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Pirimiphos-methyl Residues on/in Some Field-grown Vegetables and its Removal Using Various Washing Solutions and Kitchen Processing

M.A. RADWAN[1], M.H. SHIBOOB, M.M. ABU-ELAMAYEM AND A. ABDEL-AAL
Pesticide Chemistry Department, Residues Analysis Laboratory, Faculty of Agriculture (El-Shatby), University of Alexandria, Alexandria, Egypt
[1]Corresponding author's e-mail: mohamedradwan5@hotmail.com

ABSTRACT

Pirimiphos-methyl (Actellic 50% EC), was sprayed on field-grown pepper and eggplant at the recommended rate of 0.89 kg a.c ha^{-1}. Fruit samples were collected at 1h to 14 days after application and analysed to determine the content and dissipation rate of pirimiphos-methyl. The effect of different washing solutions and some kitchen processing on the removal of such residues from treated vegetables were also investigated. Pirimiphos-methyl residues were quantified by using gas chromatography. The results showed that the consumable safety time were 7 days on sweet pepper, 10 days on hot pepper and 14 days on eggplant fruits. The initial disappearance of pirimiphos-methyl appeared to follow first order kinetics with different rates of reaction i.e. 0.31, 0.40 and 0.37 day^{-1} for hot pepper, sweet pepper and eggplant, respectively. The corresponding half-lives ($^{t}{}_{1/2}$) were 2.20, 1.72 and 1.88 days. Results further indicated that acetic acid, potassium permenganate, sodium chloride and sodium hyroxide solution gave greater removal of pirimiphos-methyl residues from sweet pepper and eggplant fruits, while 70.16- 76.61% removal was shown in hot pepper fruit after washing with soap and acetic acid solution, respectively. In general, all tested washing solutions gave higher removal of pirimiphos-methyl residues from eggplant fruit than the two other pepper fruits. Blanching and frying of pepper and eggplant fruits resulted in almost completely removed (~ 100%) of the deposited pirimiphos-methyl. In addition, pickling process removed 86.29 and 92.34% from hot pepper fruit after one week and after two weeks, respectively.

Key Words: Pirimiphos-methyl; Residues; Eggplant; Pepper; Preparatory treatment

INTRODUCTION

Although pesticides provide numerous benefits in the production of commercial and horticulture crops, residues in commodities resulting from the heavy use of pesticides can pose potential risks to consumers. To avoid them, there is a need to monitor the pesticide residues in food commodities to assure the consumers that the maximum residue permissible limits are not exceeded. Pirimiphos-methyl is one of the most commonly used organophosphorus insecticides to protect green pepper and eggplant from the infestation by several common insect pests. There are numerous studies in the literature that have examined pirimiphos-methyl behaviour in fresh and processed edible crops such as potatoes (Abbassy *et al.,* 1998), tomatoes (Antonious & Abdel-All, 1988; Ramadan, 1991 and Radwan *et al.,* 1995) as well as to find more efficient washing reagents for removing its residues from vegetables to reduce health hazards (Awad & El-Shimi, 1993; Zohair, 2001). However, there is a scarcity of published data in for the dissipation of this insecticide on field-grown green pepper and eggplant fruits and in the processed products. Therefore, the present work was designed to study the persistence of pirimiphos-methyl in green pepper (hot and sweet) and eggplant fruits. Emphasis on the safety periods for this insecticide in the tested vegetables was considered. Also, this study aimed to throw light on the influence of different washing solutions and some kitchen processing on the removal of such residues from field-treated vegetables.

MATERIALS AND METHODS

Insecticide and chemical reagents. Pirimiphos-methyl; (O-(2-diethyl-amino-6-methyl pyrimidin-4-yl) O,O-dimethyl phosphorothioate), with acute oral LD_{50} of 1180 mg/kg for rats, 99.8% technical grade sample provided by ICI PLC, Plant Protection Division, UK, was used for GLC standardization in the present study. Formulated product (Actellic 500 g $Litre^{-1}$ EC) was employed in the field experiments. All chemicals (acetic acid, sodium chloride, sodium hydroxide and potassium permenganate) were obtained from E. Merck (Germany).

Field experiment and sampling. The experiments were carried out in a randomized block design at Abees area, Alexandria Governorate, Egypt. Green pepper (*Capsicum annuum* L.) sweet var. California wonder, hot pepper var. Long Red cayonne and eggplant (*Solanum melongena* L.) var. Balady were cultivated in plots (10 m × 6.5 m each).

