DETERMINATION OF PESTICIDES RESIDUES IN SOME VEGETABLES

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ABSTRACT

The persistence patterns of malathion, fenitrothion and deltamethrin in fruits of tomato and cucumber were determined. Residues were determined gas liquid chromatography. Results confirmed that the initial deposit of malathion and fenitrothion on and in the cucumber fruits (7.603 and 9.043 µg/g) were higher than on and in tomato fruits (5.390 and7.110) respectively. Data also indicated that the initial residue of deltamethrin on and the tomato fruits (3.660) was higher than the initial deposit of deltamethrin on and in the cucumber fruits (3.643). Results showed that, the consumable safety time was found to be 10 and 14 days after application on tomato and cucumber. This was found to be enough to reduce the residue to below the maximum residue limits (MRL). However, malathion, fenitrothion and deltamethrin appeared to have relatively longer persistence on cucumber fruits with t1/2 of 1.98, 2.04 and 1.77 days than on tomato fruits with 1.41, 1.41 and 0.4 respectively.

Keywords: Residues, Malathion, Fenitrothion, Deltamethrin, Tomato, Cucumber.

INTRODUCTION

Pesticides of different chemicals nature are currently used for agriculture all over the world. Because of their widespread, they are detected in various foods and environment matrices. Pesticides are divided into many classes, which the most important are organochlorine and organophosphorous s compounds (Leena *et. al*, 2012). The development techniques to ensure agricultural productivity, both in quality and quantity, have caused an increase of using pesticides which control harmful organisms in relevant manners. They may contaminates foods and other products (Eom, 1994). The problem of contamination of food sources, especially vegetables by pesticide residues constitutes one of the most serious challenges to public health (Khan et al., 2011). The important of using pesticide, the conducting of research and regular frequent monitoring programs are actions needed to provide direction to governments and rural extension agencies to provide accurate information to the population about their adverse effects (Lucas,1998). An important trait of these pesticides is that there use has always been targeted at major crops, specially cereals; however, in the case of vegetables, despite their short cycles and the fact that they are grown in relatively small areas, these pesticides become , in a way adapted to vegetable crops. Vegetables frequently ensure good financial return per area unit, specially because consumers often prefer products with good aspect as if that would guarantee their health and quality (Baptista and Trevizan,2007). The required rates of application of pesticides may vary, under different agricultural and climatic conditions, from country to country, and between regions of the same country (Torres et al., 1997). Among cultivated vegetables, cucumbers and tomatoes occupy a prominent position because of their importance and acceptance by the population in general. The cucumber and tomato crops has many and serious problems represented by insect pests and plant diseases. Among insects , aphids, white flies and some lepidoptrous insects, whose control are normally achieved with the use of pesticides (Gallo *et al*., 2002). In a study conducted to evaluate residues of pyrethroid insecticides in vegetables, it was observed that deltamethrin and cypermethrin residues in asparagus decreased to levels below 0.1mg/ kg on the following day after the last application of the insecticides at the recommended dose (Ripley *et al*., 2001). Pesticide residue analysis is tremendously an important process in determining the safety of using certain pesticides. Pyrethroids were reported to have relatively low toxicity as compared to organophosphorus, organochlorine or carbamate pesticides (Colume,*et al*.,2001). Pesticides polluting the earth and causing problems in human beings and wildlife, the quantity of pesticide being consumed becomes a necessary knowledge. Analytical quality requirements like trueness, precision, sensitivity and selectivity have been met to suit the need for any particular analysis (Dasika, *et al*., 2012).

The objective of this study was to carry out a systemic study on determination of selected pesticides residues in vegetable samples

MATERIALS AND METHODS

Field experiment and sampling

Field experiment was conducted during the season of 204-2015 in the Hadda El-Sham farm of Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University, Jeddah, Saudi Arabia. Plots consisting of 10 rows separated by a three row belt of tomato (*Lycopersicon eseulentum* Mill.) Var. Alfa-Hidra (Holland) ,another 10 rows cultivated with cucumber (*Cucumis sativus* L.) Var. California (U.S.A.) half feddan were allocated to randomized complete block design with three replicates, the plants were sprayed with two O'P (malathion and fenitrothion) and one pirethroide (deltamethrin) pesticides at the fruiting stage once at the recommended rate. 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.

Untreated control plot was sprayed with water only for each treatment. All agricultural management practices were done as usually practiced in commercial production of tomato or cucumber. Fruit samples were taken at intervals of 0 (1 hr), 1, 3, 5, 7, 10, and 14 days after applications. The collected samples were placed in perforated plastic bags and frozen at -18 ^{o}C until insecticide residue analysis was run.

