Available online at www.sciencedirect.com

SCIENCE DIRECT®

Food and Chemical Toxicology 43 (2005) 553–557

www.elsevier.com/locate/foodchemtox

Residual behaviour of profenofos on some field-grown vegetables and its removal using various washing solutions and household processing

M.A. Radwan *, M.M. Abu-Elamayem, M.H. Shiboob, A. Abdel-Aal

Pesticide Chemistry Department, Residues Analysis Laboratory, Faculty of Agriculture, University of Alexandria, Aflatoon st. El-Shatby, Alexandria, Egypt

Received 21 July 2004; accepted 18 December 2004

Abstract

Profenofos (Selecron 72% EC), was sprayed on field-grown pepper and eggplant at the recommended rate of 1.28 kg a,i/ha. Fruit samples were collected at 1 h to 14 days after application and analysed to determine the content and dissipation rate of profenofos. The effect of different washing solutions and some household processing on the removal of such residues from treated vegetables were also investigated. Profenofos residues were quantified by using gas chromatography. The results showed that the consumable safety time were found to be 10 days on sweet pepper and 14 days on hot pepper and eggplant fruits. The initial disappearance of profenofos appeared to follow first order kinetics with different rates of reaction of 0.38, 0.40 and 0.35 day^{-1} for hot pepper, sweet pepper and eggplant, respectively. The corresponding half-lives ($t_{1/2}$) were 1.84, 1.74 and 1.96 days. Also, the results indicated that tap water, potassium permenganate and acetic acid solution gave high percent removal of profenofos residues from hot and sweet pepper fruits, while no detectable residues was found in eggplant fruit after washing with soap and acetic acid solutions. In general, all tested washing solutions gave higher percent removal of profenofos residues from eggplant fruit than the two other pepper fruits. Blanching and frying of pepper and eggplant fruits resulted in great reduction to almost completely removed (~100%) of the deposited profenofos. In addition, pickling process removed 92.58 and 95.61% from hot pepper fruit after one week and after two weeks, respectively.

Keywords: Residues; Profenofos; Eggplant; Green pepper; Washing solutions; Household processing

1. Introduction

Green pepper and eggplant are considered as major vegetable crops which grow on a large scale in Egypt, but these crops are attacked by many insects which require frequent use of insecticides. The use of insecticides for combating insect pests in agricultural production has no doubt enhanced food production and quality of the product, but their indiscriminate use has led to undesirable side effects on environment quality and human health. Consequently, analysis of residual quantities of insecticides in raw agricultural crops and in processed food is in forefront among preventive measures of public health safety. Profenofos is an organophosphorus insecticide widely used to control various insect pests on vegetable crops in Egypt. There are numerous studies in the literature that have examined profenofos behaviour in fresh and processed edible crops such as potatoes (Habiba et al., 1992; El-Tantawy et al., 1992 and Soliman, 2001), tomatoes (Ramadan, 1991; El-Nabarawy et al., 1992 and Ismail et al., 1993) as well as to find more efficient washing reagents for removing its residues

* Corresponding author. Tel.: +20 3590 5029; fax: +20 3590 2766.
E-mail address: mohamedradwan5@hotmail.com (M.A. Radwan).

0278-6915/$ - see front matter
doi:10.1016/j.fct.2004.12.009

from potatoes to reduce health hazards (Zohair, 2001). However, there is a lack of published data in Egypt for the fate 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 profenofos 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 household processing on the removal of such residues from field-treated vegetables.

2. Materials and methods

2.1. Insecticide and chemical reagents

Profenofos; (*O*-(4-bromo-2-chlorophenyl)-*O*-ethyl-*S*-propyl phosphorothioate), with acute oral LD_{50} of 400 mg/kg for rats, 99% technical grade sample was provided by Ciba Geigy Ltd. (Swizerland), which was used for GLC standardization in the present study. Formulated product (Selecron 72% EC) was employed in the field experiment. All chemicals (acetic acid, sodium chloride, sodium hydroxide and potassium permenganate) used were obtained from E. Merck Company (Germany). In addition, local soap (Rabso) was obtained from the market.

