

## SHORT COMMUNICATION

### **Residue Levels of Pirimiphos-Methyl and Malathion on Tomato Fruits Grown in Greenhouses**

**Ahmed K. Salama, Abo-Shabana M. Mostafa and  
Ahmed A. Al-Rokaibah**

*Department of Plant Protection, College of Agriculture and Veterinary Medicine,  
King Saud University, Al-Qasseem Branch, Buraidah, Saudi Arabia*

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**Abstract.** Tomato plants grown in a greenhouse were sprayed with either pirimiphos-methyl or malathion formulation at the rate of 150 or 140 g a.i. per 100 l of water, respectively. Pesticides residues were analyzed on tomato fruits after 1st and 2nd spray at the different time intervals of zero, 1, 2, 3, 7, and 14 days. The initial deposit of malathion and pirimiphos-methyl were 114.10 and 95.20 mg/kg following a single spray, while it was 167.07 and 128.68 mg/kg after second spray, respectively. Residue of malathion were declined to 7.48 and 17.52 mg/kg after 14 days, however, in the case of pirimiphos-methyl they declined to 13.60 and 25.80 mg/kg. The residue half lives of pirimiphos-methyl and malathion were 3.65 and 5.40 and 2.15 and 3.80 days following a single and double spray, respectively. The present study indicates that the use of both compounds under the greenhouses conditions should be carried out on the young non-fruit bearing plants to avoid the high residue levels of these pesticides in tomato fruits.

### **Introduction**

Human poisoning by pesticides throughout the world has increased [1]. Food was the most common vehicle of exposure in all recorded epidemic outbreaks of pesticide poisoning [2]. Tyk and Jajh [3] reported that most accidents are caused by contaminated green leafy vegetables. Growing crops under greenhouses in Saudi Arabia is of great economic importance. Therefore, certain time should be allowed after pesticide application to produce fruits within the maximum residue limit (MRL).

Pirimiphos-methyl and malathion are recommended as insecticides and acaricides for many crop pests [4]. Many investigators have determined the residues of pirimiphos-methyl and malathion on vegetable crops under field conditions [5-10]. The initial deposits of pirimiphos-methyl and malathion on cabbage plants grown in field in Egypt were found to be varied [7]. Abo-El-Seoud *et al.* [7] found that the initial deposit of malathion was more than pirimiphos-methyl following the application at the rate of 600 and 570 g a.i. per feddan, respectively. They reported that the deposits reached the permissible limits after 12 days for both compounds under field conditions. In India, vegetables including tomatoes bought from the market, were found to be contaminated with insecticide residues. Out of 40 samples tested, 34 had residues exceeding the permissible limits, in particular malathion and organophosphate insecticides [9]. On the other hand, few studies have been carried out to determine the residue of pirimiphos-methyl, malathion and other pesticides on vegetables grown in greenhouses [11-12]. In an effort to determine the residue levels and dissipation rates of pesticides in vegetables grown in greenhouses, the present study was undertaken to determine the persistence of pirimiphos-methyl and malathion residues in tomatoes following either single or double application.

## Materials and Methods

### Treatment and sampling

Tomato plants, *Lycopersicon esculentum* Mill. grown in rows in a greenhouse located in the experimental farm of the College of Agriculture and Veterinary Medicine, King Saud University, were sprayed with aqueous dispersion of either pirimiphos-methyl (Actellic 50% EC), [*O*-2-Diethylamino-6-methyl pyrimidin-4-yl *O,O*-dimethyl phosphorothioate] or malathion (57% EC), [*O,O*-Dimethyl-*S*-1,2-di (Carboethoxy) ethyl phosphoro dithioate]. Spraying was carried out using a hand sprayer fitted with one nozzle boom at the rate of 150g a.i. from formulated pirimiphos-methyl or 140g a.i. from formulated malathion per 100ℓ of water). Untreated plants were left unsprayed as check plants. Sprayed samples, (two fruits from each replicate, approx. 250g) were collected for residue analysis at the following time intervals: zero, 1,2,3,7 and 14 days after treatment. At each time interval, three replicates were carried out where each replicate consisted of four plants. Fruits were collected in plastic bags, transported to the laboratory and stored at -20°C for two weeks. Second spray was carried out after 14 days from the first one and the double-sprayed samples were collected at the same time intervals and by the same manner mentioned above. Stored fruit samples at each time interval after spray with each pesticide were taken and left to thaw. After complete thawing, fruits were chopped and mixed thoroughly. Aliquot of the pulped tomatoes (50g) was extracted according to the method described by Lawrence and Leduc [13]. Clean up was carried out on silica gel-charcoal column (2:1, w/w) preconditioned by passing 10 ml of methanol through it. The column was eluted with 30 ml methanol and the eluate was collected and concentrated to 5 ml to be ready for determination. HPLC

