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RESIDUES OF CERTIAN INSECTICIDES ON AND IN COWPEA PLANTS AND SOIL

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ABSTRACT: Cowpea plants, Cream 7 variety, were subjected to one spray with pirimiphos-methyl, profenofos and malathion using the recommended rates during 2004 growing season. The residues of the three insecticides were determined on and in green pods, green leaves of cowpea plants and soil after spraying. The effect of washing with tap water and blenching of green pods, in boiled water, on insecticide residues were also estimated. Summarized results show the following :

The amount of initial deposits of the three tested insecticides in and on green leaves were 39.17, 18.52 and 25.82 mg/kg for pirimiphos-methyl, profenofos and malathion, respectively. These amounts decreased gradually till reached 1.13, 0.95 and 1.11 mg/kg after 14 days of spraying representing 97.12 , 94.87 and 95.70 % loss of the initial deposits, respectively. The corresponding deposits in unwashed green pods were 5.52, 3.82 and 4.13 mg/kg for pirimiphos-methyl , profenofos and malathion, respectively. These amounts decreased gradually till reached 0.11, 0.07 and 0.09 mg/kg after 14 days of spraying representing 98.01, 98.17 and 97.82% loss of initial deposits, respectively. Washing the green pods with tap water decreased the amount of initial deposits of tested insecticides by 30.8, 19.11 and 24.94% for the three insecticides, respectively. Blenching process reduced the amount of initial deposits of these insecticides by 93.19, 85.44 and 90.65%, respectively. The amounts of initial deposits of the tested insecticides in soil were 1.44, 1.2 and 1.33 mg/kg for pirimiphos-methyl, profenofos and malathion, respectively. Residues decreased gradually till reached 0.09, 0.05 and 0.07 mg/kg after 14 days of spraying showing 93.75, 95.83 and 94.74% loss, respectively. All tested insecticides exhibited a higher level of disappearance on and in cowpea plants (unwashed and washed green pods and green leaves)

compared with that in soil. Profenofos exhibited the highest rate of disappearance while pirimiphos-methyl showed the lowest one. Blenching of insecticide-contaminated green pods of cowpea could be used for human consumption directly after spraying with pirimiphos-methyl and malathion, while in case of profenofos it could be used after 7 days of spraying. Dry seeds could be used for human consumption directly after harvest.

Key words: **Pirimiphos-methyl – profenofos – malathion – cowpea-residues- soil.**

INTRODUCTION

Cowpea, (*Vigna sinensis* L.) is a very important legume crop, as a human food, in all countries. Cowpea plants liable to be infested with different insect pests. The control of these pests is considered an integral part of any strategy. Insecticides are, however, still used in a large scale throughout the world, especially in the developing countries, as a major mean for pest management. Their use open, however, the possibility of global pollution. Vegetables, like other economic crops, may be exposed to insecticides in various ways, which undoubtedly results in various levels of insecticide residues (Aioub, 1997). It is of great importance to minimize such levels of insecticide residues in crops to the permissible levels. To achieve this, waiting periods between application and harvesting should be established to be sure that the residues at time of harvesting, are below such tolerance levels.

Sometimes, initial deposits of insecticides may be removed by washing although the presence of adjuvents counteract removing such deposits (El-Nabrawy and Shalaby 1992 and Aioub, 1997). Cooking process apparently reduce more amounts of insecticide residues present in insecticide-contaminated vegetable fruits than washing with tap water (Shalaby *et al.*, 1991).

During insecticidal application, the soil is contaminated by these xenobiotics. Such insecticides may be adsorbed onto soil particles or leached to ground water depending on the partition coefficient of these toxicants and their metabolites.

Several investigations assayed the residues of pesticides in edible parts of field and vegetable crops

to find out the safety period (Balinov and Shalaby, 1986; El-Shemy and Ramadan, 1987; Ramadan, 1988; Ramadan and Amir, 1988; Ramadan and El-Shemy, 1990; Shalaby, 1992; Aioub, 1997; Gatwary 2003 and Soliman, 2004).