Extraction and clean-up

For extraction of O'P residues, the chopped fruit samples (50 gm) were taken and extracted with acetone (150 ml) for three minutes followed by partitioning using dichloromethane (Bowman, 1980). The extracts were evaporated to near dryness using a rotary evaporator at 35 ^{o}C. The concentrate was taken in 1 ml n-hexane for clean-up. The extracts were cleaned-up in a silica gel column contained 1 gm activated charcoal using 20% acetone in n-hexane as an eluting solvent (Bowman and 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) of the pure insecticide standard solution. Extraction and clean-up was performed as described earlier and the average recovery rate was found. Results were corrected according to the average of recovery.

Residue determination

Determination of O'P residues were performed at Central Laboratory, Faculty of Meteorology, Environment and Arid Land Agriculture, King Abdulaziz University on a Thermo-Trace GC Ultra FPD with an analytical Capillary column (40m X 0.18 mm X1µm.) packed with TG-624. The operating temperatures (^oC) for tested insecticides were maintained as follows: Column 220 isothermal, injector 270, detector 270 and gas flow rate (ml/min.) were: Helium 40, hydrogen 80, and air 100; the limits of detection under these conditions were 1.5 and 2.8 ng for malathion and fenitrothion, respectively. Identification of retention time (t_R) and compared with known standard at the same conditions. The quantities were calculated on a peak height basis. Using these conditions, the retention times of malathion, fenitrothion and deltamethrin were 4.36 and 10.16 and 10.19 minutes, respectively.

Statistical analysis

The obtained data were statistically analyzed and means were compared using LSD method at (0.05) according to (Steel and Torrie, 1980).

Results and Discussion

Tomato and cucumber vegetable crops were sprayed at fruit stage with malathion, fenitrothion and deltamethrin using a recommended field rate to study the persistence of any insecticides residues at different intervals. Analysis of variance of the insecticides residues are presented in Table 1. The given data showed highly significant differences among the eight periodical times on the three studies insecticides at $P \leq 0.01$ level of probability.

Table 1. Analysis of variance of the insecticide residues (µ/g) in the fruits of tomato and cucumber

Source of variation	d.f	Mean square	
		Tomato fruit	Cucumber fruit
Insecticide	2	12.51	15.34
Time	7	32.42**	58.27**
Insecticide*Time	14	1.67	2.98
Error	48	0.079	0.142

** Significant at 0.01 level

Data shown in Tables (2 and 3) demonstrate the mean of initial deposit and the residual behavior of malathion, fenitrothion and deltamethrin on and in tomato and cucumber fruits after spraying. These data demonstrated that the initial deposit found in and on tomato fruits as determined one hour after application were 5.39, 7.11, and 3.66 µg/g of malathion, fenitrothion and deltamethrin, respectively. As for cucumber it were 7.60 ,9.04 and 3.64 µg/g respectively. The amount of residue was decreased sharply to 3.44, 3.98, and 0.753µg/g for tomato and 5.74 , 6.48 and 3.24µg/g for cucumber respectively after first day of spraying within percentage of dissipation 36.5, 44.1, and 79.4% for tomato and 24.5, 29.2 and 11.0 % for cucumber respectively. This figure decreased gradually until reached 0.002, .137, and 0.005 µg/g on tomato fruits with loss of 99.9, 98.5, and 99.9% of the initial residues of malathion, fenitrothion and deltamethrin, after two weeks of application respectively. Moreover, the amount of residue were decreased to 0.002, 0.137 and 0.005 µg/g on cucumber fruits with loss of 99.9, 99.0 and 99.9% within the two weeks after spraying respectively.

When we compared the three insecticide residues we found that the deltamethrin was decreased sharply to 0.002 µg/g and 0.817 µg/g for tomato and cucumber after seven days of application followed by malathion 0.05µg/g and 0.70 µg/g and fenitrothion 0.62µg/g and 1.5 µg/g , respectively at the same interval period. Its means that the amount of residues were under MRL‘s after five to seven days of spraying (malathion MRL’s 0.5µg/g and 0.2 for tomato and cucumber, fenitrothion 1µg/g, and deltamethrin 0.3 µg/g) (Codex Alimentarius Commissioon,2003). The highest initial deposit of 7.11 µg/g and 9.04 µg/g fenitrothion was observed in the tomato and cucumber fruits, while the lowest amount was that of deltamethrin 3.66µg/g and 3.64 for tomato and cucumber, but malathion initial deposit was 5.39 µg/g and 7.60 µg/g. The concentration of the tested insecticides residues in both tomato and cucumber fruits reached to below maximum residue limits (MRL's) after 5 days of malathion, 7 days of fenitrothion and deltamethrin. The Acceptable Daily Intake values (ADI's) of malathion, fenitrothion and deltamethrin are 0.02, 0.005, and 0.01 µg/g, respectively for tested vegetables, Camoni *et. al.* (2001).

