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ORIGINAL ARTICLE

Examining the effects of Different types of Washing Techniques on the amount of Deltamethrin remained in the tomato plant by using GC mass method

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ABSTRACT
Due to the indiscriminate use of pesticides in different food products and lack of attention to the currency period, unwanted and harmful toxins are more likely remained in food products in Iran and the world. This is more serious for vegetables and fruits that can be eaten raw and can cause acute and chronic poisoning.For this reason, in the present study, we investigated the residue level of commonly used insecticide deltamethrin in the samples of tomatoes grown in Mahshahr. In this study, a total of 108 samples were collected from farms and 30 samples from fruit and vegetable wholesale markets of different cities in Khuzestan province. Spraying was done in three concentrations of 22000, 11000, and 44000 ppb and samples were collected at first, third, fifth and seventh days. The collected samples were divided into three groups of unwashed, washed with water and washed with a weak acid (vinegar). The samples were extracted via QuEChERS [Quick-Easy-Cheap-Effective-Rugged-and Saftey] method in laboratory and final extracts were measured for residue levels by GCmass device. The collected data were compared with the maximum pesticide residue levels allowed by the Food Codex and national standards and the results obtained in different washing types showed the role of washing in reducing the amount of pesticide residues in non-systemic samples. Moreover, rate of decomposition and half-life were determined using the proposed model for unwashed samples. The half-life of deltamethrin toxin for three concentrations of 1000, 22000 and 44000 ppb was equal to 2.17, 2.17, and 2.19, respectively. The present study aimed to find out the residue levels and the difference between unwashed samples and those washed with vinegar solution (one cup of vinegar with three cups of pure water).
Keywords: *deltamethrin, tomatoes, pesticide residues*

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INTRODUCTION

Tomato is one of the products that its cultivation in greenhouses has become common in recent years. Farmers are always faced with many pests during cultivation of this product, so control of the damages caused by these pests is their most important concern. Given that today chemical control methods are very commonly used [1,2], the indiscriminate use of pesticides for different products and lack of attention to the currency period result in increased unwanted pesticide residues [3,4] especially in vegetables and fruits which are eaten raw a short time after harvest and can cause acute and chronic poisoning [5, 6]. In the process of this transformation, we should also pay attention to maintenance of the population of beneficial organisms (insects). Otherwise, natural control agents are destroyed and pest outbreak occurs. Moreover, due to the adverse effects of toxins on other organisms, poisonings associated with the use of pesticides, exorbitant costs of chemical pesticides production, and effects of indiscriminate use of pesticides, the need for correct use of these products has become a very important and serious matter to be examined. In the present study, we measured residue levels of the commonly used insecticide

deltamethrin (decis) in the samples of tomatoes grown in Mahshahr. Deltamethrin belongs to the pyrethroid pesticides group and has non-systemic exposure and gastrointestinal effects. It has before taking dose of 3 to 7 days. It is fast-acting and its toxicity is lower in the artificial pyrethroids group. Insecticidal power of this toxin is five to ten times higher than other pyrethroids [7]. It affects sodium and potassium channels and causes a disturbance in the entry and exit of these ions in the nervous system [8,9].

MATERIAL AND METHODS

Test methods

a) Farm operations

1- Selection of the plant and the field

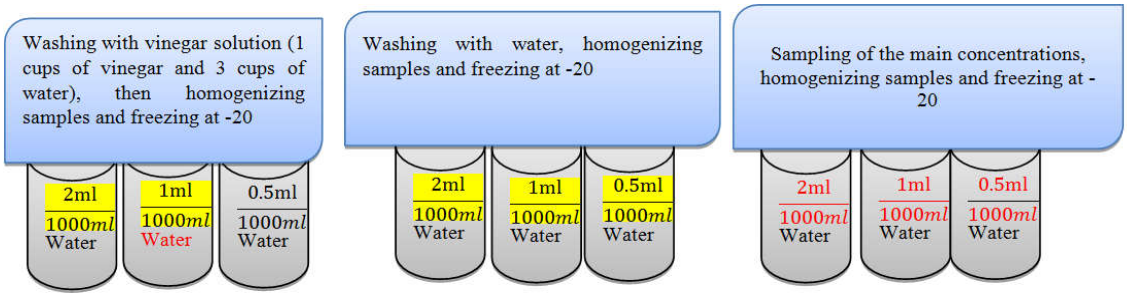
Tomato plants were grown into 15 cm bushes in a greenhouse and then transported cultured separately with a distance of 30 cmoutdoors in an area of one hectare. After watering every 3 days for two and a half months and formation of tomato on the bushes, we separated and marked three fields and determined their perimeters, and then spraying was done for the three 10 square meters fields.