Each plot consisting of 10 rows separated laterally by 3 guard rows. Treatments were replicated three times. Ripe fruits were sprayed once with pirimiphos-methyl at the recommended rate (1875 cm^3 ha^{-1}, 750 cm^3 $feddan^{-1}$), 2 days before the first harvesting. Spraying was carried out using a knapsack-sprayer (Cp-3) provided with one nozzle delivering 200 liters water/feddan, which has proved to be sufficient to give good coverage on the treated plants. An unsprayed control plot was included for each treatment. All agricultural management practices were adopted as practiced in commercial production of pepper or eggplant. Fruit samples were randomly collected (500 g per replicate). at intervals of 0 (1hr), 1, 3, 5, 7, 10 and 14 days after application, put in plastic bags and frozen at -18°C until insecticide residue analyses were carried out.

Extraction and clean-up. Each hot pepper, sweet pepper and eggplant sample (50 g) was extracted in acetone (150 mL) for three minutes followed by partitioning using dichloromethane (Bowman, 1980). The resulting extracts were evaporated to near dryness using a rotary evaporator at 35°C. The concentrate was taken in 1mL n-hexane for clean-up. The extracts were cleaned-up in a silica gel column amended with 1 g activated charcoal using 20% acetone in n-hexane as an eluting solvent (Bowman & Leuck, 1971), after which they were again concentrated and stored in the freezer until residue analysis.

To examine the efficacy of extraction and clean up, three samples from each fruit type were spiked with known concentration (2 mg kg^{-1}) of the pure insecticide standard solution. Extraction and clean-up were performed as described earlier and recovery ranges were 85.53- 88.40 %. Results were corrected according to the average of recovery.

Residue determination. Determination of pirimiphos-methyl residues was performed on a Shimadzu 4-CM (PFE) GC. FPD with an analytical glass column (2 m x 3 mm i.d) packed with 4% SE-30+6% OV-210 on 80/100 Chromosorb W. The operating temperatures (°C) were maintained as follows: Column 220 isothermal, injector 270, detector 270 and gas flow rates (mL/min) were: nitrogen 40, hydrogen 80 and air 100; the limits of detection of standard pirimiphos-methyl under these conditions was 0.30 ng. Identification of insecticide residue was accomplished by retention time (t_R) and compared with known standard under the same conditions. The quantities were calculated on peak height basis. Using these conditions, the retention time of standard pirimiphos-methyl solution was 8.6 min.

Removal of pirimiphos-methyl residues from treated vegetables. Removal tests were carried out on the 5th day treated pepper and eggplant fruits either by different washing solutions or by some home preparative procedures to evaluate their effectiveness on removing such residues. The fruit samples were divided into two parts. First part was soaked in a jar filled with any of the following solutions (tap water, soap 1%, potassium permanganate 0.01%, sodium chloride 1%, sodium hydroxide 0.1% and acetic acid 2%) for 1 min. The washed samples were allowed to dry on a clean paper before packing. Second part of treated fruits were subjected to three different household processing: (1) Blanching: the treated fruit were boiled in water for 5 minutes and then allowed to dry on a clean paper, (2) Frying: the treated fruit were fried in oil for 5 minutes and dried, or (3) Pickling: the treated fruit were pickled in 10.5% sodium chloride solution for one and two weeks. The samples were prepared for analysis as described earlier.

RESULTS AND DISCUSSION

Results in Table I showed that the initial deposits of pirimiphos-methyl on/in hot and sweet pepper fruits were 8.99 and 10.49 ppm, respectively. A rapid degradation of insecticide residues was noticed three days after application, being 55.62 and 61.20% reduction respectively in hot and sweet pepper fruits. The progression of time after application resulted in more dissipation of residues. The first week was critical, showing the highest rate of dissipation from hot and sweet pepper fruits, being 87.99 and 92.66%, respectively. By the end of experiment (two weeks), the two tested fruits contained negligible residues (~ 0.02 ppm).