2.2. Field experiment and sampling

Field experiments were conducted during the summer in the Abees area, Alexandria Governorate, Egypt. Plots consisting of 10 rows separated by a three row belt of green pepper (*Capsicum annuum* L.) sweet var. California Wonder, hot pepper var. Long Red Cayonne and eggplant (*Solanum melongena* L.) var. Balady were allocated to randomized blocks with three replicates. The plants were sprayed with profenofos once at the recommended rate of 750 ml/feddan (feddan = 0.42 hectare), 2 days before the first harvesting. Spraying was carried out using a knapsack-sprayer (Cp-3) provided with one nozzle delivering 200 l water/feddan, which has proved to be sufficient to give good coverage on the treated plants. Untreated control plots were included for each treatment. The maximum and minimum temperatures during the crops season were 30 °C and 22 °C, respectively, with average relative humidity of 63%. Average sunshine hours recorded were 10.23. There was no rainfall during the period of study. All agricultural management practices were made as usually practiced in commercial production of pepper or eggplant. Fruit samples were randomly collected (500 g were sampled per replicate). Fruit samples were taken at intervals of 0 (1 h), 1, 3, 5, 7, 10 and 14 days after profenofos application. The collected representative samples were placed in plastic bags and frozen at −18 °C until insecticide residue analysis.

2.3. Extraction and clean-up

Samples of 50 g from hot pepper, sweet pepper and eggplant were extracted with acetone (150 ml) for 3 min 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 1 ml *n*-hexane for clean-up. The extracts were cleaned-up on a column contained 10 g activated silica gel 60 (70–230 mesh) and 1 g activated charcoal. The insecticide was eluted from the column with 100 ml of a solvent mixture, 20% acetone in *n*-hexane (Bowman and Leuck, 1971). The eluate was concentrated and then analysed by gas–liquid chromatography (GLC).

To examine the efficacy of extraction and clean up, three samples from each fruit type were spiked with known concentration (2 mg/kg) of the pure insecticide standard solution. Extraction and clean-up were performed as described earlier and recoveries were 73.10–94.35%. Results were corrected according to the average of recovery.

2.4. Residue determination

Determination of profenofos residues was performed using a Shimadzu 4-CM (PFE) GC. FPD with an analytical glass column (2 m × 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 profenofos under these conditions was 2.8 ng. Identification of insecticide residue was accomplished by retention time (t_R) and compared with known standard at the same conditions. The quantities were calculated on peak height basis. Using these conditions, the retention time of profenofos was 11 min.

2.5. Removal of profenofos residues from treated vegetables

Removal tests were carried out on the 10th and 7th day treated pepper and eggplant fruits, respectively, to imitate the normal time of consuming vegetable fruits under Egyptian conditions, where it is impossible that the producer send the vegetable crops to the market before this time. The procedure was accomplished either by different washing solutions or by home processing to evaluate their effectiveness on removing such residues. The fruit samples were divided into two parts. The first part was soaked into 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. The second part of treated fruits were subjected to three different household processing: (1) Blanching: the treated fruit were boiled in water for 5 min and then allowed to dry on a clean paper, (2) Frying: the treated fruit were fried in oil for 5 min 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 before.

2.6. Statistical analysis

Data are presented as mean ± SD were subjected to analysis of variance (ANOVA). Means were compared for significance by LSD method at $P < 0.05$ (Steel and Torrie, 1980).

3. Results and dicussion

Results in Table 1 showed that the initial deposits of profenofos in/on hot and sweet pepper fruits were 11.62 and 10.67 ppm, respectively. A rapid degradation of insecticide residues was noticed, after one day of application with values of 46.04% and 46.29% reduction, respectively. 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 87.35% and 91.48%, respectively. At the end of experiment (two weeks), hot pepper fruit contained negligible residues (0.021 ppm), whereas no residues were detected in sweet pepper fruit.

The extractable residues of profenofos in/on eggplant fruit ranged from 4.50 ppm (one hour after application) to 0.27 ppm in 7 days samples when applied at the field rate. The percent dissipation at 1 and 7 days were found to be 26.67% and 94.00%, respectively. After two weeks, no detectable residues of profenofos were measured on eggplant fruit.

The initial disappearance of profenofos appeared to follow first order kinetics with different rates of reaction of 0.38, 0.40 and 0.35 day^{-1} for hot pepper, sweet pepper and eggplant, respectively. The corresponding half-lives ($t_{1/2}$) were 1.84, 1.74 and 1.96 days (Table 2).