Dilution and spraying step

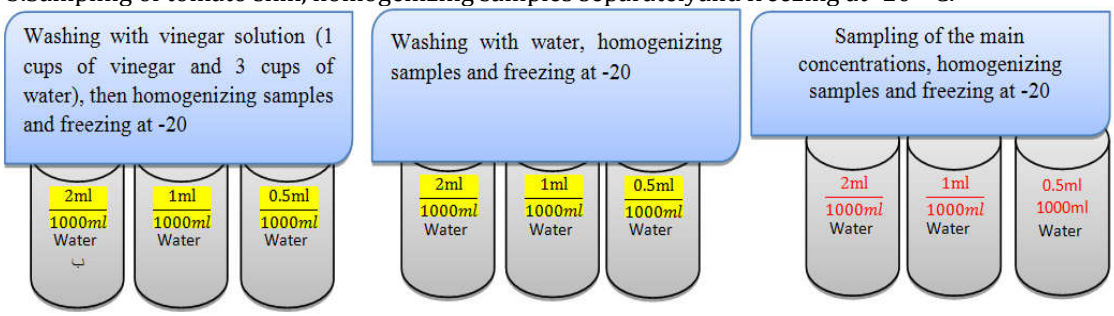
(According to the toxin manufacturer's instructions, 500 ml per thousand liters of water for fruits and vegetables) per a hectare.

Based on the desired cultivation field, 10 square meters, and the dilution solution, we dissolved 0.5 ml of toxin from a tank containing 2.5% deltamethrin into 1 l of water spraying was done with the obtained 0.5 per thousand ml of water solution. In order to doubling the concentration, we dissolved 1 ml taken from the 1 l tank into 1000 ml of water, and to quadruple the initial concentration, we dissolved 2 ml taken from the main tank into 1000 ml of water. Sampling was done in several steps after spraying. In each step, the samples were prepared in three ways: unwashed, washed with water and washed with a solution of vinegar (a cup of vinegar and three cups of water), and then they were homogenized and frozen at -20 ° C (the effect of washing with vinegar was based on the instructions issued by Food and Drug Administration of America).Because deltamethrin is a non-systemic (non-intrusive) toxin and takes place on skin of tomatoes, it is expected that washing is more effective in reducing this toxin. Various steps of testing are summarized in the following tables.

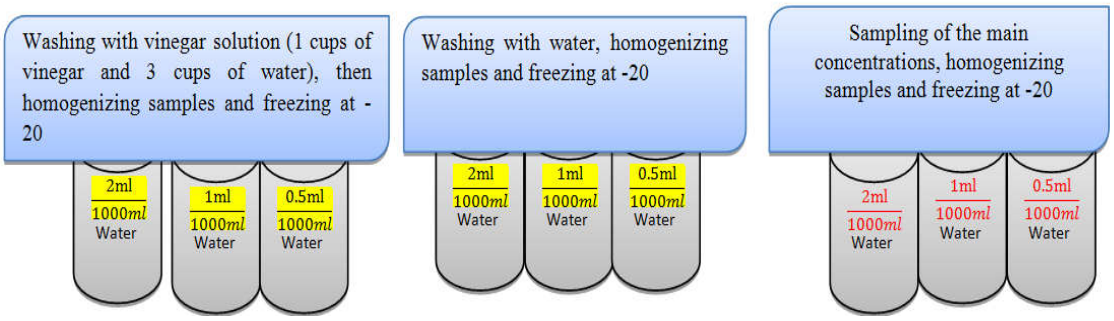
Day 1.Spraying, sampling of tomato skin with an interval of 2 hours, homogenizing samples separatelyand freezing at -20 ° C.