The present study aimed determining the residues of pirimiphos-methyl, profenofos and malathion insecticides on and in green cowpea plants (pods and leaves) and soil as well as the role of washing and blenching processes in reducing insecticides residues in contaminated cowpea pods.

MATERIALS AND METHODS

A- Field Experiments:

Cowpea seeds, *V. sinensis*, Karim-7 variety were cultivated at Abu-Kaber, Sharkia governorate, Egypt on May 1, 2004. The experimental area was divided into plots of 1/200 of a feddan each arranged in randomized blocks design with three replicates for each treatment and untreated control. The normal agricultural practices were adopted. The three used insecticides and their rates in gram active ingredients (a.i.) per feddan, were:

1) Pirimiphos-methyl 50% EC., (Actelic); 750.
2) Profenofos (Selecron 72% EC.), 540.
3) Malathion 57% EC., 570.

A Knapsack hand sprayer, fitted with one nozzle, was used. Each recommended volume of the used insecticides was diluted with 400 L. per fed. Each insecticide was sprayed once on july 15, 2004. The untreated control plots were left unsprayed

B- Determination of Insecticides Residues :

1- Preparation of samples:

Representative samples of green pods and green leaves were taken 1 h, 1,3,7,10, and 14 days after spraying for residues determinations (at this time the mature green pods may be collected by farmers for marketing and consumption). Each sample of green pods was divided into three sub samples (100g each), the first one was washed with tap water and air dried, the second was left unwashed while the third one was washed with tap water, air dried and then boiled in water for 20 minutes. Samples of dry seeds obtained from insecticide-treated plants were taken for residue

analysis. At the same time, representative samples of soil (0.5 kg) were taken from the upper 15 cm surface layer of insecticide-treated cowpea field. Soil samples were air dried, cleaned from plant parts, thoroughly mixed, crushed, sieved through 2 mm sieve and subjected to residue analysis.

2- Extraction

Pirimiphos-methyl, profenofos and malathion residues were extracted from plant and soil samples according to the method of Macnell *et al.* (1975).

3- Clean- up

Purification by thin layer chromatography was adopted according to Soliman *et al.* (1982). TLC plates 20X 20 cm coated with Silica gel 60 F_{254} (Merck) were used for the clean up of extracted samples.

4- Residue determination

The residues of pirimphos-methyl, profenofos and malathion insecticides were determined colorimetrically using the methods of Getz and Watts (1964). In this method the absorbance of the formed colour was read at wave length 520 nm using spectronic 20 D spectrophotometer. The author was obliged to use this old method of determination due to the shortage of the well equipped laboratories.

Results of the three tested insecticides were corrected using their respective recovery rates in green pods, green leaves, dry seeds and soil which were 85.73, 89.27, 94.28 and 92.57% for pirimiphos-methyl; 84.13, 91.45, 93.78 and 95.43% for profenofos and 86.35 , 88.47, 91.18 and 90.63% for malathion, respectively.

In order to study the rate of degradation and half life period of each of the used pesticide, the following steps were conducted:

The relation between the logarithm of ppm recovered and time intervals were plotted. A straight line was fitted, then the slope of this line was calculated. The rate of degradation was obtained from the following equation :

Rate of degradation (K) = 2.303 x slope. Finally, the half life period ($t½$) was obtained from the following equation:

$T ½ = 0.693/k$ (Gomaa and Belal, 1975).

RESULTS AND DISCUSSION

Data summarized in Tables (1, 2 and 3) represent the amounts of pirimiphos-methyl, profenofos and malathion in green pods

Table (1): Residues (in ppm) of pirimiphos-methyl (750 g a.i./fed.) on and in green pods and green leaves of cowpea plants and soil.

Days after spraying	Green pods						Green leaves		Soil	
	Unwashed		Washed		Blenched		Residues	% of Dissipataion	Residues	% of Dissipataion
	Residues	% of Dissipation	Residues	% loss by washing	Residues	% loss by Blenching				
*Initial	5.52	-	3.82	30.80	0.26	93.19	39.17	-	1.44	-
1	4.14	25.00	3.00	27.54	0.29	90.33	14.08	64.05	1.32	8.33
3	3.00	45.65	2.30	23.33	0.45	80.43	6.20	84.17	1.04	27.78
7	0.92	83.33	0.75	18.48	0.15	80.00	2.57	93.44	0.29	79.86
10	0.25	95.47	0.21	16.00	0.023	89.05	2.08	94.69	0.18	87.50
14	0.11	98.01	0.10	9.09	0.013	87.00	1.13	97.12	0.09	93.75

- Figures are the average of three replicates.

