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# Determination of Pirimiphos-Methyl and Chlorpyrifos-Ethyl Residues on Tomato and Pepper Fruits Grown in Greenhouse

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**Abstract:** The objective of this reserch is to determine the residues of pirimiphos-methyl and Chlorpyrifos-ethyl insecticides on greenhouse tomato and pepper fruits, a green house trial was carried out at the King Faisal Research Station, King Faisal University, Al-Hassa, Saudi Arabia. The experiment was designed in randomize block design. Samples of tomato and pepper fruits were randomly collected from treated and non-treated plants after a time elapse of one hour, 1, 3 and 7 days post insecticide treatments. Fruit extracts were analyzed for pirimiphos-methyl and Chlorpyrifos-ethyl residues using gas chromatography. The data showed that pirimiphos-methyl was vastly degraded when compared with Chlorpyrifos-ethyl. Chlorpyrifos-ethyl degradation of 8.2, 14.2 and 73.2% were recorded as compared with 30.4, 89.5 and 94.8% for pirimiphos-methyl after one, three and seven days, respectively. Chlorpyrifos-ethyl residues on tomato or pepper fruits after 3 days, represented more than ten folds of the maximum residue limits on vegetables (50 μg kg$^{-1}$). The data also showed that the rates of degradation were 0.14 and 0.44 day$^{-1}$ and 0.28 and 0.18 day$^{-1}$ and the $t_{1/2}$ was 4.8 and 1.6 day for pirimiphos-methy l and 2.5 and 3.9 day for chlorpyrifos-ethyl on tomato and pepper, respectively.

**Key words:** Pirimiphos-methyl, chlorpyrifos-ethyl, insecticide residues, tomato, pepper fruits

## INTRODUCTION

Insect pests are major challenge to greenhouse and open field vegetables production all over the world. These damaging pests are important because symptoms of feeding often go unnoticed until serious damage has occurred (Daughtrey *et al.*, 1997). The controls of such insects are mainly relying on the use of chemical pesticides (Prabhaker *et al.*, 1985). Many organophosphorus insecticides remain highly effective in reducing insect infestation (Prabhaker *et al.*, 1998). The extensive use of synthetic organic pesticides for this purpose has inevitably been followed by many problems. One of the most problems is a remaining residue in vegetables and fruits especially with highly stable and persistent insecticides. It could cause a health hazard to the ultimate consumers, particularly when the fruits are freshly consumed (Emico and Tomoke, 1982; Zidan *et al.*, 1996). Many publications revealed the existence of pesticide residues in various food items (Sullivan, 1980; Gartrell *et al.*, 1985). Abdel-Gawaad and Shams El-Deen (1989) detected residues of 23 pesticide and their degradation metabolites in many foodstuff samples. Judicate and Geoff (2005) found that pesticide residues in table ready foods in Tanzania were detected in 29% of all samples analysed. Chavarri *et al.* (2004) cleared that Sprayed crops of tomato and red peppers harvested after controlled field trials with six insecticides (organochlorine, organophosphorus and pyrethroids) contained residues well below the maximum residues levels. They added that washing removed all residual lindane, chlorpyrifos and cypermethrin from tomatoes. Chlorpyrifos residues were reduced by 67% during wood-fire roasting of peppers and subsequent peeling removed all the remains. Mayank and Ajay (2005) resulted that The concentration of organochlorine pesticides in summer and winter vegetables from Agra, India were well below the established tolerances but continuous consumption of such vegetables even with moderate contamination level can accumulate in the receptor's body and may lead to chronic effects that could be fatal.

The objective of this research is to determine the residues of pirimiphos-methyl and Chlorpyrifos-ethyl on greenhouse tomato and pepper fruits after one week of insecticides treatments.

## MATERIALS AND METHODS

**Chemicals:** Two organophosphorus insecticides were purchased locally and used for the field trials at the recommended rates. Actellic (pirimiphos-methyl) O-(2-diethylamino-6-methylpyrimidin-4-yl) O,O-dimethyl phosphoro-thioate, 50% EC and Dursban (chlorpyrifos-ethyl) O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate, 48% EC, at rates of 2.0 mL L$^{-1}$.

**Field trials:** The experiment was carried out at the King Faisal Research Station, Al-Hassa, Saudi Arabia. The experiments were designed in Randomize Block Design. Cultural practices were applied as recommended for commercial production of tomato and pepper. Insecticide applications were repeated four times at 15 days intervals to control the chewing and piercing-sucking insects on greenhouse tomato and pepper plants. Three replicates were set up for the six treatments. A hand operated knapsak sprayer was used to apply insecticides. Samples were taken after the last application of the two insecticides.

**Residue analysis**

**Sampling:** About 3 kg samples of tomato and pepper fruits were collected at random from each treatment, then placed in perforated cardboard boxes and transferred to the laboratory. The representative samples of non-treated and treated fruits were taken from each treatment at different intervals after treatment (zero (one hour), 1, 3 and 7 days). Fruits were cut into small pieces and three sub samples (100 g of each) were weighed into polyethylene sacs and kept deep-frozen until extraction.