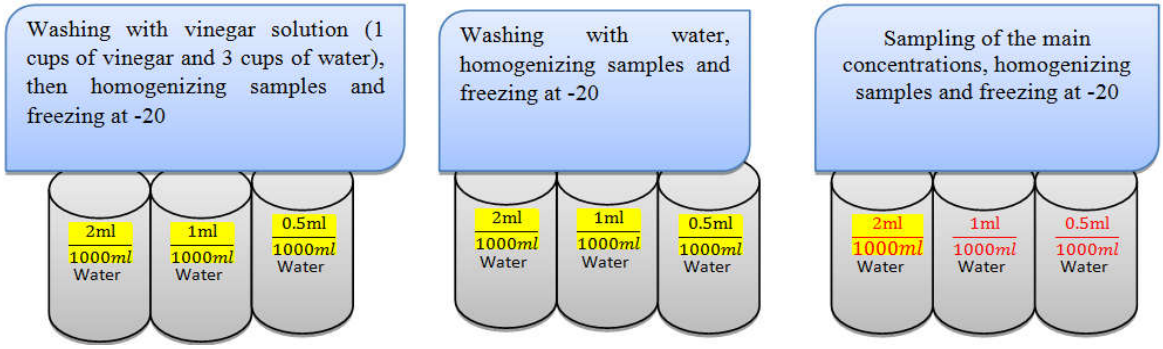
Day 3.Sampling of tomato skin, homogenizing samples separatelyand freezing at -20 ° C.



Day 5.Sampling, homogenizing samples separately and freezing at -20 ° C.



Day 7.Sampling of skin, homogenizing samples separately and freezing at -20 ° C.



Sampling

Sampling was done randomly.

Storage of samples

The samples were stored in plastic containers(Falcon 50 ml conical tubes) at low temperatures because high temperatures increase the risk of sample corruption and decomposition of toxin [12].

Extraction of chemical pesticides

First, chemical pesticides existed in the sample should be fully extracted and measured.Fats and pigments existed in agricultural productions are dissolved into most solvents used to extract chemical pesticide residues and cause problems in later steps. High performance gas and liquid chromatography systems are widely used as two preferred methods for measurement of chemical pesticide residues [11]. Due to the harmful effects of chemical pesticides on the environment and the health of organismsand, above all, human, the special place of tomatoes in our food basket, cultivation of this crop in the southern regions, and the effects of deltamethrin, which is widely used for tomatoes, on human health, we decided to measure the pesticide residues in tomatoes in three modes of unwashed, washed with water, and washed with acid (vinegar) for three different doses of 2, 1, 0.5 ml per thousand ml of water at concentrations of 22000, 11000, and 44000 ppb.

b) Laboratory procedures

Laboratory procedures were conducted via QuEChERS method [13, 14, 15] which is now a suitable standard method alternative to other extraction methods and is widely used in many laboratories around the world. In short, this procedure was performed in the following steps in Kaj laboratory in Tehran. Samples were freezing out of the cold chain in Falcon tubes and placed in open space to be defrosted in the ambient temperature of the laboratory. The tubes contained 50 ml homogenized samples which were separated into two phases after centrifuging. 10 g of the upper layer was separated by Sartorius balance and transferred into Erlenmeyer and then 10-15 ml of n-hexane solvent was added on the samples. A magnet was placed in the Erlenmeyer for better dissolution and then the samples were placed on a heater for 20 minutes. In this step, tomato extracts remained at the bottom of the container and the top layer was removed with a syringe. This layer contained n-hexane, deltamethrin, tomato extracts with the seeds of tomatoes andfatty acids, water, etc. Before injection into the device, additional matters were entirelyseparated by c18 cartridge. Then washing process was performed twice, each time with 5 ml of distilled water by a Manny Feld device equipped with a vacuum pump with 20 cartridge stands and the liquid was gathered under the Manny Feld. By putting a 50-mm balloon under the Manny Feld the solution of toxin and n-hexane passed through the cartridge and gathered in the balloon, then 15 mm of hexane passed through the cartridge and gathered in the 50-ml container. The balloon containing 25 ml was placed in a vacuum evaporation device to reduce the volume (about 1 cc or less). Finally,1 ml of

hexane was added and the sample was prepared in a 2-ml vial for being injected into the device. About one micro literwas taken from the vialand injected into GC/Mass by the auto sampler [15].