analysis was carried out in a Varian-VISTA 5500 High Performance Liquid Chromatograph equipped with  $\mu$ Bondapak C<sub>18</sub> stainless steel column (30x 5 mm I.D.) and an ultra-violet detector. Analysis was conducted using an isocratic elution system with methanol at a flow rate of 2 ml/min. UV detector set at wavelengths of 254 and 224 nm for pirimiphos-methyl and malathion, respectively.

Rate of recoveries of pirimiphos-methyl from tomato fruits at the fortification levels of 10, 50, and 100  $\mu$ g/g were 90.12, 85.86, and 80.05 %, respectively, with an average of 85.34 %. Whereas in the case of malathion, they were 94.95, 80.90 and 75.99 % with an average of 83.95 %.

### Results and Discussion

Table 1 shows the analytical values of the contents of either pirimiphos-methyl or malathion residues in tomato fruits following a single or double application. The results revealed that the initial deposits of pirimiphos-methyl were 95.20 and 128.68 mg/kg, however those of malathion were 114.10 and 167.07 mg/kg following a single and double application, respectively. These results indicate that the initial deposits of malathion were higher than that obtained from pirimiphos-methyl.

**Table 1. Levels of pirimiphos-methyl and malathion residues in tomato fruits following a single and double spray**

Time in days	Pirimiphos-methyl amount (mg/kg)		Malathion amount (mg/kg)	
	Single spray	Double spray	Single spray	Double spray
Zero	95.20 $\pm$ 10.2	128.68 $\pm$ 12.0	114.10 $\pm$ 7.5	167.07 $\pm$ 11.9
1	57.36 $\pm$ 1.4	103.88 $\pm$ 7.0	83.62 $\pm$ 5.5	130.62 $\pm$ 7.7
2	54.20 $\pm$ 4.0	83.20 $\pm$ 6.6	61.65 $\pm$ 12.6	113.62 $\pm$ 6.7
3	50.10 $\pm$ 1.2	79.42 $\pm$ 4.4	34.05 $\pm$ 2.3	86.13 $\pm$ 7.1
7	36.00 $\pm$ 0.2	47.80 $\pm$ 10.8	12.17 $\pm$ 1.0	49.16 $\pm$ 3.8
14	13.60 $\pm$ 1.4	25.80 $\pm$ 2.4	7.48 $\pm$ 1.0	17.52 $\pm$ 1.4

Each value represents the mean of three samples  $\pm$  S.D.

As can be seen, the residue of both compounds in tomatoes decay with time and low levels of residue are reached more quickly following a single application of either pirimiphos-methyl or malathion. After one day, the remaining amounts of both compounds were reduced to reach 57.36 and 103.88 mg of pirimiphos-methyl/kg tomato fruits and 83.62 and 130.62 mg malathion per kilogram fruits following a single and double spray, respectively. The results also showed that the residue levels of both

pesticides after a single spray were lower than that obtained from double treatment throughout the all time point. Finally, residue levels of 13.60 and 25.80 mg of pirimiphos-methyl and 7.48 and 17.52 mg of malathion per kilogram tomato fruits are achieved at 14 days following a single and double application, respectively.

In general, it seems that the disappearance rate of both compounds is very slow and they need more time to reach the permissible dose in tomato fruits under the greenhouses conditions. Some differences were observed between the different compounds.

