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DETERMINATION OF METHOMYL AND PROFENOFOS RESIDUES ON AND IN TOMATO FRUITS UNDER FIELD CONDITIONS

BY

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ABSTRACT

Field trial was conducted at a private farm at Bany-Shible, Zagazig, Sharkia Governorate, during the summer cultivation of 1999 and 2000 seasons to control some insect pests infesting tomato crop using methomyl and profenofos insecticides. Residues of both insecticides were determined in unwashed and tap water-washed tomato fruits at 0, 1, 3, 5, 7, 10 and 15 days of spraying. The most prevailing insects in two seasons were *Bemisia tabaci*, *Phthorimaea operculella*, *Spodoptera littoralis* and *Nezara viridula*. Seven days after methomyl and profenofos had been applied to tomato crop during summer of 1999 season, their residue levels in unwashed tomato fruits reached 0.92 and 0.643 p.p.m with actual loss of 88.26 and 83.34%, respectively. The corresponding residue values of both insecticides during the summer of 2000 season reached 1.07 and 0.805 p.p.m with actual loss of 89.11 and 82.61%, respectively. Results showed that washing treated tomato fruits with tap water removed considerable amounts of these insecticides residues from 28.93 to 71.54% and from 26.47 to 67.88% loss during 1999 and 2000 seasons, respectively.

INTRODUCTION

In Egypt, tomato crop grown in summer cultivation is severely attacked by many insect pests including Egyptian cotton leaf worm (*Spodoptera littoralis* Boisd.), whiteflies (*Bemisia tabaci* Genn.) potato tubermoth (*Phthorimaea operculella* Zeller). Methomyl: S – methyl – N – (methyl carbamoyloxy) thioacetimidate and profenofos: *O* - 4 – bromo – 2 – chlorophenyl *O* – ethyl – S – Propyl phosphorothioate, have been recommended to control these pests as a confirmative and satisfactory treatment (PCP, 2001). However, on several occasions, incidents were attributed to negligence in observing a safety interval before harvest. Pesticide residues determination in treated vegetable fruits and foodstuffs is required to give an idea about the post harvest interval (PHI) that should pass after application and before marketing and for setting maximum residue limits to protect the consumer against the possible health hazard of exposure to pesticides (Bates, 1979). Therefore, the object of this study was to determine the disappearance rate of both methomyl and profenofos after application to tomatoes to establish the (PHI) under Sharkia Governorate conditions. Another target for this study was to assess the effect of washing treated tomato fruits with tap water in order to remove methomyl and profenofos residues.

MATERIALS AND METHODS

Pesticides used:

Methomyl (Lannate 90% WSP) and profenofos (Selecron 72% E.C) were applied at their recommended rates, i.e. 300 gm. and 750 ml. per fed., respectively, using a knapsack sprayer fitted with a single-nozzle boom.

Field Experiments:

Field experiments were conducted during the summer cultivations of 1999, and 2000 seasons at a private tomato field at Bany Shible Village, El-Zagazig, Sharkia Governorate. Treatments were arranged in randomized complete block's design with four replicates. Tomato (*Lycopersicon esculentum* var. Super Marmand) seeds were sown on 1/1/1999 and 15/1/2000. Then, tomato seedlings were transferred into the permanent soil on 15/2/1999 and 29/2/2000 for the first and the second seasons, respectively. The plants were sprayed three times (1/4, 22/4 and 8/5/1999 and 18/4, 8/5 and 24/5/2000) with each of methomyl and profenofos at their recommended rates to control some insects infesting tomatoes and for residue analysis.

Sampling:

Samples of tomato fruits (four fruits for each) were randomly collected from treated and untreated plots at 0, 1, 3, 5, 7, 10 and 15 days after spraying. Samples collected at each appointed time were added together and thoroughly mixed. Then 0.5 kg was placed in polyethylene bags and kept in deep freezer at -18°C until analyzed.

Analytical method:

Methomyl and profenofos residues were determined in the tomato fruit samples at 0, 1, 3, 5, 7, 10 and 15 days after application according to the method adapted by El-Nabarawy and Carey (1988).