Preparation of standard solutions

To prepare standard solutions, a Stoke standard was derived from the basic standard and when necessary, precise standards were daily obtained from this standard. Deltamethrin with purity higher than 99% was used for preparation of the mother standard solution. Solutions with different concentrations were prepared from the mother solution each time and 0.5 ml of them were injected into the device. To prepare a standard curve, the corresponding peaks were obtained and the curves of injected poison concentrations vs the area under the peaks were plotted. Then, using the area under the peak related to the sample and the standard curve,we determined sample's concentration (Figure 1).

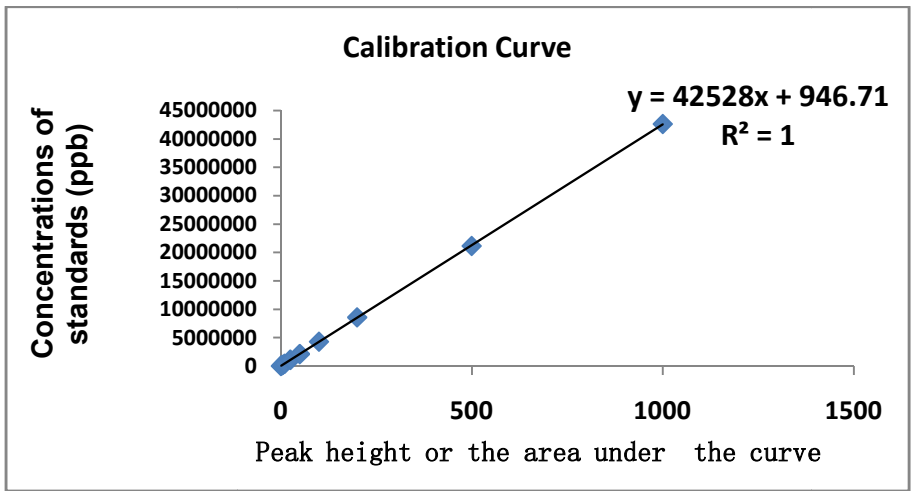


Figure 1: Deltamethrin calibration curve

Statistical Methods

All the factors considered in this test were expressed as the mean ± the standard error of the mean. ANOVA and Duncan's test were used to analyze the differences between different groups. These tests were performed via SPSS and the values with $p<0.05$ were considered as acceptable differences(significant at $P<0.05$).

RESULTS

A-The difference in toxin extracted from samples after washing with different matters

After spraying, three samples were selected in each group (based on dose and day). One sample were washed with water, one washed with vinegar and one was remained unwashed. After analyzing and extracting toxin residuesin samples, the means of 8.23± 3.116, 5.21±3.105, and 1.14± 1.69 were reported for unwashed samples, samples washed with water, and samples washed with acid, respectively (ppb or µg / kg). Statistically, as shown in Figure 2, a significant difference was observed between the data.