**Extraction:** Samples (100 g/each) were extracted and cleaned-up according to the method adopted by Bullock (1984) and Al-Sarar (1996) by blending with 150 mL of acetonitrile at high speed for 3 min. The whole extract decanted through a glass wool plug in a glass funnel containing 20-30 g anhydrous sodium sulfate. The filtrate was concentrated to about 50 mL using rotary evaporator then shacked vigorously for 2 min with 150 mL of petroleum ether in a separatory funnel. The aqueous layer was taken and another 50 mL of petroleum ether was added and shacked again for another 2 min. The two organic layers were taken and concentrated using rotary evaporator to about 5-10 mL.

**Clean up:** Activated florisil 60-100 mesh (20 gm activated at 130°C for 16 h) was added to 300x25 mm chromatographic column in small portions, while tapping the column. A layer of anhydrous sodium sulfate was placed at the top of the florisil. The column, pre wet by allowing 40-50 mL of petroleum ether. Samples extract was transferred to the column. A total of 70 mL of the eluting mixtures 15 and 50% diethylether in petroleum ether were used. The eluent was concentrated to 5 mL.

**Determination:** Determination of insecticides was carried out by gas liquid chromatography (GC-14 Shmiadzo) equipped with FPD and ECD detectors. The conditions were: column (4% OV-210 on chromosorb WHP80-100 mesh), 220°C, injector 250°C and detector 250°C. Nitrogen was carrier gas (99.99% purity) at flow rate of 60 mL $min^{-1}$. The residue analysis was calculated according to the method of Goodspeed and Chestnut (1991). The average rate of recovery was 91% of pirimiphos-methyl while it was 93% for chlorpyrifos-ethyl. The quantification of the residues was corrected according to the rate of recovery. The data was subjected to statistical analysis (Snedecor and Cochran, 1967).

## RESULTS AND DISCUSSION

**Determination of pirimiphos-methyl residues in/on tomato and pepper fruits:** Table 1 shows that the maximum amount of detected residues was after one hour from insecticide application where it reached 83.6 and 34.3 μg $kg^{-1}$ in/on tomato and pepper fruits, respectively. The amount of residues reduced after a day from application where it reached 37.4 and 23.2 μg $kg^{-1}$ in/on tomato and pepper fruits, respectively. The lowest amount of residues recorded after one week from treatments where it was 24.1 and 1.8 μg $kg^{-1}$ in/on tomato and pepper fruits, respectively. Data revealed a rapid degradation of pirimiphos-methyl since degradation percentage was 55.2 within a day from application compared with that determined in/on tomato fruits after 1 h. However, degradation percentage was 89.5 and 94.8 of the initial deposit after 3 and 7 days on pepper fruits. In addition, degradation percentage reached 30.4 on pepper after one day compared with that determined after 1 h.

**Determination of Chlorpyrifos-ethyl residues in/on tomato and pepper fruits:** The maximum amount of residues was detected after an hour from insecticide application, where it was 878.8 and 678.3 μg $kg^{-1}$ in/on

Table 1: Pirimiphos-methyl residues on fruits of greenhouse tomato and pepper at different intervals from insecticide application

| Time post application | Residues (μg $kg^{-1}$) | | Residues (%) | | Degradation (%) | |
|---|---|---|---|---|---|---|
| | Tomato | Pepper | Tomato | Pepper | Tomato | Pepper |
| 1 h | 83.60 | 34.30 | 100.0 | 100.0 | 0.0 | 0.0 |
| 1 day | 37.40 | 23.20 | 44.8 | 69.6 | 55.2 | 30.4 |
| 3 days | 37.40 | 3.60 | 44.8 | 10.5 | 55.2 | 89.5 |
| 7 days | 24.10 | 1.80 | 28.8 | 5.2 | 71.2 | 94.8 |
| $LSD_{0.05}$ | 0.24 | 0.13 | | | | |

Table 2: Chlorpyrifos-ethyl residues on fruits of greenhouse tomato and pepper at different intervals from insecticide application

| Time post application | Residues (μg $kg^{-1}$) | | Residues (%) | | Degradation (%) | |
|---|---|---|---|---|---|---|
| | Tomato | Pepper | Tomato | Pepper | Tomato | Pepper |
| 1 h | 878.80 | 678.30 | 100.0 | 100.0 | 0.0 | 0.0 |
| 1 day | 864.80 | 622.40 | 98.4 | 91.8 | 1.6 | 8.2 |
| 3 days | 662.00 | 582.80 | 75.3 | 85.9 | 25.7 | 14.2 |
| 7 days | 130.50 | 181.80 | 14.9 | 26.8 | 85.2 | 73.2 |
| $LSD_{0.05}$ | 2.15 | 2.69 | | | | |