Apparatus and Reagents:

a) High performance liquid chromatograph (HPLC) Bechman 432 equipped with an injector model 210, a fixed wave length ultraviolet detector model 160 and an ultraphase C 18 analytical column (ODS): 25 cm × 4.6 mm id. The mobile phase was acetonitrile + water (60 + 40 by volume) and the solvent flow rate was 0.7 ml./min. The minimum detectable level of methomyl by the apparatus was 0.75 ng.
b) Gas chromatograph "GC" Hewlett-Packed HP. model 5890 equipped with ^{63}Ni electron capture detector and integrator 3395. HP capillary column (methyl silicon gum) 30m × 0.25mm × 0.2μm film thickness. Operating conditions: nitrogen carrier gas 120 ml./min.; Temperature: oven 220 °C.

injector 220 °C and detector 300 °C. The lowest amount of profenofos could be detected by the apparatus was 0.1 PPb.

c) Solvents: acetone, acetonitrile, n-hexane, diethylether and petroleum ether. All solvents were distilled twice and subjected to general purity tests as mentioned in the PAM (1990).

d) Florisil: PR grade, 60-100 mesh, activated on 650 °C for 4 hrs and kept over night at 140 °C, handled and tested as in sec. 121-3 in the PAM (1990).

Extraction:

A representative weight of about 100 gm. of each tomato sample was washed with tap water and homogenized in a suitable glass jar with 200 ml. of acidic acetone (385 ml. acetone + 15 ml. of 50% H_2SO_4 in distilled water) for 2 min. at high speed and filtered through a Buchner funnel fitted with S & S Shark skin filter paper into a 250 ml. graduated cylinder. The glass jar and filter cake were washed twice with 15 ml. of acidic acetone. A measured volume of filtrate which represents 20 gm of the fruit sample was transferred to 100 ml. quickfit flask and the acetone was evaporated using a rotary evaporator under vacuum in a water bath at 30 °C. Acetone – free extract was re-extracted twice with 50 ml. petroleum ether using a 250 ml. separatory funnel. The layers were allowed to separate, the aqueous layer was discarded and the solvent layer was transferred to a 100 ml. quickfit flask and concentrated to ca. 1.0 ml. using a rotary evaporator. The remaining solvent was allowed to evaporate under fume hood and the residues was dissolved in 10 ml. n – hexane.

Clean - up:

Methomyl and profenofos extracts were quantitatively transferred to a chromatographic column (40×10 cm) containing 5 mm of glass wool, 4.0 gm activated florisil 60/100 mesh and topped by 2.0 gm anhydrous sodium sulphate using two 5 ml. portions of n-hexane. Residues were eluted in a 250 ml. quickfit flask using 35 ml. of n-hexane and 65 ml. of a mixture of diethylether and petroleum ether (1:1). The solvent was concentrated to about 2.0 ml. using a rotary evaporator and left to be completely evaporated under a fume hood. Methomyl and profenofos residues were dissolved in known amounts of n-hexane for injection into HPLC and GC equipped with UV and EC detectors, respectively.

Determination:

The cleaned extracts of methomyl and profenofos residues were injected in HPLC and GC apparatus, respectively. Under the conditions previously mentioned for each apparatus, the retention times of methomyl and profenofos were 2.60 and 14.43 min., respectively. Amount of residues in the injected aliquot was determined by comparing residue peaks with those of standard solutions of both insecticides. Methomyl and profenofos residues were corrected according to their recoveries which ranged from 90.06-91.0% and from 90.23-91.23%, respectively, (Table 1).

Recovery studies:

Recovery experiments were conducted with fortified samples of untreated tomato fruits at level ranged from 0.1 to 1.0 ppm. The fortified samples were processed through all steps of the analytical method to validate the assay procedure. The percentages of recoveries of both methomyl and profenofos from tomato fruits are shown in (Table 1).

Table (1): Recovery percentages* of methomyl and profenofos from unwashed tomato fruits.

Added ppm	Methomyl		Profenofos	
	Unwashed tomato fruits	Washed tomato fruits	Unwashed tomato fruits	Washed tomato fruits
1.0	91.2	92.0	90.0	92.5
0.5	90.0	88.0	91.2	93.1
0.1	89.0	93.0	89.5	88.1
Average	90.06	91.0	90.23	91.23

* These figures are the mean of 4 replicates.

RESULTS AND DISCUSSION

a) Residues of methomyl and profenofos on and in tomato fruits produced during the summer cultivation of 1999 season:

Data presented in Table (2) show methomyl and profenofos residues detected on and in unwashed and tap water-washed tomato fruits obtained from treated crop during summer cultivation of 1999 season.