It could be concluded that, 0.31 ppm of profenofos residues was detected on sweet pepper fruit, 10 days after application, while minute amounts of insecticide residues (0.025 ppm) was detected on hot pepper, 14 days after spraying. This indicated that only 10 and 14 days were long enough to reduce the residues below the permissible limits (0.5 ppm) on peppers (Anonymous, 1999). The Codex maximum residue limits (MRLs) for profenofos residues in/on several commodities ranged from 0.05 to 2 mg/kg (Anonymous, 1999). The list, however, lacks MRLs for this insecticide on eggplant. Therefore, eggplant fruit could be marketed with apparent safety for human consumption.

Profenofos residues in/on vegetable fruits are reported in earlier studies; the initial deposits of profenofos in/on unwashed tomato and okra fruits were 10.18 and 11.56 ppm, respectively. These figures were decreased to 0.04 and 0.025 ppm after 15 days of spraying (Ramadan, 1991). Tomatoes treated with profenofos could be marketed, 8 days after application, while green

Table 2
Calculated half life values of profenofos on the tested vegetables

Crop	Apparent rate constant (K)[a]	Half-life time ($t_{1/2}$)[b] (day)
Hot pepper	0.38	1.84
Sweet pepper	0.40	1.74
Eggplant	0.35	1.96

[a] K = 1/2 ln a/m where k = apparent rate constant, a = intial concentration, m = concentration after t, and t = time in days.
[b] $t_{1/2} = \ln(2)/k = 0.693/\mathrm{k}$.

Table 1
Residues of profenfos detected in hot pepper, sweet pepper and eggplant fruits at periodic intervals

Time (days)	Hot pepper		Sweet pepper		Eggplant	
	Mean*	Reduction (%)	Mean	Reduction (%)	Mean	Reduction (%)
0 (1 h)**	11.62 ± 0.75^{a}		10.67 ± 0.46^{a}		4.50 ± 0.21^{a}	
1	6.27 ± 0.63^{b}	46.04	5.73 ± 0.66^{b}	46.29	3.30 ± 0.32^{a}	26.67
3	4.49 ± 0.61^{bc}	61.36	3.42 ± 0.27^{bc}	67.95	1.49 ± 0.04^{b}	66.89
5	2.49 ± 0.17^{cd}	78.57	2.59 ± 0.25^{cd}	75.73	0.79 ± 0.04^{bc}	82.44
7	1.47 ± 0.17^{cd}	87.35	0.91 ± 0.09^{cd}	91.48	0.27 ± 0.02^{c}	94.00
10	0.66 ± 0.16^{d}	94.32	0.31 ± 0.10^{d}	97.09	0.15 ± 0.01^{c}	96.67
14	0.025 ± 0.02^{d}	99.78	ND	∼100	ND	∼100

Means ± SD within each crop having the same letter are not significantly different at $P < 0.05$.
ND = Non detectable
* Mean = mg/kg ± S.D. Values given are mean of three analysis.
** Initial deposits of the insecticide.

beans could be consumed safely, 11 days after spraying (Abd-Alla et al., 1993). Tomatoes had considerable amounts of profenofos (26.6–8.7 ppm) depending on the time from pesticide application (Ismail et al., 1993). Minute amounts (0.02 ppm) of profenofos were detected in pods of cowpea, 15 days after spraying (Soliman, 1994).

When the preharvest intervals between treatments and harvest are not respected by the farmers, the risk of having higher pesticide levels is not negligible. 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 household processing in removing the pesticide residues from plants may be a solution to overcome this problem.

Profenofos residues and removal percent as affected with different washing solutions and processing treatments on green pepper and eggplant fruits are shown in Table 3. The residue of profenofos on raw unwashed hot pepper, sweet pepper and eggplant fruits after application were 0.66, 0.31 and 0.27 ppm, respectively. The washing of treated fruits with tap water reduced these residue levels to 0.125, 0.046 and 0.002 ppm, respectively, with corresponding percent removal of 81.06, 85.16 and 99.26, respectively. Soap solution washing eliminated the initial residues of profenofos from eggplant fruit, but it was the lowest removing method in the case of hot and sweet pepper fruits with concentration levels of 0.313 and 0.116 ppm (52.58 and 62.58% loss), respectively. The results obtained by Ramadan (1991); Ismail et al. (1993) and Tejada et al. (1995), indicated that washing profenofos-treated vegetable fruits with tap water removed magnitude amounts of its residues.