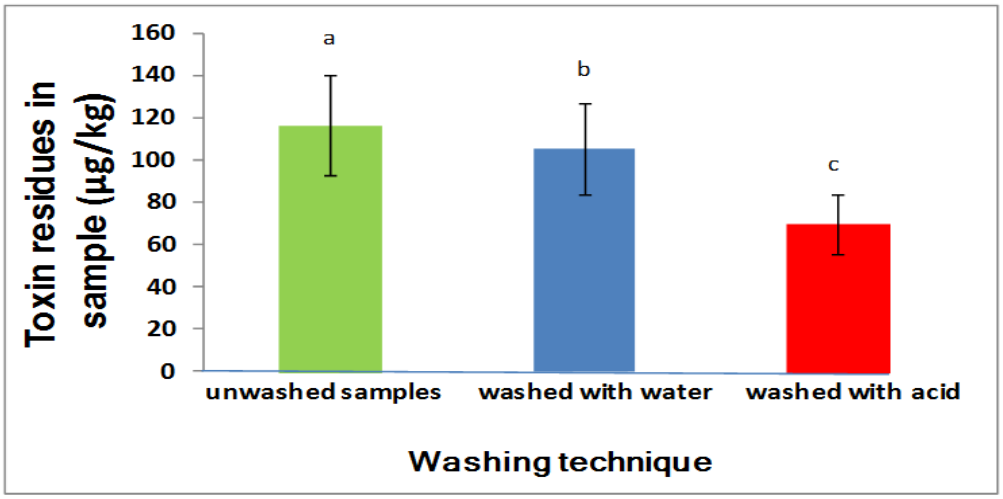


Figure 2: The difference in deltamethrin residues in samples due to different techniques of washing

B-The difference in toxin residues in different samples based on MRL (standard level of toxins in tomato) for different test conditions (day, dose and washing technique)After analyzing and extracting the toxin residues in samples, the means of 99/0±77.128, 07/1±5.254, and 4/1±501 ppb were reported for doses of 22000, 11000, and 44000 ppb, respectively, for unwashed samples acid on day 1. This was greater than the national maximum allowed deltamethrin residues in tomato (MRL) which is equal to 50 ppb (0.05 ppm). For the cases of washing with water and washing with vinegar (acid), all values were greater than the maximum allowed cut-off. (Figure 3).On the third day, the values of 3.0±1.0, 109.0±3.54, and 0±218.03 ppbwere reported respectively for unwashed samples which are greater than MRL. In the case of washing with water on day 3, the results were equal to 3.0±9.48, 3.0±4.98, and 3.0±3.195 ppb, respectively. So, only dose 11000 on day 3 was less than the maximum limit. In the case of washing with acid on day 3, the results were equal to7.0±7.33, 3.0±01.65, and 2.0±6.127, respectively. So, only dose 11000 on day 3 was less than the maximum limit (Figure 4). On day 5, in the case of unwashed samples, the results were equal to 0.0±0.17, 2.0±5.33, and 2.0±9.64 ppm, respectively. Compared with MRL, except for the concentration of 44000, the values were less than the maximum limit. In the case of washing with water, except for the concentration of 44000, the values were less than the maximum limit. In the case of washing with acid, the values were less than the maximum limit (Figure 5). On day 7, in the case of unwashed samples, the results were equal to 0.03±97.03, 4.0±1.07, and 8.0±17.09, respectively, which are all less than the maximum limit. Also, in the cases of washing with acid and washing with water, all values were less than the maximum limit (Figure 6).

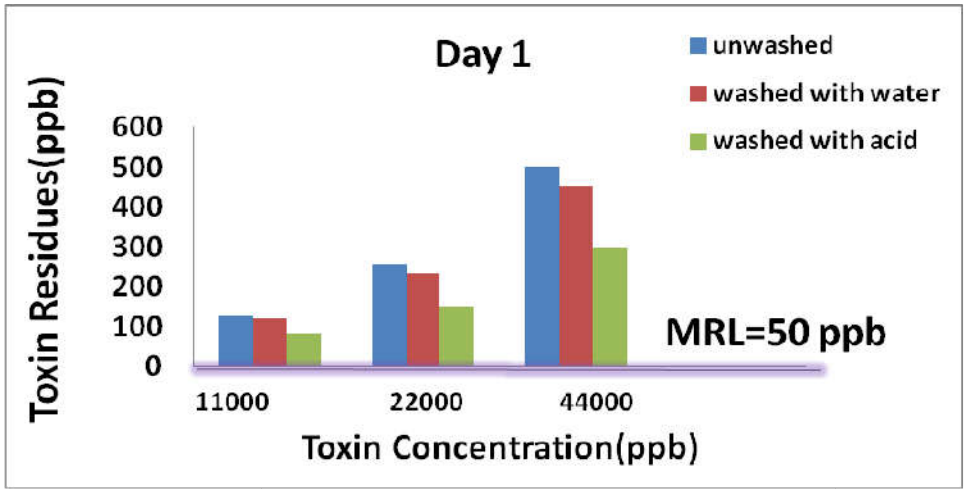


Figure 3: A comparison between MRL and toxin residues in tomato samples for different concentrationsand different washing conditions on the first day