Table I. Residues of pirimiphos-methyl detected in hot pepper, sweet pepper and eggplant fruits at periodic intervals

Time (days)	Hot pepper		Sweet pepper		Eggplant	
	Mean[a]	Reduction (%)	Mean	Reduction (%)	Mean	Reduction (%)
0 (1h)[b]	8.99 ± 0.11		10.49 ± 0.95		4.26 ± 0.10	
1	7.99 ± 0.40	11.12	5.61 ± 0.98	46.52	2.89 ± 0.13	32.16
3	3.99 ± 0.27	55.62	4.07 ± 0.58	61.20	1.16 ± 0.01	62.21
5	2.48 ± 0.56	72.41	2.09 ± 0.38	80.08	0.85 ± 0.08	80.05
7	1.08 ± 0.14	87.99	0.77 ± 0.28	92.66	0.40 ± 0.01	90.61
10	0.05 ± 0.03	99.43	0.36 ± 0.04	96.57	0.07 ± 0.01	98.38
14	0.025 ± 0.06	99.72	0.02 ± 0.01	99.79	0.01 ± 0.00	99.77

[a]Mean = mg / kg ± S.D. Values given are mean of three analysis.
[b]Initial deposits of the insecticide

Table Π. Calculated half life values of pirimiphos-methyl on the tested vegetables using GC method

Crop	Apparent rate constant (K)[a]	Half-life time ($t_{½}$)[b] (day)
Hot pepper	0.31	2.20
Sweet pepper	0.40	1.72
Eggplant	0.37	1.88

[a]K = ½ ln a/m where k = apparent rate constant,
a = intial concentration
m = concentration after t, and t = time in days
[b]$t_{½}$ = ln (2)/k = 0.693/k

The extractable residues of pirimiphos-methyl on/in eggplant fruit ranged from 4.26 ppm (one hour after application) to 0.40 ppm in 7 days samples when applied at the field rate. The percent dissipation at 1 and 7 days were found to be 32.16 and 90.61%, respectively. After two weeks, minute amount of residues (0.01 ppm) were measured on eggplant fruit.

The initial disappearance of pirimiphos-methyl appeared to follow first order kinetics with different rates of reaction 0.31, 0.40 and 0.37 day^{-1} for hot pepper, sweet pepper and eggplant, respectively. The corresponding half-lives ($^{t}{}_{1/2}$) were 2.20, 1.72 and 1.88 days (Table Π).

It could be concluded that the preharvest intervals (PHI= safety period) were 7 and 10 days for sweet pepper and hot pepper, respectively. This indicated that sweet and hot pepper fruits could be safely marketed 7 and 10 days after treatment with pirimiphos-methyl, respectively, and was long enough to reduce the residues below the permissible limits (1 ppm) on peppers (CAC/PR, 1993). Also, the negligible amount (0.01 ppm) was detected on eggplant fruit after 14 days of spraying. The Codex maximum residue limits (MRLs) for pirimiphos-methyl residues on/in several commodities ranged from 0.05 to 20 mg kg^{-1} (CAC/PR, 1993). The list, however, lacks MRLs for this insecticide on eggplant. Therefore, eggplant fruit could be marketed with apparent safety for human consumption when free from any residues of pirimiphos-methyl.

Present results of pirimiphos-methyl residues on/in pepper and eggplant fruits are comparable to those reported in earlier studies; tomato and squash fruits could be safely consumed 3 days after Actellic application (Antonious & Abdel-All, 1988). The initial deposits of pirimiphos-methyl on/in unwashed tomato and okra fruits were 13.71 and 14.24 ppm, respectively. These figures were decreased to 0.049 and 0.56 ppm after 15 days of spraying (Ramadan, 1991). Tomatoes treated with actellic could be marketed one day after application, while green beans could be consumed safely 4 days after spraying (Abd-Alla *et al*., 1993). Pirimiphos-methyl was undetectable in the whole pods of cowpea 10 days after spraying (Soliman, 1994). The level of pirimiphos-methyl residues on broad bean seeds was found to be within the MRLs 5 days after application, while exceeding the MRLs on tomatoes for that time (Radwan *et al.,* 1995). The waiting period of 21 days after Actellic spraying on grapes is enough to reduce residues below the MRLs (Radwan *et al.,* 2001). Pepper and chili fruits could be safely marketed one and five days after treatment with pirimiphos-methyl, respectively (Nasr, 2002).

When the waiting peroid between applications and harvesting are not respected by the farmers, the risk of having higher pesticide levels remains there. In this case, the higher levels of pesticides can involve considerable economic losses if the maximum residue limits established by FAO/WHO are surpassed. So the effect of washing by different solutions or using some kitchen processes in removing the pesticide residues from plants may be a solution to overcome this problem.