Half-life values and elimination rates were calculated and illustrated in Table 2. The half-life ( $T_{1/2}$ ) of each pesticide was calculated using the following formula [14],

$$T_{1/2} = 0.693 / K$$

where 0.693 is constant and  $K$  is the elimination rate constant which was obtained by linear regression of terminal linear exponential decline in pesticide concentration.

**Table 2. Half-life values and elimination rates of pirimiphos-methyl and malathion in tomato fruits**

Pesticide	Elimination rate constant, $K$ ( $\text{day}^{-1}$ )		Half-life value, $T_{1/2}$ (days)	
	Single spray	Double spray	Single spray	Double spray
Pirimiphos-methyl	0.19	0.13	3.65	5.40
Malathion	0.32	0.18	2.15	3.80

The disappearance phase of pirimiphos-methyl had rate constants ( $k$ ) of 0.19 and 0.13  $\text{day}^{-1}$  following a single and double spray, respectively, and as a consequence, half-life ( $t_{1/2}$ ) values of 3.65 and 5.40 day. In the case of malathion, the elimination rate constants were 0.32 and 0.18  $\text{day}^{-1}$  following a single and double treatment. The corresponding half-life values were 2.15 and 3.80 day.

The obtained data showed that the spray of pirimiphos-methyl and malathion on tomato plants as the same conditions of this experiment will reveal levels of residues in tomato fruits above the maximum residue limits (1 ppm for pirimiphos-methyl and 0.5 ppm for malathion [15]) until 14 days after treatment. These findings may be due to the condition of planting in plastic houses where there is no direct contact between the compound and climate conditions such as light, moisture and/or heat. Thus the study shows clearly that the use of these pesticides under the greenhouses conditions should be carried out on the young non-fruit bearing plants.

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## مستويات متبقيات البريميغوس - ميثايل والملاثيون على الطماطم المزروعة في البيوت المحمية

أحمد حميس سلامة، أبوشبانة مصطفى، وأحمد على الرقبة  
قسم وقاية المزروعات، كلية الزراعة والطب البيطري  
جامعة الملك سعود، القصيم، بريدة

(قدم هذا البحث للنشر في ١٤١٧/١٢/٢٧ هـ، وقبل للنشر في ١٤١٨/٢/٧ هـ)

ملخص البحث. تم تقدير متبقيات مبيد ميثايل-بريميغوس و ملاثيون على ثمار الطماطم المزروعة في البيوت المحمية وذلك بعد معاملة النبات في طور الإثمار برشة واحدة أو رشتين متتاليتين لكل مبيد على حدة بمعدل ١٥٠، ١٤٠ جم من المادة الفعالة لكل ١٠٠ لتر ماء على الترتيب. وقد أوضحت النتائج أن التركيز الابتدائي المتخلف عن مبيد الملاثيون (١٠، ١١٤، ١٦٧، ٠٧ جم/كجم من الثمار) أعلى منه في حالة مبيد الميثايل بريميغوس (٢٠، ٩٥، ٦٨، ١٢٨ جم/كجم ثمار) سواء بعد رشة واحدة أو رشتين على الترتيب نفسه. ثم بدأت هذه الكميات في التناقص مع مرور الوقت حتى وصلت إلى ٧، ٤٨، ١٧، ٥٢ جم/كجم ثمار في حالة مبيد الملاثيون، بينما كانت ١٣، ٦٠، ٢٥، ٨٠ جم/كجم ثمار في حالة مبيد ميثايل-بريميغوس وذلك بعد ١٤ يوما من الرش. وقد تم حساب الزمن الذي تختفي عنده نصف كمية الميثايل-بريميغوس منذ بداية الرش فكانت ٣، ٦٥، ٥، ٤٠ يوم، وذلك بعد رشة واحدة ثم رشتين على الترتيب، بينما في حالة مبيد الملاثيون كان هذا الزمن ٢، ١٥، ٣، ٨٠ يوما على الترتيب نفسه. وتوضح هذه الدراسة أنه يجب استخدام هذه المبيدات على النباتات الصغيرة غير المثمرة وذلك حتى نتجنب المتبقيات العالية لهذه المبيدات على ثمار الطماطم.