Table(2) Mean of residues of malathion, fenitrothion and deltamethrin in tomato fruits at periodic intervals

Periodic intervals (days)	Residue[µg/g(%Dissipation)]		
	Malathion	Fenitrothion	Deltamethrin
zero time (1 hr.)	5.390#[b]	7.110[a]	3.660[cd]
1	3.440[d] (36.53)	3.977[c] (44.06)	0.753[h] (79.43)
3	2.257[f] (58.36)	2.903[e] (59.17)	0.550[hij] (84.97)
5	0.350[hij] (93.54)	1.360[g] (80.87)	0.117[ij] (96.80)
7	0.048[j] (99.11)	0.620[hi] (91.28)	0.002[j] (99.95)
12	0.002[j] (99.96)	0.500[hij] (92.97)	0.001[j] (99.97)
14	N.D**[j] (~100)	0.063[j] (99.11)	N.D[j] (~100)

*Initial deposits of the insecticide.
**N.D =Not detected. #Means followed by the same letter(s) are not significantly different according to L.S.D.(0.05).

Table (3) Mean of residues of malathion, fenitrothion and deltamethrin in cucumber fruits at periodic intervals.

Periodic intervals (days)	Residue[µg/g(%Dissipation)]		
	Malathion	Fenitrothion	Deltamethrin
zero time (1 hr.)	7.603[b]	9.043[a]	3.643[fe]
1	5.738[d] (36.53)	6.480[c] (28.34)	3.238[f] (11.12)
3	2.257[f] (58.36)	4.007[e] (55.69)	2.133[g] (41.45)
5	1.078[ij] (85.82)	1.917[gh] (78.80)	1.049[ij] (71.21)
7	0.704[jkl] (90.74)	1.463[hi] (83.82)	0.817[ijk] (77.57)
12	0.279[kl] (96.33)	0.613[jkl] (93.22)	0.130[kl] (96.43)
14	0.002[l] (~99.95)	0.137[kl] (98.49)	0.005[l] (99.86)

*Initial deposits of the insecticide.
#Means followed by the same letter(s) are not significantly different according to L.S.D.(0.05).

The calculated half-life (t1/2) values of malathion were 1.41 and 1.98 days on tomato and cucumber fruits, respectively. The corresponding half–life values of fenitrothion and deltamethrin were 1.41, 2.04 and 0.4, 1.77 days, for tomato and cucumber, respectively (Table 4).

Table (4). The value of apparent rate constant (k) and the half –life (t1/2) of tested insecticides on tomato and cucumber fruits using GC methods

Insecticides	sample	Apparent rate Constant(K)a	Half-life Time(t1/2)b
Malathion	Tomato	0.49	1.41
	Cucumber	0.35	1.98
Fenitrothion	Tomato	0.49	1.41
	Cucumber	0.34	2.04
Deltamethrin	Tomato	1.72	0.4
	Cucumber	093	1.77

ak=1/t In a/m, where k= apparent rate constant, a=initial concentration, m=concentration after t,t=time in days; bt1/2 =In 2/k= 0.693/k

The results obtained from the present study exceeded this Acceptable Daily Intake values and this may be attributed to the common use of this pesticide for pest control in the study area. Akan *et. al.*(2013).

The different levels of initial deposits of tested insecticides on fruits of tomato and cucumber mainly due to many factors; the ratio of surface to mass area and character of treated surface, systemic and non-systemic character of compounds, high wax content of fruit surface and

hydrophilic-lipophilic balance of applied of agrochemicals into fruit tissues (*Cabras, et. al., 1988*)
Degradation and dissipation residues of malathion, fenitrothion and deltamethrin from these vegetable fruits happened because the initial deposits and residues at different intervals of these pesticides are influenced by different factors; evaporation of the surface residue which is dependent on temperature condition, biological dilution which is due to the increase mass of fruits, chemical or biochemical decomposition, metabolism and photolysis. Great interest to note that the same factors were studied by several investigators, *Christensen (2004)* reported that the decline of pesticides may due to biological, chemical or physical processes, or if still in field, due to dilution by growth of the crop. Plant growth, particularly for fruits is also responsible to a great extent for decreasing residue concentrations due to growth dilution effects (*Walgenbach et. al., 1991*). In addition, the rapid dissipation of originally applied pesticide are dependent on a variety of environmental factors such as sunlight and temperature (Lichtenstenin, 1972).
However, high temperature is reported to the major factor in reducing the pesticides from plant surfaces. Light plays an important role in the behavior of pesticide in the environment (*Zepp and Cline, 1977*).

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