Table 3: Kinetic parameters of insecticides degradation on tomato and pepper fruits

| Insecticides | Rate of constant degradation (k) $(day)^{-1}$ | | $T_{1/2}$ (day) | | Slope | | r* | |
|---|---|---|---|---|---|---|---|---|
| | Tomato | Pepper | Tomato | Pepper | Tomato | Pepper | Tomato | Pepper |
| Pirimiphos-methyl | 0.14 | 0.44 | 4.8 | 1.6 | 0.06 | 0.19 | 0.85 | 0.94 |
| Chlorpyrifos-ethyl | 0.28 | 0.18 | 2.5 | 3.9 | 0.12 | 0.08 | 0.96 | 0.95 |

* correlation coefficient

tomato and pepper fruits, respectively (Table 2). The amount of residues reduced afterwards and reached 622 and 582.8 μg $kg^{-1}$ in/on tomato and pepper fruits, respectively after three days. The lowest amount of residues was recorded after one week from treatments (130.5 and 181.8 μg $kg^{-1}$) in/on tomato and pepper fruits, respectively.

Data revealed that chlorpyrifos-ethyl degradation was less at all the intervals compared with that of pirimiphos-methyl since degradation percentages were 1.6, 25.7 and 85.2 after 1, 3 and 7 days, respectively for Chlorpyrifos-ethyl compared with 55.2, 55.2 and 71.2 of pirimiphos-methyl at the previous intervals in/on tomato fruits. Same trend of degradation was recorded for both insecticides on pepper fruits where 8.2, 14.2 and 73.2% of Chlorpyrifos-ethyl compared with 30.4, 89.5 and 94.8% of pirimiphos-methyl after 1, 3 and 7 days from insecticides application, respectively (Table 2).

**Kinetic parameters of decay of insecticide residues:** The degradation behavior of the insecticides under the greenhouse condition was deduced from the logarithmic linear relationship between insecticide residues versus the time. The data showed linear correlation since the correlation coefficient (r) equal 0.85 and 0.94 for pirimiphos-methyl and 0.96 and 0.95 for chlorpyrifos-ethyl on tomato and pepper, respectively. Accordingly, the kinetic of degradation approximately follows the first order reaction. Data showed that the rates of degradation were 0.14 and 0.44 $day^{-1}$ for pirimiphos-methyl and 0.28 and 0.18 $day^{-1}$ for chlorpyrifos-ethyl on tomato and pepper, respectively (Table 3). The time require to degrade the half amount of the initial residues ($t_{1/2}$) was 4.8 and 1.6 day for pirimiphos-methyl and 2.5 and 3.9 day for chlorpyrifos-ethyl on tomato and pepper, respectively. Data revealed that the rate of pirimiphos-methyl degradation was higher compared with that of chlorpyrifos-methyl on pepper and vise versa on tomato. In general, about half of the organophosphorus insecticides decayed within 2 to 5 days under the greenhouse condition. The results are in agreement with that reported by Khan *et al.* (1985) and Al-Khalaf *et al.* (1992). They mentioned that the time required to reach the acceptable residue limits is 3-6 days for the organophosphorus compounds. Moreover, Hegazy *et al.* (1989) reported that the $t_{1/2}$ was 3 days for pirimiphos-methyl on tomato under the indoor conditions. In addition Al-Sarar (1996) reported that the $t_{1/2}$ of pirimiphos-methyl was 2.31 days on tomato.

From the previous data it is apparent that both organophosphorus insecticides have same behavior of degradation in/on tomato and/or pepper fruits in greenhouse. Residues of Chlorpyrifos-ethyl were about 10 and 20 fold when compared with that of pirimiphos-methyl in/on tomato and pepper fruits after one hour from application. However, after 3 days, Chlorpyrifos-ethyl residues in/on tomato or pepper fruits represented more than ten fold of Maximum residue limits (50 μg $kg^{-1}$) on vegetables (FAO/WHO, 1993). The different degradation percent might due to dissimilar chemical structure and physicochemical properties of the two insecticides, which affect their persistence in the environment against climatic parameters (temperature, humidity, sunshine hours, evaporation and saturation deficit). The results in line with that of (Abdalla *et al.*, 1993) who reported high level of organophosphorus residues on fruits of some vegetables and they mentioned that pirimiphos-methyl residues diminished within a day from insecticide application in/on tomato where the degradation percent was 83.7 and they added that tomato fruits could be consumed after four days from treatments. Moreover, Antonius *et al.* (1994) reported that, the half-life of pirimiphos-methyl on cabbage leaves was about 2.13 days. Furthermore Antonius and Snyder (1994) mentioned that greenhouse conditions elongate the half life of pirimiphos-methyl in/on tomato fruits. Also, Al-Samariee *et al.* (1987) and Al-Sarar (1996) mentioned that pirimiphos-methyl is rapidly degraded on cucumber fruits. They claimed that the quick decay might due to the temperature, humidity inside the protected house and the higher water contents of the cucumber fruits.

The present investigation suggests that the control of greenhouse insect pests on vegetables that consumed freshly should not depend mainly on the use of more persistent insecticides such as Chlorpyrifos-ethyl.

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