Methomyl residues detected at 0, 1, 3, 5, 7, 10 and 15 days of spraying were 7.837, 6.656, 4.568, 1.193, 0.92, 0.483 and 1.103 ppm for unwashed tomatoes while those of washed tomatoes were 4.113, 2.669, 1.3, 0.85, 0.562, 0.343 and N.D ppm, respectively. The corresponding values of profenofos residues for unwashed tomatoes were 3.86, 2.74, 1.907, 1.15, 0.643, 0.204 and 0.103 ppm while those of washed tomatoes were 2.01, 1.65, 1.075, 0.734, 0.325, 0.108 and N.D ppm. Washing of tomato fruits with tap water removed the surface residues of methomyl and profenofos by average losses of about 50 and 44%, respectively.

Data obtained indicated that methomyl and profenofos residues in both tomato samples clearly diminished as time lapsed science 84.78 and 70.20% of such residues, respectively, were disappeared at the 5th day of spraying (Table 3 and Fig. 1 and 2). The disappearance of the residues of both insecticides, however, was nearly similar after this period and gradually decreased until the fifteenth day of spraying. After the 10th day of spraying, the initial deposits of methomyl and profenofos were lost by about 94 and 95%, respectively. Those figures show that the first 5 days after spraying are the critical period in dissipation of the used insecticides.

Table (2): Methomyl and profenofos residues "ppm" in and on tomato fruits samples at indicated periods of spraying during the summer cultivation of 1999 season.

Days after spraying	Methomyl residues (ppm)			Profenofos residues (ppm)		
	Unwashed samples	Washed samples	% of loss by washing	Unwashed samples	Washed samples	% of loss by washing
Initial *	7.837	4.113	47.52	3.86	2.01	47.92
1	6.656	2.669	65.14	2.74	1.65	39.78
3	4.568	1.3	71.54	1.907	1.075	43.62
5	1.193	0.85	47.21	1.15	0.734	36.71
7	0.92	0.562	38.91	0.643	0.325	49.96
10	0.4826	0.343	28.93	0.206	0.108	47.06
15	0.103	N.D **	-	0.103	N.D	-
			avg.= 49.88			avg.= 44.18

* Initial : Just after spraying ** N.D : none detected

Generally, data presented in Table (3) indicated that the actual loss in methomyl and profenofos residues during the first three periods (1^{st}, 3^{rd}, and 5^{th} day of spraying) was higher than that occurred during the other last two periods (7^{th} and 10^{th} day of spraying).

Table (3): Loss percentages of methomyl and profenofos from tomato fruits at the indicated periods of spraying during the summer cultivation of 1999 season.

Days after spraying	Methomyl		Profenofos	
	% of actual loss	% loss by washing	% of actual loss	% loss by washing
Initial *	-	47.52	-	47.92
1	15.07	65.14	29.02	39.78
3	41.71	71.54	50.60	43.78
5	84.78	47.21	70.20	36.17
7	88.26	38.91	83.34	49.96
10	93.84	28.93	94.72	47.06
15	98.69	-	97.33	-

* Just after spraying

b) Residues of methomyl and profenofos on and in tomato fruits produced during the summer cultivation of 2000 season:

Data shown in Table (4) revealed that methomyl and profenofos residues detected on or in tomato fruits collected during summer cultivation of 2000 season were higher than those detected during the previous season. Methomyl residues for unwashed tomatoes at 0, 1, 3, 5, 7, 10 and 15 days of spraying were 9.827, 7.037, 3.72, 1.85, 1.07, 0.531 and 0.211 ppm, respectively. The corresponding values for washed tomatoes at the same time intervals were 4.213, 2.821, 2.321, 1.321, 0.738, 0.231 and 0.117 ppm. On the other hand, profenofos residues for unwashed tomato fruits ranged between 4.63 ppm at zero time and 0.108 ppm at 15 days of spraying. These values became 2.97 and 0.067 ppm when tomato fruits were washed with tap water at the same time intervals.

