were more stable in the soil than in the green pods.

In green pods the maximum residues level (MRL) was 0.5 ppm for pirimiphos-methyl and the preharvest intervals (safety period) were 3 and 3.3 days for green pods and peels, respectively.

Peeling the green pods removed most of the two insecticide residues. For pirimiphos-methyl the residues were brought to a level below the Codex MRL, so that the green seeds could be used safely at any time after spraying. The dry seeds were found to contain 0.009 ppm of prothiofos. On the contrary, no residues of pirimiphos-methyl were detected in dry seeds so, they could be marketed safely for human consumption at any time after harvest. Also, dry peels and dry trellis contained 4.208 and 1.945 ppm of prothiofos and 0.033 and 0.037 ppm of pirimiphos-methyl, respectively.

INTRODUCTION

Broad bean crop plays an important role in the Egyptian diet either as green pods or dry seeds. This crop is attacked with many insect species which cause serious injury and thus the final yield is reduced. Pirimiphos-methyl (O-2-diethylamino-6-methyl pyrimidin-4-yl 0,0-dimethyl phosphorothioate) and prothiofos (O-2, 4-dichlorophenyl 0-ethyl S-propyl phosphorodithioate) insecticides are known to be efficient against insect species infesting broad bean.

The aim of the present investigation was to study the persistence of these insecticides in the green pods of the broad bean plants and the contamination of the soil.
under these plants and to determine the intervals between application and harvest (safety period) for human consumption.

MATERIALS AND METHODS

The experiment was conducted from November 1997 to April 1998 in the Giza region (farm of Faculty of Agriculture, Cairo University). Broad bean seeds of the Giza 2 variety were planted on November 13th 1997. Pirimiphos-methyl (Actellic E.C. 50%) and prothiofos (Tokuthion E.C. 50%) were applied on March 10th 1998, at rates of 300 ml/100L water (recommended dose) using a knapsack sprayer equipped with one nozzle. Samples, 500g each, of green pods were taken at intervals of one hour after application (zero time), 1, 3, 6, 9, 12, 15 and 20 days. Then sub-samples, 50g each of green pods, peels and green seeds, were taken for residue analysis. At harvest time 200g each of dry seeds, dry peels and dry trellis were grinded and 50g were taken for residue analysis. Soil samples, 500g each from the area under the sprayed plants were taken at 5 cm depth at intervals of one hour after application (zero time), 9, 20 and 35 days.

Analytical Procedures

A. Extraction

Plant Samples: The extraction procedure used is the general method suitable for organophosphorus compounds (Ministry of Welfare, Netherlands 1988). According to the method, 50g homogenized sample were mixed with 50g anhydrous sodium sulphate and 100 ml ethylacetate. The mixture was blended for 3 min. and the extract filtered, then evaporated just to dryness using a rotary evaporator at 40°C.

Soil Samples: Soil samples (clay) were ground then 100 g. were placed in 500 ml conical flask containing 50g. anhydrous sodium sulphate and 200 ml chloroform. The flasks were shaken for one hour using an electrical shaker. Then the chloroform layers were filtered through anhydrous sodium sulphate, then evaporated just to dryness using a rotary evaporator at 40°C, and the residues were ready for chromatographic determination without clean-up.

B. Clean-up of Extracts

The clean-up procedure was done according to the method of Mills et al. (1972). An elution solvent system used a mixture of 50% methylene chloride-1.5% acetoni-
trile- 48.5% hexane (v/v/v). A Column chromatographic containing 10g. activated florisil for pirimiphos-methyl extract and 10g. 3.5% deactivated florisil for prothiofos extract was used. Then the residues from the column were eluted with 200 ml of this mixture.

**C. Gas liquid chromatography determination**

A Pye Unicam 4500 gas chromatograph equipped with a flame photometric detector operated in the phosphorus mode (526 nm filter) was used for determination pirimiphos-methyl and prothiofos. The column (1.5m x 4mm i.d. pyrex) was packed with 4% SE-30 + 6% OV-210 on gas chromosorb Q (80-100 mesh); temperature degrees were 230°C. for column, 240°C. for detector and 235°C. for injector and gas flow was 30, 30 and 30 ml/min for nitrogen, hydrogen and air, respectively. Retention time for pirimiphos-methyl and prothiofos under these conditions was 4.22 and 7.64 minutes, respectively.

Results were corrected according to the rates of recovery which were determined in fortified untreated samples. Following the techniques previously mentioned, the rates of recovery for pirimiphos-methyl were 89.7% and 93.56% and for prothiofos 97.4% and 96.34% in plant parts and soil, respectively.