* Samples were taken one hour after application.

(unwashed, washed and blenched) and green leaves of cowpea plants and soil.

Results show that the initial deposits of tested insecticides in unwashed green pods were 5.52, 3.82 and 4.13 ppm for pirimiphos-methyl, profenofos and malathion, respectively. These figures decreased gradually till reached 0.11, 0.07 and 0.09 ppm after 14 days of spray indicating 98.01, 98.17 and 97.82% loss of the initial deposits, respectively.

Washing the green cowpea pods with tap water decreased the amount of the initial deposits (zero time) of tested insecticides by 1.7, 0.73 and 1.03 ppm, which represent 30.80 , 19.11 and 24.94% loss of the initial deposits of pirimphos-methyl, profenofos and malathion, respectively.

The capacity of washing in removing the residues of the three sprayed insecticides decreased as time lapsed between the onset of spraying till 2 weeks later; the loss% ranged between 30.8 – 9.09, 19.11 – 0.0 and 24.94 – 0.0 for pirimiphos-methyl, profenofos and malathion, respectively. The effect of washing process was obvious with pirimiphos-methyl (30.8% loss) compared with profenofos (19.11%) and malathion (24.94%) that due to the differences in partition coefficient.

Data show that cooking process did reduce the amount of insecticide residues in green cowpea pods. Blenching of cowpea pods in boiled water removed magnitude amounts of insecticides residues.

Great interest to note that the highest amount of loss took place in the samples taken just after spraying, loss percentages in pirimphos-methyl, profenofos and malathion contaminated cowpea pods were 93.19, 85.44 and 9.65, respectively.

It is obvious that cowpea leaves contained higher residues than those obtained with pods; this may be due to differences in surface area contaminated with insecticides in the same weight. Amount of residues were 39.17, 18.52 and 25.82 ppm just after spraying for pirimphos-mehtyl, profenofos and malathion, respectively. The corresponding amounts in pods were 5.52, 3.82 and 4.13 ppm. Dissipation percentages were much higher, especially in the first two samples. Such difference may be due to differences in the amount of residues.

Table (2): Residues (in ppm) of profenofos (450 g a.i./fed.) on and in green pods and green leaves of cowpea plants and soil.

Days after spraying	Green pods						Green leaves		Soil	
	Unwashed		Washed		Blenched		Residues	% of Dissipation	Residues	% of Dissipataion
	Residues	% of Dissipation	Residues	% loss by washing	Residues	% loss by Blenching				
*Initial	3.82	-	3.09	19.11	0.45	85.44	18.52	-	1.20	-
1	2.97	22.25	2.52	15.15	0.43	82.94	10.34	44.17	0.96	20.00
3	1.86	51.31	1.65	11.29	0.30	81.82	6.77	63.44	0.73	39.17
7	0.62	83.77	0.57	8.06	0.14	75.44	3.12	83.15	0.25	79.17
10	0.18	95.29	0.17	5.56	0.04	76.47	1.81	90.23	0.09	92.50
14	0.07	98.17	0.07	0.00	0.02	71.43	0.95	94.87	0.05	95.83

- Figures are the average of three replicates.

* Samples were taken one hour after application.

It worth mentioned that in dry seed at harvest time, one month after spraying, contained undetectable amounts of insecticide.

In contrary with leaves, initial deposit of pesticides in soil were much lower than those with pods. Pirimiphos-methyl, profenofos and malathion residues were 1.44, 1.2 and 1.33 ppm, respectively. Theses amounts decreased gradually by time till reached 0.09, 0.05 and 0.07 ppm after 14 days of spraying. Dissipation percentage were much lower in insecticide-contaminated soil, compared with those of pods and green leaves, especially in the first two samples. It is obvious that loss in residues differed from insecticide to another which reflect the role of sorbance capacity of the tested insecticides.

