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

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Abstract

These studies were carried out to determine the residual behaviour of pirmiphosmethyl and prothiofos organophosphorus insecticides on green pods of broad bean plants and the contamination of soil under these plants. The residue half-life values (RL_{50}) determined on green pods, peels and soil were ,15.6,15.6 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 pirimiphosmethyl and the preharvest intervals (safety period) were 3 and 5.3 days for green pods and peels, respectively.

Peeling the green pods removed most of the two insecticide residues. For pirimiphos-m ethyl 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 pirimiphosmethyl 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.

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 (0-2-diethylamino-6-methyl pyrimidin-4-yl 0,0-dimethyl phosphorothioate) and prothiofos (0-2, 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 13 th 1997. Pirimiphos-methyl (Actellic E.C. 50%) and prothiofos (Ţokuthion E.C. 50%) were applied on March 10 th 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^{o}C.

Soil Samples: Soil samples (clay) were ground then 100 g. were placed in 500 ml conical flask containing 50g. ar hydrous 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^{o}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 prothoifos 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 ($1X10^{-4}$ mmHg at 30 °C) than prothiofos ($<7.5 X10^{-6}$ 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 appication. 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-Donia (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 resdiues of profenophos, pirimiphos-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 safety used at any time after harvest.

Data in table 2 indicate the amount of pirimiphos-methy 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, thay could be marketed safely for human consumption at any time after harvest. Also, dry peels and dry trellis contatined 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, thay 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 0.049,0.489 and 0.117 ppm and 0.716,0.227 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 1. Residues of pirimiphos-methyl and prothiofos on and in broad bean pods.

Time after application (Days)	Residues (ppm)					
	Pirimiphos-methyl			prothiofos		
	Green Pods	Peels	Green seeds	Green Pods	Peels	Green seeds
Zero Time*	8.500	11.560	0.000	6.175	7.933	0.000
1	1.930	2.508	0.013	3.095	5.505	0.024
3	0.465	0.860	0.017	2.530	4.712	0.025
6	0.298	0.351	0.008	2.306	4.700	UND
9	0.083	0.270	0.007	2.192	4.514	UND
13	0.070	0.119	UND	1.2287	4.031	UND
20	0.025	0.102	UND	0.560	1.338	UND
RL_{50} in hours	15.6	15.6		24	316.8	

*One hour after application

Table 2. Residues of pirimiphos-methyl and prothiofos in dry seeds, dry peels and dry trellis

Insecticide	Residues (ppm)		
	Dry seeds	Dry peels	Dry trellis
Pirimiphos-methyl	UND	0.033	0.057
Prothiofos	0.009	4.208	1.945

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

Time after application (Days)	Residues (ppm)	
	Pirimiphos-methyl	Prothiofos
Zero Time*	4.392	3.680
9	0.949	0.716
20	0.489	0.227
35	0.117	0.096
RL_{50} in hours	144	120

*One hour after application.

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متبقيات البيريموفوس – ميثيل والبروثيوفوس على وفى نباتات الفول والتربة

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

يهدف هذا البحث لدراسة سلوك متبقيات مبيدى البيريموفوس ميثيل والبروثيوفوس على وفى قرون نباتات الفول ودراسة مدى تلوث التربة أسفل النباتات نتيجة عملية الرش. أوضحت الدراسة أن فترات نصف العمر بالنسبة لمبيد البيريموفوس ميثيل كانت ١٥,٦، ١٥,٦، ١٤٤، ساعة ولمبيد البروثيوفوس كانت ٢٤,٨ ، ٣١٦,٠ ، ١٢٠ ساعة على القرون الخضراء لنباتات الفول وقشور القرون الخضراء والتربة على التوالى. كان مبيد البروثيوفوس أكثر ثباتاً من مبيد البريموفوس ميثيل على القرون الخضراء لنباتات الفول وقشور القرون الخضراء ، وأيضاً كان البروثيوفوس والبيريموفوس ميثيل أعلى ثباتاً فى التربة عند مقارنتها بالثبات على القرون الخضراء لنباتات الفول.

بالنسبة لمبيد البريموفوس ميثيل كان الحد المسموح به من المتبقيات على قرون الفول ٠,٠٥جزء في المليون كما حددته الكودكس وكانت فترة الأمان بعد المعاملة بهذا المبيد هى ٣ ، ٣ ، ٥ يوما بالنسبة لقرون الفول الخضراء وقشور القرون الخضراء على التوالى. سببت عملية تقشير القرون الخضراء أزالة عالية لمتبقيات المبيدين ، حيث كانت البذور الخضراء تحتوى على كمية من المبيد أقل من الحد المسموح به بالنسبة لمبيد البريموفوس ميثيل ولذلك فهى تصلح للاستهلاك فى أى وقت بعد المعاملة.

احتوت البذور الجافة على ٠,٠٩ جزء فى المليون من مبيد البروثيوفوس وعلى العكس من ذلك لم تكتشف أى متبقيات من مبيد البريموفوس ميثيل فى البذور الجافة وبذلك يمكن تسويقها للاستهلاك بأمان بعد الحصاد مباشرة . أيضاً أحتوت القشور الجافة وعرش النبات الجاف على كميات ٢٠٨ و ٤ و ١,٩٤٥ جزء فى المليون بالنسبة لمبيد البروثيوفوس و ٠,٣٣ و٠,٠٥٧ جزء فى المليون بالنسبة لمبيد البريموفوس ميثيل على التوالى.