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Determination and analysis of pesticide residues in field-grown and greenhouse-grown tomatoes using liquid chromatography-mass spectrometry

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ABSTRACT

The present study aimed to extract pesticide residues in the field and greenhouse-grown tomatoes and homemade paste based on the quick, easy, cheap, effective, rugged, and safe sample preparation method (QuEChERS) before determined by the liquid chromatography-mass spectrometry (LC-MS). The mean difference in percentage reduction of deltamethrin (DLM) and acetamiprid (ACT) in raw tomatoes of greenhouse-grown was obtained at 91.42 and 90.00%, respectively, which was insignificantly more than filed condition (84.91% and 86.34%). Maximum reduction percentages of the DLM in paste under greenhouse and field tomato conditions were achieved by more than 95.86% and 93.11%, respectively. The residual concentration of both DLM (91.42%) and ACT (90.00%) in the greenhouse decreased more than the field (84.91% and 86.34%), respectively. Abamectin(ABA) reached below the MRL in a shorter time after spraying (2 days). Considering the pre-harvest interval (PHI) period of deltamethrin and abamectin can reach their residual concentration to the MRL in both conditions, which were determined by LC-MS. According to the results of the current study, 7 and 5 days can be suggested as the PHI period of the acetamiprid for field and greenhouse-grown tomatoes, respectively. Therefore, using pesticides in the proper dosage, considering appropriate PHI, and harvesting can reduce their residues in agricultural products.

1. Introduction

Tomato, scientifically known as *Solanum Lycopersicum*, is one of the world's most widely used and popular vegetables. It's used as raw and processed due to having high antioxidants such as ascorbic acid, vitamins E and A, carotenoids, flavonoids, and phenolic acid that can reduce the risk of cardiovascular diseases and prevent diabetes and cancer [1, 2]. Several pesticides are used to maintain agricultural products. Improper consumption of pesticides in farm products and non-compliance with the pre-harvest interval (PHI) period can

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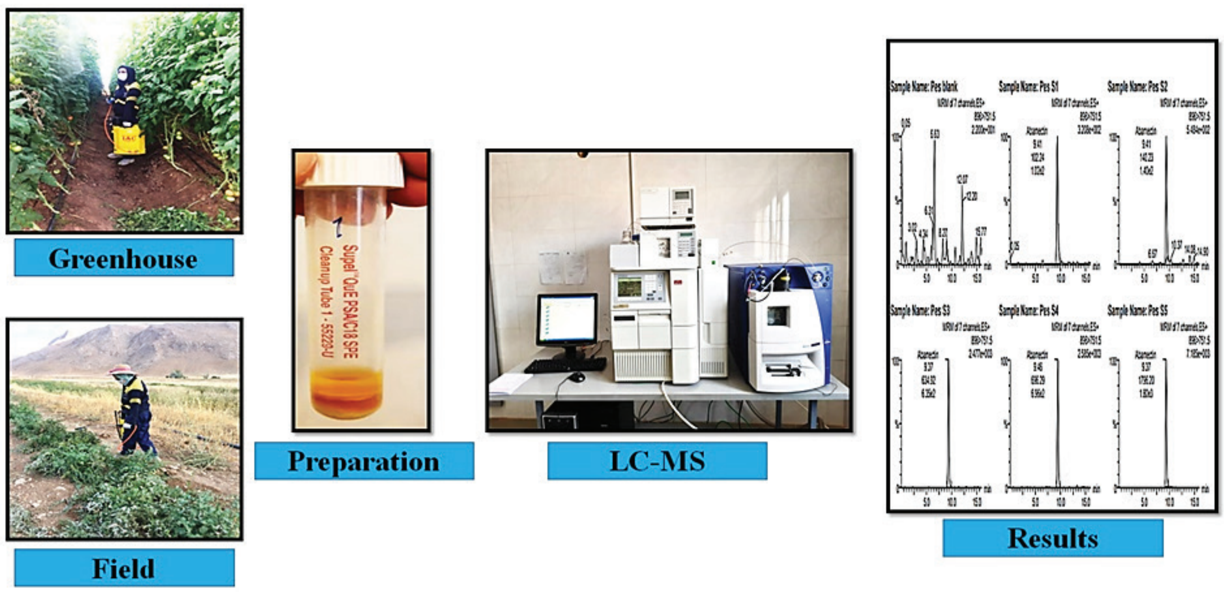
cause adverse effects due to the presence of residual pesticides in the crops [3]. Therefore, the European Union (EU) has set a maximum pesticide residue limit (MRL). The MRLs for studied pesticides in the present study included acetamiprid, deltamethrin, and abamectin in tomatoes are defined as 500, 70, and 90, respectively, regardless of the growth conditions [4, 5]. Ratnamma et al.'s study on the residual acetamiprid in okra showed that using 10 g and 20 g of 20% acetamiprid per hectare led to the residual of 2.034 and 4.044 mg kg^{-1}, respectively [6]. The results of Yazdan Pak et al.'s study on the residual pesticides in the greenhouse tomatoes during 2, 5, 7, 10, 14, 17, and 21 days after spraying showed that the residual of acetamiprid, diazinon, imidacloprid, and pirimicarb declined after the PHI period approached [7]. Mohamed et al. reported that imidacloprid decomposed faster than acetamiprid in tomatoes grown under greenhouse conditions [8]. Iran ranks seventh globally, accounting for 4.7% of the total world production of tomatoes, with an annual production of 5.8 million tons and an average yield of 38 tons per hectare [9]. According to the high production and consumption of raw and processed tomatoes in Iran and the use of high levels of pesticides in their cultivation, this study aimed to determine deltamethrin, abamectin, and acetamiprid residues in cultivated tomatoes in the field and greenhouse as raw and home processed using QuEChERS (quick, easy, cheap, effective, rugged, and safe) method and analysis of residual pesticides by liquid chromatography-mass spectrometry (LC-MS) method.