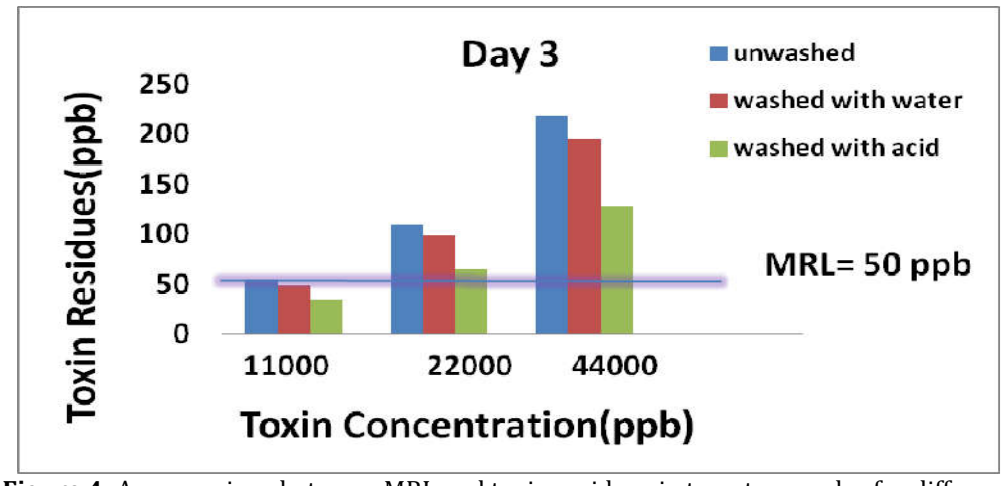


Figure 4: A comparison between MRL and toxin residues in tomato samples for different concentrationsand different washing conditions on the third day

Currency period was 3 to 5 days.

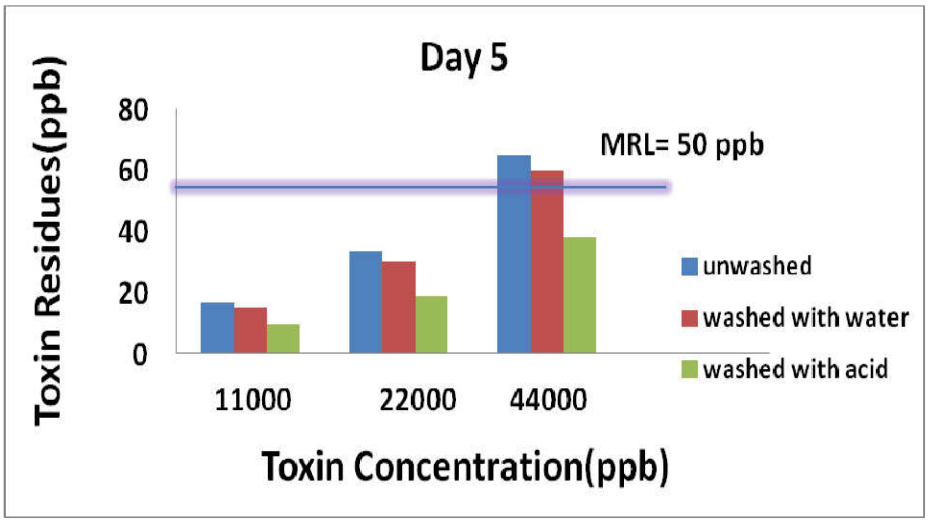


Figure 5: A comparison between MRL and toxin residues in tomato samples for different concentrations and different washing conditions on the fifth day