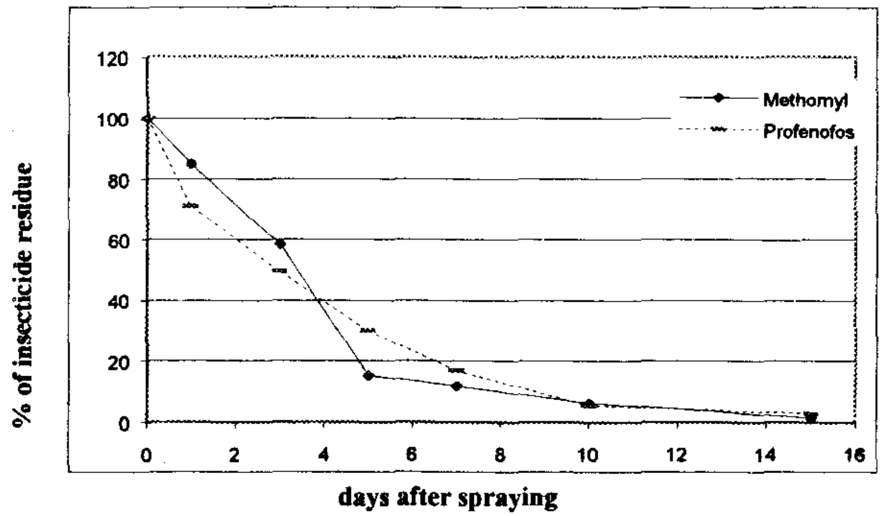

Fig. (1): Persistence of methomyl and profenofos in and on unwashed tomato fruits during the summer cultivation of 1999 season.

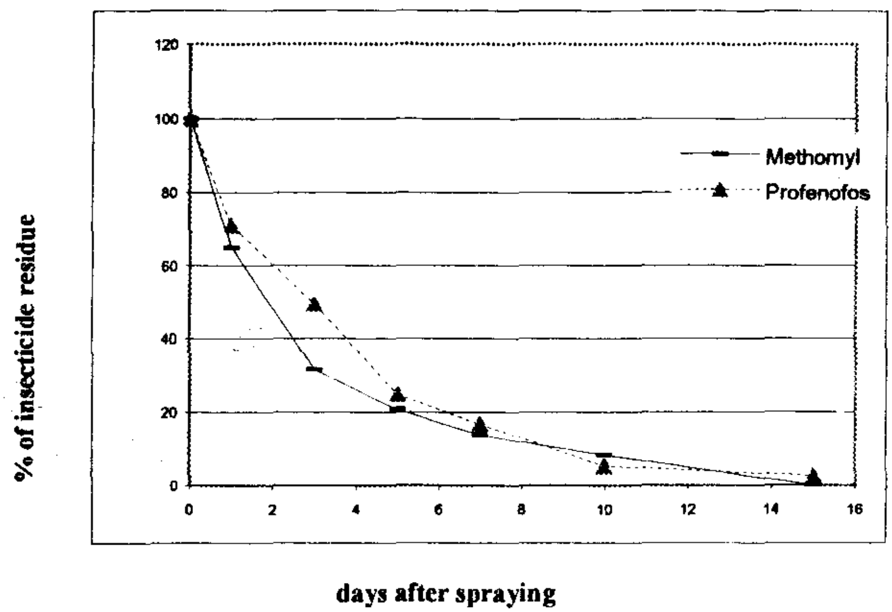

Fig. (2): Persistence of methomyl and profenofos in and on washed tomato fruits during the summer cultivation of 1999 season.

Table (4): Methomyl and profenofos residues (ppm) in and on tomato fruits samples at indicated periods of spraying during the summer cultivation of 2000 season.

Days after spraying	Methomyl residues (ppm)			Profenofos residues (ppm)		
	Unwashed samples	Washed samples	%of loss by washing	Unwashed samples	Washed samples	% of loss by washing
Initial *	9.827	4.213	57.13	4.63	2.97	38.01
1	7.037	2.821	59.91	2.98	1.97	33.89
3	3.72	2.321	37.61	1.95	1.173	39.85
5	1.85	1.132	38.81	1.36	1.0	26.47
7	1.07	0.738	31.03	0.805	0.401	50.19
10	0.531	0.231	59.89	0.358	0.115	67.88
15	0.211	0.117	44.55	0.108	0.067	37.96
			avg.= 46.99			avg.= 42.04

* Initial: Just after spraying

Data listed in Table (5) and illustrated in Fig. (3) and (4) show that the actual loss of methomyl residues progressively increased up to the 10th day post treatment reaching more than 94% of initial deposits.

Table (5): Loss percentage of methomyl and profenofos at indicated period of spraying in and on tomato fruits during the summer cultivation of 2000 season.