In this study, the residual concentrations of pesticides, including acetamiprid, deltamethrin, and abamectin, were extracted and determined by the QuEChERS procedure coupled to LC-MS. The residual concentration of three high-consumption pesticides of Iran in raw and processed tomatoes was determined and compared. Also, the residual concentration of the three mentioned pesticides in outdoor-grown (field-grown) and greenhouse tomatoes were studied and compared together. The current study was innovative in comparing the residual pesticides.

2. Material and Methods

This study was done in several stages included planting and spraying of tomatoes in field and greenhouse and harvesting, preparation of the samples through the QuEChERS method and their analysis of samples via LC-MS and statistical analysis of the data. Study stages are illustrated in Schema 1.



Schema 1. Study stages of sampling, the QuEChERS preparation method and determination by LC-MS

2.1. Instrumental

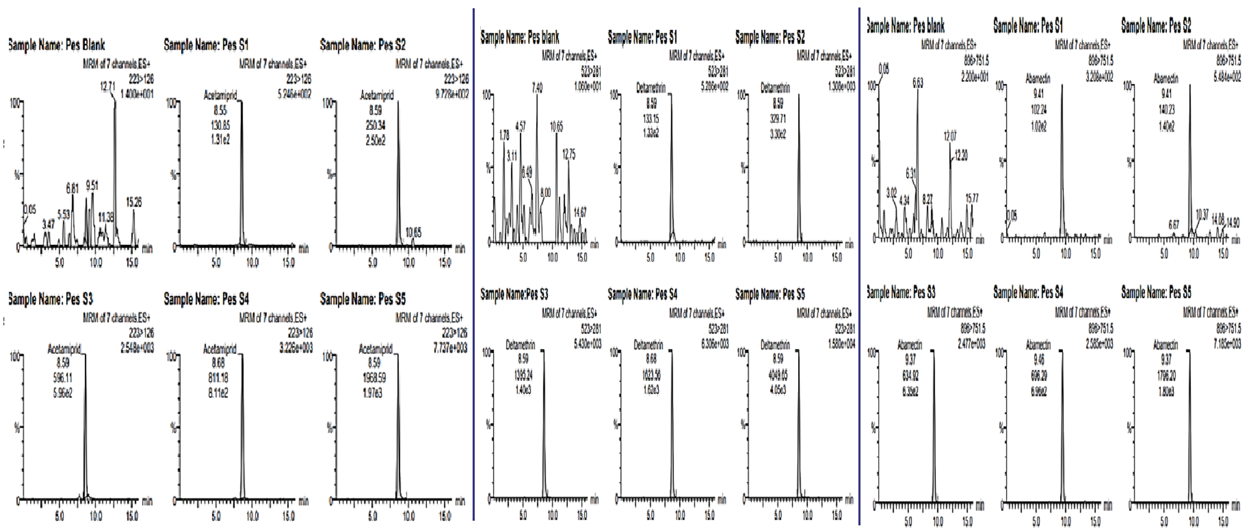
LC-MS is an accurate and precise method to separate, identification and analysis of compounds. It can be successfully and efficiently adopted for quality control analysis of compounds. It can also be used in combination with other analytical methods to further elucidate the components of mixtures [17]. LC-MS (model: Waters Alliance 2695 (UK)) using a matrix-matched method was used to analyze samples in the present study. The type of detector was Micromass Quattro Micro API Triple Quadruple Mass Spectrometer (UK). Column specifications were Waters Sunfire C18 Column 100 Å, 150 mm × 2.1 mm × 1.5 µm. The samples of 20 µL were injected into the device. Chromatograms of the standard samples to provide calibration curve have been illustrated in Schema 2.

2.2. Chemicals and reagents