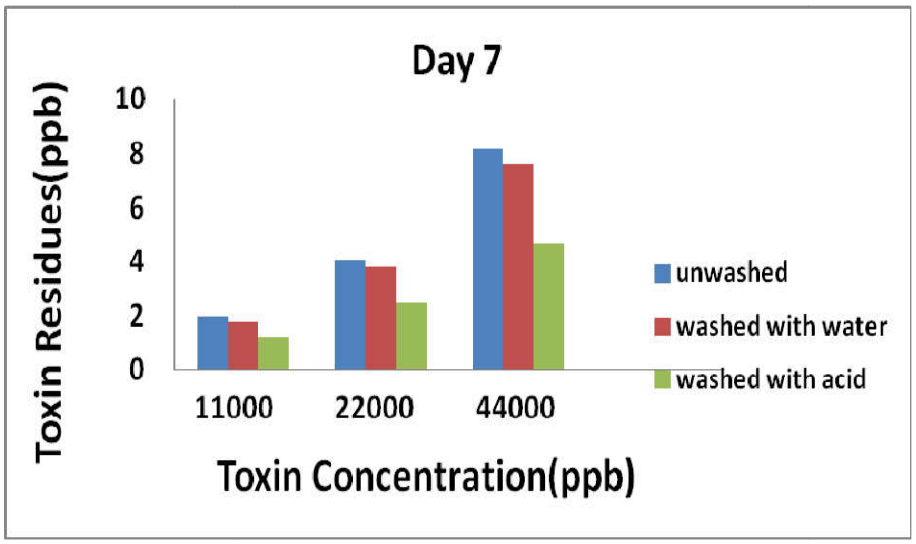


Figure 6: A comparison between MRL and toxin residues in tomato samples for different concentrationsand different washing conditions on the seventh day

C- Determination of rate of decomposition and half-lifeusing the proposed model in the case of unwashed samples

As can be seen, toxin residues for dose 11000 ppb decrease in plant samples over time, so that after three days, toxin residues become less than the maximum cut-off (MRL). After 11 days, this value tends to zero. The half-life at a dose of 11000 ppb was 17.2 days (Figure 7). Toxin residues for dose 22000 ppb decreases decrease over time, so that after four days, toxin residues become less than the maximum cut-off (MRL). After 12 days, this value tends to zero. The half-life at a dose of 22000 ppb was 17.2 days (Figure 8). Toxin residues for dose 44000 ppb decreases decrease over time, so that after five days, toxin residues become less than the maximum cut-off (MRL). After 13 days, this value tends to zero. The half-life at a dose of 44000 ppb was 19.2 days (Figure 9).

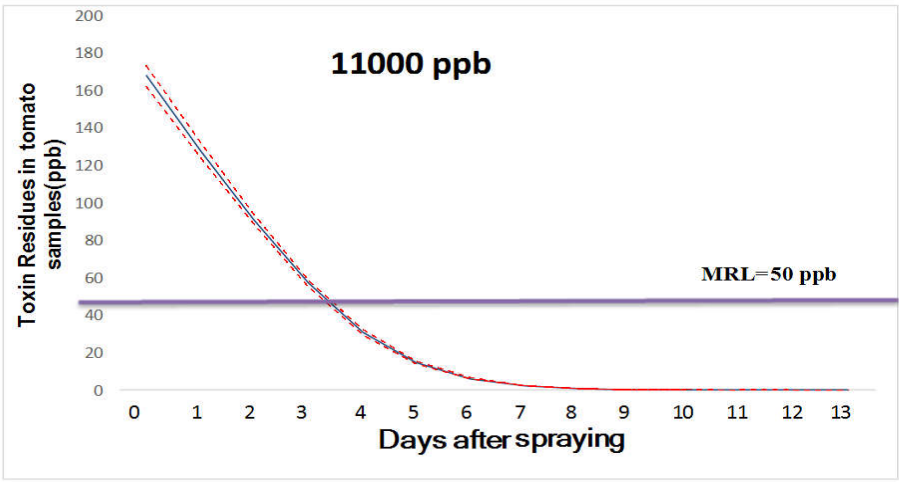


Figure 7: Rate of decomposition and toxin residues after several days of spraying at concentration 11000 ppb (unwashed samples).