The most efficient removal from hot pepper fruit was observed using potassium permenganate solution (95.75% reduction), while washing with sodium chloride solution reduced the initial residues found on unwashed fruit to 0.113 ppm (79.89% reduction). The other types of washing treatments removed about 53–65% of the deposited profenofos. Frying reduced profenofos residues to 0.01 ppm (98.48% removal) as well as pickling the fruit reduced its residues and the reduction was more pronounced after two weeks with the level of 0.049 ppm (95.61%) than after one week with the concentration of 0.029 ppm (92.58%). Also, the most efficient removal from sweet pepper fruit was occurred using acetic acid solution, it gave reduction of the amount of residues to 0.045 ppm (85.48% loss). This was followed by potassium permenganate, sodium hydroxide and sodium chloride. The blanching process removed 98.06% of the deposited profenofos, whereas frying almost completely removed its residues.

Moreover, no detectable residues of profenofos (~100% removal) was found in eggplant fruit after washing with soap solution and acetic acid solution. Eggplant fruit contained small amount of profenofos residues of 0.007 ppm (97.41% reduction) after washing with sodium chloride solution, while 0.025 ppm (90.74% reduction) and 0.021 ppm (29.22% reduction) were found after washing with potassium permenganate and sodium hydroxide solution, respectively. Blanching and frying of eggplant fruit almost eliminated profenofos residues. These data indicated that the tested different washing solutions or home processing procedures had varied effects on reducing or removing of profenofos residues from the tested vegetable fruits depending upon the type of processing methods and the type of crops fruits. Removal studies are reported in the litera-

Table 3
Effect of different washing solutions and household processing on the removal of profenofos residues from the tested vegetables

Treatment	Hot pepper		Sweet pepper		Eggplant	
	Mean*	Reduction (%)	Mean	Reduction (%)	Mean	Reduction (%)
Control	0.66 ± 0.160[a]		0.31 ± 0.100[a]		0.27 ± 0.020[a]	
Washing solutions						
Tap water	0.125 ± 0.013[d]	81.06	0.046 ± 0.008[d]	85.16	0.002 ± 0.0[c]	99.26
Soap 1%	0.313 ± 0.032[b]	52.58	0.116 ± 0.004[b]	62.58	ND	~100
Acetic acid 2%	0.260 ± 0.015[c]	60.61	0.045 ± 0.008[d]	85.48	ND	~100
Potassium permnganate 0.01%	0.028 ± 0.002[e]	95.75	0.052 ± 0.004[d]	83.22	0.025 ± 0.005[b]	90.74
Sodium hydroxide 0.1%	0.230 ± 0.020[c]	65.15	0.064 ± 0.012[cd]	79.35	0.021 ± 0.002[b]	92.22
Sodium chloride 1%	0.113 ± 0.011[d]	79.85	0.078 ± 0.007[c]	74.84	0.007 ± 0.008[c]	97.41
Household processing						
Blanching	NT	–	0.006 ± 0.001[e]	98.06	ND	~100
Frying	0.01 ± 0.0[f]	98.48	ND	~100	ND	~100
Pickling						
One week	0.049 ± 0.005[e]	92.58	NT	–	NT	–
Two week	0.029 ± 0.001[e]	95.61	NT	–	NT	–

Means ± SD within each crop having the same letter are not significantly different at $P < 0.05$. ND = Non detectable.
NT = Non tested.
* Mean = mg/kg ± S.D. Values given are mean of three analysis.

ture by several investigators (Awad and El-Shimi, 1993; Youssef et al., 1995; Schattenberg et al., 1996; Soliman, 2001 and Zohair, 2001). They found that washing with water and/or other solutions as well as the cooking processes 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).

More recently, Michaels et al. (2003) studied the effectiveness of cleaning methodologies used for removal of organophosphorus and organochlorine residues from produce. Tests were performed on apple, cucumber and lemons using water wash, produce brush, produce cleaner, produce cleaner with paper towel wipe and water wash and paper towel wipe. They stated that water rinse and paper towel dry were found superior to all other methods tested.