Standards of Acetamiprid (99.9%), abamectin (95%), deltamethrin (98.5%), deltamethrin (2.5%EC), acetamiprid (20%SP), abamectin (1.8%EC) and other chemicals and reagents included acetonitrile, anhydrous magnesium sulfate, the internal standard of triphenyl phosphate, sodium chloride, trisodium citrate dihydrate, disodium hydrogen citrate, primary, secondary amine (PSA), and carbon adsorbent (C18) were purchased from Sigma Aldrich, Germany. Dilutions of 50, 100, 250, 500, and 1000 ng g^{-1} were used to plot the calibration curve of the pesticides using a matrix-matched method. The limit of detection (LOD), the limit of quantification (LOQ), the regression equation of calibration, and the MRL for the studied pesticides are mentioned in Table 1.

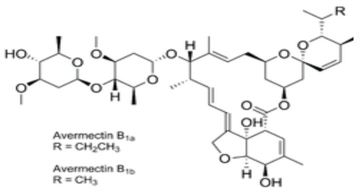
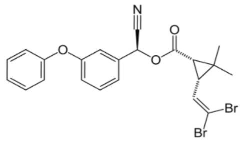
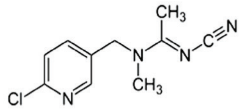
2.3. Planting and spraying of tomatoes in the field and greenhouse

A field and a greenhouse were respectively considered for planting tomatoes outdoors and in a greenhouse in the summer of 2020. The average temperature in the study period, namely the summer and fall of 2020, in the greenhouse and field was 20±3 and 8.9 °C. Four terraces were allocated for each treatment in the greenhouse and the field. The distance between tomato plants was considered to be 40 cm. Distances of 120 and 100 cm were defined between terraces in the greenhouse and field, respectively. An empty terrace was spaced between the terraces to eliminate the effects of overlap and possibly dispersion of pesticides through the wind. The control samples were grown on the unsprayed terrace. Randomized spraying was performed with a 20 L calibrated rechargeable back sprayer (model: IAC CODE: E2) according to the doses recommended by the Iran Plant Protection Organization, including 0.6 liters per hectare for abamectin, 300 cc per hectare for deltamethrin, and



Schema 2. Chromatograms of the five standard pesticides, including acetamiprid, deltamethrin, and abamectin for calibration curve

Table 1. Limit of detection (LOD), the limit of quantification (LOQ), the regression equation, and the maximum residue limit (MRL) for the studied pesticides