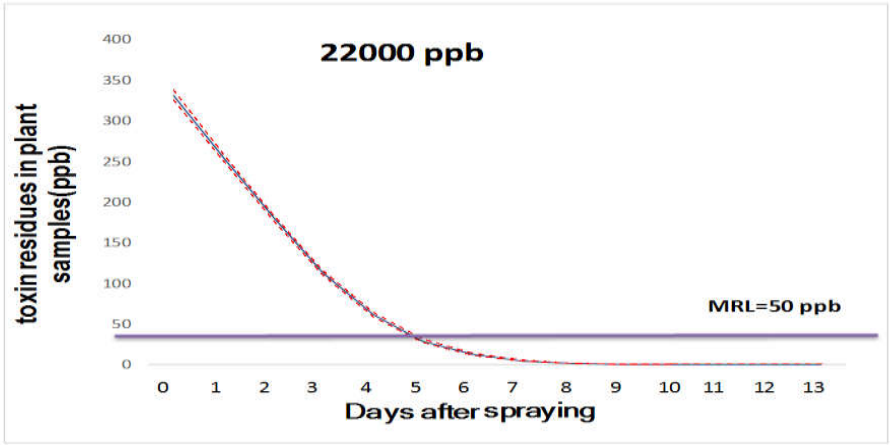


Figure 8: Rate of decomposition and toxin residues after several days of spraying at concentration 22000 ppb (unwashed samples).

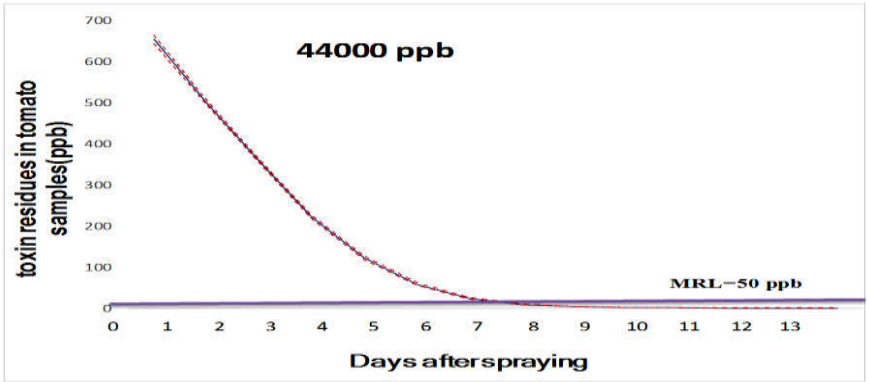


Figure 9: Rate of decomposition and toxin residues after several days of spraying at concentration 44000 ppb (unwashed samples).

DISCUSSION AND CONCLUSION

The test results indicate a statistically significant difference between toxin residues in plant after washing with different techniques. These results are in consistent with the results obtained from other studies (16). One of the objectives of the present study was to determine rate of decomposition and toxin residues in tomatoes at different conditions (different days after spraying, different toxin concentrations, different washing techniques). As shown in Figure 7, toxin residues in tomatoes with the concentration of 0.5 per thousand (11000 ppb) after three days reached less than the maximum national allowable cut-off and tended to zero after 12 days. Figure 8 shows toxin residues at the concentration of 22000 ppb which

reached less than the maximum limit after 4 days. This value tended to zero after 11 days. After six days, 14.12 ppb of the toxin residues, i.e. 96.3% was decomposed within this period. In this test, the half-life was 17.2. decomposition of the sprayed toxin at the concentration of 44000 ppb is shown in Figure 9. The toxin residues reached to 23.98 after 6 days, i.e. 96.3% of the toxin was decomposed within this period. For decomposition of the toxin at the concentration of44000 ppb, the half-life was equal to 19.2.

The results indicated decomposition of deltamethrin on tomatoes surface. An average half-life of 18.2 days was obtained for this decomposition rate. According to decomposition equations and the average half-life of deltamethrin, i.e. 18.2 days, it can be said that deltamethrin can be a good alternative for high-risk pesticides with a long half-life such as diazinon and malathionoxydemeton methyl. However, low-risk toxins such as IGR pesticides can also be a good alternative [17].The important thing about this pesticide is that because of less persistence in the environment, it is widely used for vegetables.

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