**RESULTS AND DISCUSSION**

Results in table 1 represent the residues of pirimiphos-methyl and prothiofos on and in green pods, peels and green seeds. The data showed that the concentration of the initial deposits was 8.500 and 11.560 ppm for pirimiphos-methyl and 6.175 and 7.933 ppm for prothiofos on and in green pods and peels, respectively, one hour after application. The amount of residues decreased to 1.930, 2.508 ppm and 3.095, 5.505 ppm, respectively within the first 24 hours after spraying. The residues of these insecticides dropped to 0.025, 0.102 ppm and 0.560, 1.338 ppm after 20 days, respectively from treatment. The half-life values of pirimiphos-methyl and prothiofos were 15.6, 15.6 hours and 24,316.8 hours green pods and peels, respectively. It was in accordance with degradation data indicating that prothiofos was more persistent in green pods and peels that pirimiphos-methyl.

The fast disappearance of pirimiphos-methyl could be attributed to its higher vapour pressure ($1 \times 10^{-4}$ mmHg at 30°C) than prothiofos ($<7.5 \times 10^{-6}$ mmHg at 20°C) and also the other factors such as weathering, metabolic conversions or other pro-
cesses. The obtained data are in agreement with those of Shokr (1997) who found that prothiofos was persistent 2.5 times more than pirimiphos-methyl in green bean pods, where the rate of loss one day after application was 18.4% and 45.05%, respectively.

The residues of pirimiphos-methyl and prothiofos were concentrated in the peels and migrated in low concentration to the green seeds in the first 9 days after application for pirimiphos-methyl and first 3 days after application for prothiofos. The results obtained agreed with findings of Abdel Rahman (1996) who found that the residues of pirimiphos-methyl in green pea pods were concentrated in the peel and migrated in low concentration to the seeds 9 days after application. Similar results were reported by Barakt et al., (1994) who studied the persistence of pirimiphos-methyl in whole cowpea pods, peels and green seeds. They found that residues of pirimiphos-methyl migrated from peels to green seeds in first five days after application. Abdel-Razik et al. (1985) found that pirimiphos-methyl residues were mainly found in the peels of potato tuber and small amounts penetrated to the pulp.

According to the Codex Alimentarius Commission (1990), the maximum residue level (MRL) for pirimiphos-methyl on broad bean pods was 0.5 ppm and the preharvest intervals (safety period) were 3 and 5.3 days for green pods and peels, respectively.

El-Nabarawy and Abou-Donaia (1992) reported that the green cowpea pods could be consumed 5 days after profenophos spraying and 1 day after pirimiphos-methyl application. Green beans could be used safely for consumption 4 and 11 days after spraying with either pirimiphos-methyl or profenofos, respectively (Abdalla et al.1993). Shokr (1997) studied the residues of pirimiphos-methyl and fenitrothion in green beans pods. He found that the preharvest intervals (safety period) were 10.7 and 13.6 days after application, respectively.

Peeling the green pods removed most of the two insecticide residues. For pirimiphos-methyl, the residues were brought to a level below the Codex MRL, so that the green seeds could be used safely at any time after spraying. El-Nabarawy (1992) studied the residues of profenophos, pirimphos-ethyl and pirimiphos-methyl on and in broad bean pods. He found that most of the insecticide residues are removed with the peel so that the green seeds could be safely used at any time after harvest.

Data in table 2 indicate the amount of pirimiphos-methyl and prothiofos residues in dry seeds, dry peels and dry trellis. The dry seeds were found to contain 0.009 ppm of prothiofos. On the contrary, no residues of pirimiphos-methyl were detected in dry
seeds so, they could be marketed safely for human consumption at any time after harvest. Also, dry peels and dry trellis contained 4.208 and 1.945 ppm of prothiofos and 0.033 and 0.057 ppm of pirimiphos-methyl, respectively. El-Sayed et al. (1975) determined the persistence of monocrotophos (azodrin and nuvacron) under field conditions on snap bean and found that the dry bean seeds contained 1.28 and 1.03 ppm, respectively, of azodrin and nuvacron as parent compounds. El-Sayed et al. (1980) studied the persistence of profenophos inside the mature seeds of soybean at harvest and found that mature seeds did not contain detectable amounts of this compound.

The dried seeds of broad bean plants did not have any detectable residues of profenophos, pirimiphos-ethyl and pirimiphos-methyl after spraying on broad bean plants so, they could be marketed with apparent safety for human consumption at any time after harvest (El-Nabarawy 1992).

The data obtained in table 3 show that the residue levels in soils under broad bean plants, one hour after application were 4.392 and 3.680 ppm for pirimiphos-methyl and prothiofos, respectively. The amount of residues decreased to 0.049, 0.499 and 0.117 ppm and 0.718, 0.227 and 0.096 ppm 9,20 and 35 days after spraying pirimiphos-methyl and prothiofos, respectively.

The residue half-life values in soil under broad bean plants were 144 and 120 hours for pirimiphos-methyl and prothiofos, respectively.