Concerning the residual half lives (RL_{50}) of the three tested insecticides in cowpea plats and soil, result in Table (4) show that profenofos, however, had the highest rate of disappearance while pirimphos-methyl was the lowest one; it could be noticed that both insecticides exchanged their position in case of green leaves. All tested insecticides exhibited higher level of disappearance on and in cowpea plants (unwashed and washed green pods and green leaves) compared with that of soil. Such difference in rates of disappearance may be due to surface area of the treated plant and soil as well as intensity of exposure to solar radiation which play an important role in degradation (Shokr *et al.*, 2000 and Nasr, 2002).

Maximum residue levels (MRL) of pirimphos-methyl, profenofos and malathion in common bean (pods and/ or immature seeds) were 0.5 , 0.1 and 2 ppm, respectively, as published by (CAC/PR, 1997). Comparing these figures with those presented in Tables 1,2 and 3 show that cooking green pods, washed and unwashed pods, could be however, used for human consumption, directly after spray, 10 and 10 days of spray with pirimiphos-methyl; 7, 14 and 14 days of spray with profenofos and directly after spray, 3 and 7 days of spray with malathion, respectively.

Similar results were obtained by Ramadan (1988); Aioub (1997 and 1998); Shalaby (1992); Nasr (2002); Gatwary (2003) and Soliman (2004). Ramadan (1988) reported that unwashed and washed snap bean pods treated with pirimiphos-methyl (750gm a.i./fed.) could be marketed safely after 15 days post-treatment , while cooked fruits could be used safely after nine

Table (3): Residues (in ppm) of malathion (570 g a.i./fed.) on and in green pods and green leaves of cowpea plants and soil.

Days after spraying	Green pods						Green leaves		Soil	
	Unwashed		Washed		Blenched		Residues	% of Dissipataion	Residues	% of Dissipataion
	Residues	% of Dissipation	Residues	% loss by washing	Residues	% loss by Blenching				
*Initial	4.13	-	3.10	24.94	0.29	90.65	25.82	-	1.33	-
1	3.20	22.52	2.56	20.00	0.30	88.28	13.97	45.89	1.05	21.05
3	2.11	48.91	1.79	15.23	0.25	86.03	8.15	68.44	0.95	28.57
7	0.67	83.78	0.57	14.93	0.10	82.46	4.92	80.95	0.32	75.94
10	0.23	94.43	0.21	8.69	0.013	93.81	2.13	91.75	0.15	88.72
14	0.09	97.82	0.09	0.00	0.016	82.22	1.11	95.70	0.07	94.74

- Figures are the average of three replicates.
* Samples were taken one hour after application.

Table (4): Residual half lives (in days) of pirimiphos-methyl, profenofos and malathion insecticides on cowpea plants and soil.

Insecticides	Green pods		Green leaves	Soil
	Unwashed	Washed		
Pirimiphos-methyl	4.07	3.89	0.95	5.40
Profenofos	2.68	2.58	1.64	3.81
Malathion	3.39	3.07	1.07	5.02

days of application. Aioub (1997) reported that pirimiphos-methyl and methomyl-contaminated pea plant could be harvested however, just after spraying with the two insecticides since the residue levels of each insecticide fell below the maximum residue limits. Nasr (2002) studied the persistence of pirimiphos-methyl residues, at the rate of 375 ml per 100 L water) on and in pepper and chili fruits and soil. Residue analysis showed that initial deposits were 2.05 amd 6.59 ppm on and in pepper and chili fruits, respectively. The auther showed that washing process was very effective, it removed 70.73 and 79.21% of intial deposits on pepper and chili fruits, respectively. It was found that pirmiphos-mehyl had a low disappearance in the soil than on and in pepper and chili fruits. Soliman (2004) studied the residues of profenofos and carbosulfan in and on green pods of cowpea plants. He reported that the residue amounts were depends mostly on the rate of pesticide application. Rinsing treated fruits with tap water removed considerable amounts of profenofos and carbosulfan residues. It was found the loss of pesticide residues by washing was decreased with the decease in the residues on the fruits before washing.