Days after spraying	Methomyl		Profenofos	
	% of actual loss	% loss by washing	% of actual loss	% loss by washing
Initial *	-	57.13	-	38.01
1	28.39	59.91	35.63	33.89
3	62.15	37.61	57.88	39.85
5	81.17	38.81	70.63	26.47
7	89.11	31.03	82.61	50.19
10	94.60	59.89	92.27	67.88
15	97.85	44.55	97.67	37.96

* Just after spraying

Moreover, sharp decrease in methomyl residues was observed at the 3rd day of its spraying since more than 62% of initial deposits was disappeared. On the other side, disappearance manner of profenofos residues was similar to that of methomyl. It was shown that there was an obvious fluctuation in the rate of profenofos dissipation from one period to another since it recorded 35.63 – 92.27% loss through the first 10 days after spraying.

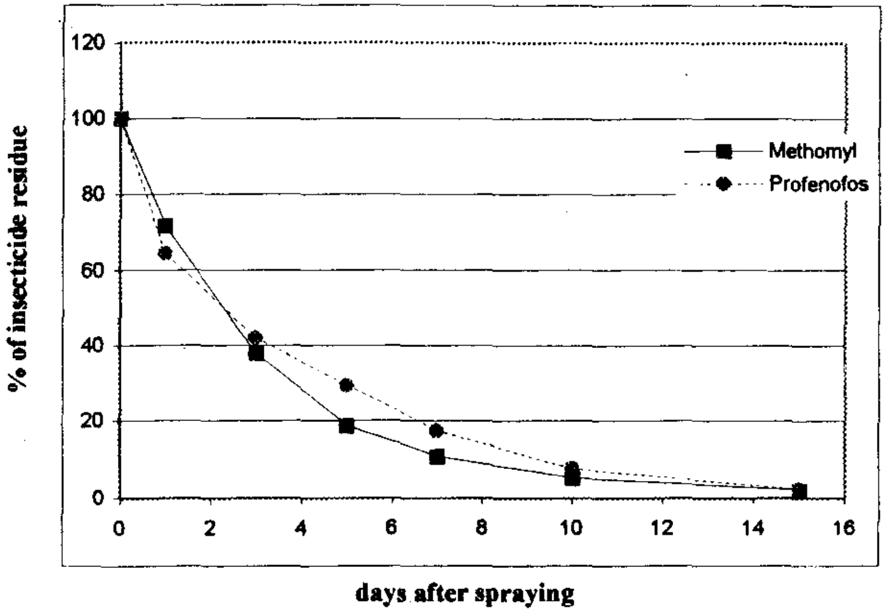

Fig. (3): Persistence of methomyl and profenofos in and on unwashed tomato fruits during the summer cultivation of 2000 season.

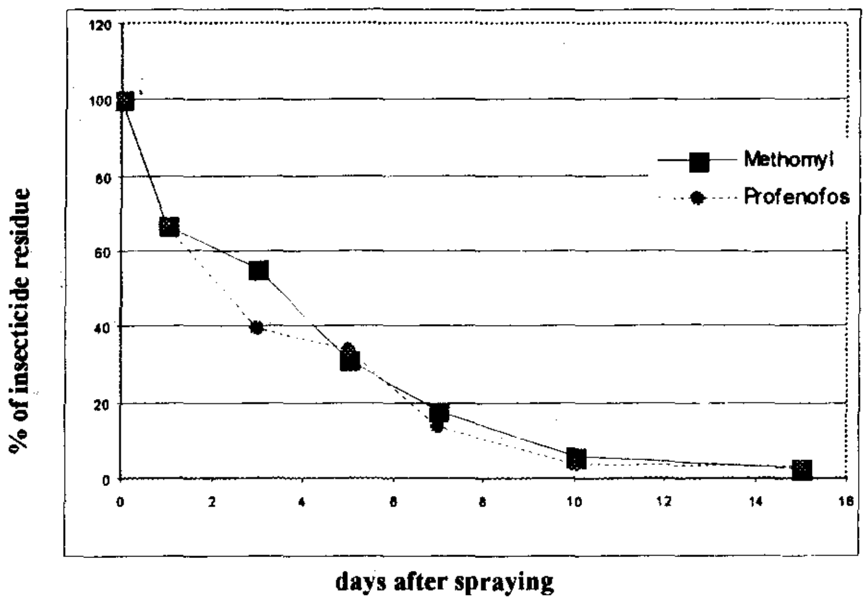

Fig. (4): Persistence of methomyl and profenofos in and on washed tomato fruits during the summer cultivation of 2000 season.