Pirimiphos-methyl residues and removal percent as

Table Ш. Effect of different washing solutions and household processing on the removal of pirimiphos-methyl residues from the tested vegetables

Treatment	Hot pepper		Sweet pepper		Eggplant	
	Mean[a]	Reduction (%)	Mean	Reduction (%)	Mean	Reduction (%)
Control	2.48 ± 0.08		2.09 ± 0.01		0.85 ± 0.01	
Washing solutions						
Tap water	1.17 ± 0.04	52.82	0.99 ± 0.01	52.63	0.35 ± 0.06	58.82
Soap 1%	0.74 ± 0.02	70.16	1.20 ± 0.03	42.58	0.14 ± 0.01	83.52
Acetic acid 2%	0.58 ± 0.04	76.61	0.09 ± 0.02	95.74	0.05 ± 0.01	94.58
Potassium permnganate 0.01%	0.83 ± 0.03	66.53	0.14± 0.05	93.30	0.03 ± 0.02	96.82
Sodium hydroxide 0.1%	1.95 ± 0.05	21.37	0.36 ± 0.02	82.77	0.09 ± 0.02	89.76
Sodium chloride 1%	1.56 ± 0.06	37.10	0.30 ± 0.01	85.64	0.07 ± 0.02	92.00
Household processing						
Blanching	----[b]	----	0.018 ± 0.01	99.14	____[c]	~ 100
Frying	0.097 ± 0.00	96.08	____	~ 100	____	~ 100
Pickling						
One week	0.34 ± 0.02	86.29	----	----	----	----
Two week	0.19 ± 0.01	92.34	----	----	----	----

[a]Mean = mg / kg ± S.D. Values given are mean of three analysis.
[b]Non tested
[c]Non detctable

affected by different washing solutions and processing treatments on pepper and eggplant fruits (Table Ш) showed that washing remarkably reduced the insecticide residues in the tested vegetable fruits. Washing the treated fruits with tap water led to 52-58% removal of the initial residues from the tested fruits. Washing with soap greatly reduced the initial residues of pirimiphos-methyl from hot pepper and eggplant fruits (70.16 and 83.52% loss, respectively), but its efficiency was the lowest in case of sweet pepper fruit (42.58% loss). These findings agree with those of Antonious and Abdel-All (1988), Ramadan (1991) and Abbassy *et al.* (1992), who found that washing the pirimiphos-methyl treated vegetable fruits with tap water or soap solution significantly reduced its residues and the reduction was more pronounced using soap solution.

The most efficient removal from hot pepper fruit was observed due to acetic acid solution (76.61% reduction), while washing with potassium permenganate solution removed 66.53% of the initial residues found on unwashed fruit. Frying caused 96.08% removal as well as pickling the fruit reduced its residues, and the reduction was more pronounced after two weeks (92.34%) than after one week (86.29%). Also the most efficient removal from sweet pepper fruit occurred using acetic acid solution giving a reduction of 95.74%. This was followed by potassium permenganate, sodium chloride and sodium hydroxide. The blanching removed 99.14% of the deposited pirimiphos-methyl, while frying almost completely removed it.

Potassium permenganate was the best solution for removing the insecticide residues from eggplant fruit (96.82%), whereas washing of the treated fruit with acetic acid, sodium chloride and sodium hydroxide solution removed 94.58, 92.00 and 89.76%, respectively. Blanching and frying of eggplant fruit almost eliminated pirimiphos-methyl residues completely. These data indicated that the different washing solutions or kitchen procedures that are used in the present study had varied effects on reducing or removing of pirimiphos-methyl residues from the tested vegetable fruits depended upon the type of processing methods and the type of crop fruits. The present data coincide with those reported by several investigators (Awad & El-Shimi, 1993; Youssef *et al.,* 1995; Schattenberg *et al.,* 1996; Zohair, 2001; Nasr, 2002). They reported that washing with water and/or other solutions as well as the cooking peocesses resulted in a great reduction of pesticide residues from treated vegetable fruits and lead to the residue level lower than the Maximum Residue Limits (MRLs).

In conclusion, the data from the present study may be useful for establishing MRL and assessing the amount of pirimiphos-methyl residues in these vegetables under field conditions. The data suggest the need to implement these safety intervals before harvesting and marketing such crop fruit. Moreover, washing these fruits with suitable solution before using has to be strictly observed by the consumer.

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