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متبقيات بعض المبيدات الحشرية على وفى نباتات اللوبيا والتربة

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تم رش نباتات اللوبيا رشة واحدة بثلاث مبيدات حشرية (بيريميفوس – ميثيل، بروفينوفوس وملاثيون) بالمعدلات الموصى باستخدامها خلال موسم النمو ٢٠٠٤ وقد تم تقدير متبقيات هذه المبيدات عقب الرش مباشرة وعلى فترات من الرش على وفى قرون اللوبيا الخضراء والأوراق الخضراء وكذلك فى التربة. كما تم دراسة تأثير عمليات الغسيل بماء الصنبور والسلق فى ماء مغلى للقرون الخضراء على متبقيات المبيدات فيها.

أوضحت النتائج المتحصل عليها ما يلى:

كمية المترسب الأولى فى الأوراق الخضراء كانت ٣٩,١٧ ، ١٨,٥٢ و ٢٥,٨٢ جزء فى المليون لمبيدات بيريميفوس – ميثيل، بروفينوفوس وملاثيون على التوالى. انخفضت هذه الكميات مع الوقت تدريجياً حتى وصلت الى ١,١٣ ، ٠,٩٥و ١,١١ جزء فى المليون بعد ١٤ يوم من الرش مسجلة نسبة فقد مقدارها ٩٧,١٢ ، ٩٤,٨٧ و ٩٥,٧٠% على التوالى من المترسب الأولى. كمية لمترسب الأولى فى القرون الخضراء الغير مغسولة كانت ٥,٥٢، ٣,٨٢ و ٤,١٣ جزء فى المليون لمبيدات بيريميفوس – ميثيل، بروفينوفوس وملاثيون على التوالى. انخفضت هذه الكميات بمرور الوقت تدريجياً حتى وصلت الى ٠,١١، ٠,٠٧ و ٠,٠٩ جزء فى المليون بعد ١٤ يوم من الرش مسجلة نسبة فقد مقدارها ٩٨,٠١، ٩٨,١٧ و ٩٧,٨٢% على التوالى من المترسب الأولى. غسيل القرون بماء الصنبور أحدث انخفاضا فى كمية المترسب الأولى بمقدار ٣٠,٨، ١٩,١١ و ٢٤,٩٤% لمبيدات بيريميفوس- ميثيل، بروفينوفوس وملاثيون على التوالى. عملية السلق للقرون الخضراء أحدثت نقصاً فى كمية المترسب الأولى بمقدار ٩٣,١٩، ٨٥,٤٤ و ٩٠,٦٥% لمبيدات بيريمفيوس – ميثيل، بروفينوس وملاثيون على التوالى. كمية المترسب الأولى فى التربة كانت ١,٤٤ ، ١,٢ و ١,٣٣ جزء فى المليون لمبيدات بيريميفوس – ميثيل، بروفينوفوس وملاثيون على التوالى. انخفضت هذه الكميات بمرور الوقت تدريجياً حتى وصلت الى ٠,٠٩ ، ٠,٠٥ ، ٠,٠٧ جزء فى المليون بعد ١٤ يوم من المعاملة مسجلة نسبة فقد قدرها ٩٣,٧٥ ، ٩٥,٨٣ و ٩٤,٧٤% من المترسب الأولى على التوالى. لوحظ أن جميع المبيدات المختبرة تختفى بمعدل أسرع فى الأوراق الخضراء والقرون مقارنة بالتربة وأن بروفينوفوس كان أكثرهم سرعة فى الاختفاء بينما مبيد بريميفوس – ميثيل كان أقلهم. القرون الخضراء المسلوقة والملوثة بمبيدات بيريميفوس – ميثيل والملاثيون يمكن استخدامها للاستهلاك الآدمى بأمان بعد الرش مباشرة أما فى حالة بروفينوفوس فيتم ذلك بعد ٧ يوم من الرش. بذور اللوبيا الجافة يمكن استخدامها للاستهلاك الآدمى بعد الحصاد مباشرة.