In the soil, pirimiphos-methyl migrates poorly, its half-life in various soils fluctuating with four weeks (Gruzdyev et al. 1983).

pirimiphos-methyl and prothiofos had high stability in the soils under broad bean plants when compared with their stability in the green pods of broad bean plants.
<table>
<thead>
<tr>
<th>Time after application (Days)</th>
<th>Residues (ppm)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Pirimiphos-methyl</td>
<td>Peels</td>
<td>Green seeds</td>
<td>prothiofos</td>
<td>Green Pods</td>
<td>Peels</td>
<td>Green seeds</td>
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<tr>
<td>Zero Time*</td>
<td>8.500</td>
<td>11.560</td>
<td>0.000</td>
<td>6.175</td>
<td>7.933</td>
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<td>1</td>
<td>1.930</td>
<td>2.508</td>
<td>0.013</td>
<td>3.095</td>
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<tr>
<td>3</td>
<td>0.465</td>
<td>0.860</td>
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<td>4.712</td>
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<td>6</td>
<td>0.298</td>
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<td>2.306</td>
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<td>9</td>
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<td>0.270</td>
<td>0.007</td>
<td>2.192</td>
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<td>13</td>
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<td>1.2287</td>
<td>4.031</td>
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<td>20</td>
<td>0.025</td>
<td>0.102</td>
<td>UND</td>
<td>0.560</td>
<td>1.338</td>
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<tr>
<td>$R_{50}$ in hours</td>
<td>15.6</td>
<td>15.6</td>
<td>24</td>
<td>316.8</td>
<td></td>
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</tbody>
</table>

*One hour after application
Table 2. Residues of pirimiphos-methyl and prothiofos in dry seeds, dry peels and dry trellis

<table>
<thead>
<tr>
<th>Insecticide</th>
<th>Residues (ppm)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Dry seeds</td>
<td>Dry peels</td>
<td>Dry trellis</td>
</tr>
<tr>
<td>Pirimiphos-methyl</td>
<td>UND</td>
<td>0.033</td>
<td>0.057</td>
</tr>
<tr>
<td>Prothiofos</td>
<td>0.009</td>
<td>4.208</td>
<td>1.945</td>
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</table>

Table 3. Residues of pirimiphos-methyl and prothiofos in soil.

<table>
<thead>
<tr>
<th>Time after application (Days)</th>
<th>Residues (ppm)</th>
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<tr>
<td></td>
<td>Pirimiphos-methyl</td>
<td>Prothiofos</td>
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<td>Zero Time*</td>
<td>4.392</td>
<td>3.680</td>
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<td>9</td>
<td>0.949</td>
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<td>20</td>
<td>0.489</td>
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<tr>
<td>35</td>
<td>0.117</td>
<td>0.096</td>
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<tr>
<td>R50 in hours</td>
<td>144</td>
<td>120</td>
<td></td>
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</tbody>
</table>

*One hour after application.
REFERENCES


ставлен في المليون بالتساوي لصيد البذور. مثبطات البيريموفوس ميثيل والبروثيوفوس
على وفي تشتت القول والنشرة

شكر عبد السلام على شكر ، محمد عبد الرؤف السيد، محمد السعيد على حفظي،
مصطفى محمد أبو زهير، نيفين صلاح الدين أحمد

العمل المرئي للمبيدات - مركز البترول الزراعية - المدي – الجيزة.

يهدف هذا البحث لدراسة سلوك مثبطات مبيد البيريموفوس ميثيل والبروثيوفوس
على وفي قرون نباتات القول والعصارة مدى تلوث النبات للأسلاف المزروعية نشيطة القول.

أوضحت الدراسة أن مثبطات النبات الإبلية للبيريموفوس ميثيل كانت 1.7 15.7 16.7 17.7 18.7
وينور القرون الخضراء، والنشرة على التوالي. كان مبيد البيريموفوس أكثر ثباتاً من مبيد
البروثيوفوس ميثيل على القرون الخضراء لنباتات القول، وينور القرون الخضراء، وأيضاً كان
البروثيوفوس والبيريموفوس ميثيل أعلى ثباتاً في النباتات عند مقارنتها بالثبات على القرون
الخضراء لنباتات القول.

بالنسبة لصيد البيريموفوس ميثيل كان الحد المسموح به من المنترقات على قرون القول
5.7 جزء في المليون كذلك البدنوس وكانت فترة الأمان بعد الملاحة بهذا المنتج 2.5.

عوماً بالنسبة لقرن النبات الخضراء، وتسلق البيريموفوس ميثيل، حيث كانت البدن النبات الخضراء تحتوي على كمية من
المبيد اقل من الحد المسموح به بالنسبة لصيد البيريموفوس ميثيل، وثلك فهي تصلح للاستهلاك في
أي وضع بعد الملاحة.

احصت البذور الجانبية على 6.9 جزء في المليون من مبيد البيريموفوس وعلى الغرس من
ذلك لم تكشف أي تشتتات من مبيد البيريموفوس ميثيل في البذور الجانبية وقد يذكر تسويعها
للبيكربال بناء جيد الحصاد مباشرة. أيضاً احتوت القرون البذور الخضراء ورخة النبات البذور على
كميات 1.48 و 0.74 جزء في المليون بالنسبة لصيد البروثيوفوس و3.72 و 0.57 جزء في
المليون بالنسبة لصيد البيريموفوس ميثيل على التوالي.