In conclusion, the present study provides residue data which may be useful for establishing MRL and assessing the amount of profenofos residues in these vegetables under Egyptian field conditions and suggests the need of implementation of these safety intervals before harvesting and marketing such crop fruit. Moreover, washing these vegetables with suitable solution before using has to be strictly considered by the consumer.

References

Abd-Alla, E.F., Sammour, E.A., Abd-Allah, S.A., El-Sayed, E., 1993. Persistence of some organophosphate insecticide residues on tomato and bean plants. Bull. Fac. Agric. Cairo Univ. 44 (2), 462–476.

Anonymous, 1999. List of Codex Maximum Residue Limits. August, 31. WHO/FAO.

Awad, O.M., El-Shimi, N.M., 1993. Influence of different means of washing and processing on removing of Actellic residue from spinach and eggplant and its in-vivo action on mice hepatic biochemical targets. J. Egypt Public Health Assoc. 68 (5–6), 671–686.

Bowman, M.C., 1980. Analysis of organophosphorus pesticides. In: Moye, H.A. (Ed.), Analysis of Pesticide Residues. John Wiley, Sons Inc., pp. 263–332, Chapter 7.

Bowman, M.C., Leuck, D.B., 1971. Determination and persistence of phoxim and its oxygen analog in forage corn and grass. J. Agric. Food Chem. 19 (6), 1215–1218.

El-Nabarawy, I.M., Abou-Donia, M.A., Amra, H.A., 1992. Determination of profenofos and malathion residues in fresh tomatoes and paste. Egypt J. Appl. Sci. 7, 106–111.

El-Tantawy, M.A., El-Nabarawy, I.M., Sallam, A.A., 1992. Determination of profenofos residues in fresh and blanched potatoes. Delta J. Sci. 16, 114–122.

Habiba, R.A., Ali, H.M., Ismail, S.M.M., 1992. Biochemical effects of profenofos residues in potatoes. J. Agric. Food Chem. 40, 1852–1855.

Ismail, S.M., Ali, H.M., Habiba, R.A., 1993. GC–ECD and GC–MS analysis of profenofos residues and biochemical effects in tomatoes and tomato products. J. Agric. Food Chem. 41, 610–615.

Michaels, B., Gangar, V., Schattenberg, H., Blevins, M., Ayers, T., 2003. Effectiveness of cleaning methodologies used for removal of physical, chemical and microbiological residues from produce. Food Service Technol. 3 (1), 9 (Abstract).

Ramadan, R.A., 1991. Residues of profenofos and pirimiphos-methyl in tomato and okra fruits as influnced by certain technologial processes. Fourth Nat. Conf. of Pests and Diseases of Vegetables & Fruits, Ismallia, Egypt, October, pp. 303–316.

Schattenberg, H.J., Geno, P.W., Hsu, J.P., Fry, W.G., Parker, R.P., 1996. Effect of household preparation on levels of pesticide residues in produce. J. Assoc. Off. Anal. Chem. 79 (6), 1447–1453.

Soliman, K.M., 2001. Changes in concentration of pesticide residues in potatoes during washing and home preparation. Food Chem. Toxicol. 39 (8), 887–891.

Soliman, M.M.M., 1994. Efficiency of some insecticides against leguminous pod borer *Etiella zinckenella* Treitschke on cowpea with special reference to pesticide residues. M.Sc. Thesis, Fac. Agric. Cairo Univ., Egypt.

Steel, R.C.D., Torrie, J.H., 1980. Principles and Procedures of Statistics: A Biomatrical Approach, second ed. Mc-Graw Hill Kogakusha Ltd., pp. 633.

Tejada, A.W., Varca, L.M., Calumpang, S.M.F., Bajet, C.M., 1995. Pesticide residues in food affected by crop protection practices. Asean Food J. 10 (3), 94–98.

Youssef, M.M., Abdel-Aal, A., Radwan, M.A., El-Henawy, G.L., Marei, A.M., 1995. Removal of pirimiphos-methyl and chlorpyrifos-methyl residues from treated tomatoes and broad beans by commercial and home preparative procedures. Alex. Sci. Exch. 16 (4), 461–469.

Zohair, A., 2001. Behaviour of some organophosphorus and organochlorine pesticides in potatoes during soaking in different solutions. Food Chem. Toxicol. 39 (7), 751–755.