Great interest to note that the initial deposit of methomyl (a carbamoyloxime compound) was much higher (2.08 times) than that of the phosphorothionate profenofos. Also, it is known that there is a positive correlation between the lipophilicity of the used compound and its ability to uptake onto the recipient plant surface. In this ranged, Steven *et al.*, (1988) measured the uptake of fourteen agrochemicals for four plant species and concluded that the total uptake into the leaf ranged from 1 – 97% at 24 hrs. after application depending on the partition coefficient the compound as well as the plant species. Moreover, the insecticide uptake is positively correlated with the coverage of the used insecticide droplets onto the recipient target and climatic temperature (Ambrus, 1987). Therefore, the higher uptake of both methomyl and profenofos during the summer cultivation of 2000 may be attributed to the high temperature recorded during this season (avg. ca. 44 °C) comparing with that recorded during the summer cultivation of 1999 (avg. ca. 26 °C) (CLAC, 2000). On the contrary, several investigators (eg. Harper *et al.*, 1993; Willis and Mc Dowell, 1987 and Willis *et al.*, 1992) reported that the weather factors including temperature were effective factors of pesticide deterioration from foliage. The obvious fluctuation in the rate of insecticide disappearance from period to another may be attributed to the fluctuation in the metabolizing enzymes as well as the interference of the metabolites present during detection time which may affect the titer of the metabolizing enzymes. The same conclusion was pointed out by Rafa (1988) when calculated the actual loss of four organophosphorus insecticides in and on several vegetable and fruit crops.

On the other hand, washing of tomato fruits with tap water removed considerable amounts of the surface residues of both examined insecticides. Similar findings were outlined by other investigators. Ramadan (1991) and Ismail *et al.*, (1993) reported that washing of profenofos contaminated – tomatoes by tap water removed substantial portions of its residues. Badawy *et al.*, (1995) found that washing of tomato fruits by tap water just after spraying with profenofos and pirimiphos – methyl resulted in 44.5 and 51.03% loss in both insecticides, respectively. Herbert *et al.*, (1996), Zidan *et al.*, (1996), El-Nabarawy *et al.*, (2000) and Sohair (2002) recorded similar findings but with other insecticides and other raw agricultural products.

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تقدير متبقيات الميثوميل والبروفينوفوس على وفى ثمار الطماطم تحت الظروف الحقلية

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تم إجراء تجربة حقلية فى مزرعة خاصة بقرية بنى شبل مركز الزقازيق محافظة الشرقية وذلك بهدف مكافحة بعض الآفات الحشرية التى تهاجم الزراعات الصيفية لمحصول الطماطم خلال موسمى ١٩٩٩ ، ٢٠٠٠ وذلك باستخدام مبيدى الميثوميل والبروفينوفوس ، وللوقوف على مستويات متبقيات هذين المبيدين على وفى ثمار الطماطم فى ظل الظروف الحقلية السائدة فقد تم تقدير متبقيات هذين المبيدين فى عينات من تلك الثمار جمعت عشوائياً من المعاملات المختلفة وذلك بعد الرش مباشرة وأيضاً بعد ١ ، ٣، ٥ ، ٧ ، ١٠ ، ١٥ يوماً من الرش ، بالإضافة إلى ذلك فقد تم تقدير متبقيات هذين المبيدين على الثمار المعاملة بهما وذلك بعد غسيل تلك الثمار بماء الصنبور. ولقد اتضح من الدراسة أن متبقيات مبيدى الميثوميل والبروفينوفوس على وفى ثمار الطماطم وصلت إلى ٠,٩٢ ، ٠,٦٤٣ جزء فى المليون بعد سبعة أيام من الرش بعد أن كانت ٧,٨٣٧ ، ٣,٨٦ جزء فى المليون بعد الرش مباشرة وبمعدل فقد مقداره ٨٨,٢٦ ، ٨٣,٣٤% على التوالى وذلك خلال موسم ١٩٩٩. أما فى موسم ٢٠٠٠ فقد وصلت هذه المتبقيات بعد سبعة أيام من الرش إلى ١,٠٧ ، ٠,٨٠٥ جزء فى المليون بعد أن كانت ٩,٨٢٧ ، ٤,٣٦ جزء فى المليون بعد الرش مباشرة وبمعدل فقد مقداره ٨٩,١١ ، ٨٢,٦١% على التوالى. كذلك اتضح من الدراسة أن استعمال ماء الصنبور فى غسيل الثمار المعاملة بهذين المبيدين أسفر عن إزالة كميات من متبقيات هذين المبيدين تراوحت بين ٢٨,٩٣–٧١,٥٤% خلال موسم ١٩٩٩ وبين ٢٦,٤٧–٦٧,٨٨% خلال موسم ٢٠٠٠.