Pesticide	Abamectin	Deltamethrin	Acetamiprid
Chemical structure			
Chemical formula	$C_{95}H_{142}O_{28}$	$C_{22}H_{19}Br_2NO_3$	$C_{10}H_{11}C_1N_4$
MW (g mol^{-1})	1732.1	505.21	222.68
Water solubility	1.21 mg L^{-1} at 25 ºC	<0.002 mg L^{-1} at 25 ºC	4.25 g L^{-1} at 25 ºC
Octanol/water partition coefficient	4.4	6.10	0.8
Chemical Family	Insecticide, a natural fermentation product of soil-dwelling actinomycete, Streptomyces avermitilis	Pyrethroid insecticide	Neonicotinoid insecticide

0.5 kg per 1000 liters of water for acetamiprid. The physical and chemical characteristics of the studied pesticides [10-12] are reported in Table 2.

2.4. Sample harvesting

According to the manufacturer's instrument, the PHI period for deltamethrin and abamectin was defined as three days. Therefore, sample harvesting in the case of deltamethrin and abamectin was done in the suggested PHI period and before and after that, 1, 2, 3, 4, and 5 days after spraying. The manufacturer did not define the PHI period for acetamiprid. Thus, sample harvesting in the case of acetamiprid was done according to similar studies [13, 14], and the farmers' performance was 3, 5, 7, 9, and 11 days after spraying. After time elapsed, 2 kg samples harvested from different terraces were mixed and, after coding, placed in a black bag and maintained at 4 °C. Then, part of the samples was homogenized after washing to measure the residual pesticide in the raw sample, and the other part was used to prepare homemade tomato paste. To make tomato paste, the washed tomatoes were chopped, salted, and stored at room temperature for 24 hours. Then, the tomato juice was strained and heated at 96 °C for one hour. After cooling, the samples were packaged and coded separately.

Also, one sample of each treatment was taken one hour after spraying to compare the amount of pesticide residues in washed and unwashed tomatoes. Then, the samples were divided into two equal parts; one part was washed with tap water, and another part was reserved unwashed. Finally, the samples were maintained at -21 °C until experiments.

Table 2. Physical and chemical characteristics of the studied pesticides

Pesticide	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	Regression equation of calibration	R^2	*MRL
Abamectin	13.2	40	y=3.37761x +0.313794	0.9848	0.09
Deltamethrin	13.2	40	y=7.78742x-7.7343	0.9931	0.07
Acetamiprid	13.2	40	y=11.8763x-8.70884	0.9946	0.50

***MRL**: maximum residue limit of the European Union

2.5. Preparation and analysis of samples

The QuEChERS method, with its high sensitivity, is used to extract the residual pesticides in the products in many reference laboratories [15]. To extract pesticides in the current study by the QuEChERS method, each sample was homogenized in a blender, and 10 g of samples were transferred to the centrifuge tube. Then, 10 mL of acetonitrile and 100 µL of the internal standard of triphenyl phosphate were added to each centrifuge tube at the concentration of 10 ppm. Next, 4g anhydrous magnesium sulfate, 1.0 g sodium chloride, 1.0 g Trisodium citrate dehydrate, and 0.5 g disodium hydrogen citrate were added to each centrifuge tube after a vigorous shake for one minute. Again, the mixture was vortexed for one minute at 5000 rpm for 5 minutes at -10 °C. Then, 3 mL of the transparent top layer was transferred into the tube containing 75 mg PSA, 450 mg anhydrous magnesium sulfate, and 75 mg C18 adsorbent. Samples were finally moved into a vial after vortex for one minute and re-centrifuged [16]. Residual concentrations of pesticides in the samples were measured by the method of LC-MS. LC is an accurate and precise method to separate, identify and analyze compounds. It can be successfully and efficiently adopted for quality control analysis of compounds. It can also be combined with other analytical methods to further elucidate the components of mixtures [17].

2.6. Statistical analysis

Statistical analysis was performed using R software version 3.4.1. Results were reported as the mean ± standard deviation. The mean concentration of pesticides in different samples was compared via ANOVA. P-value < 0.05 was considered as the significance level.

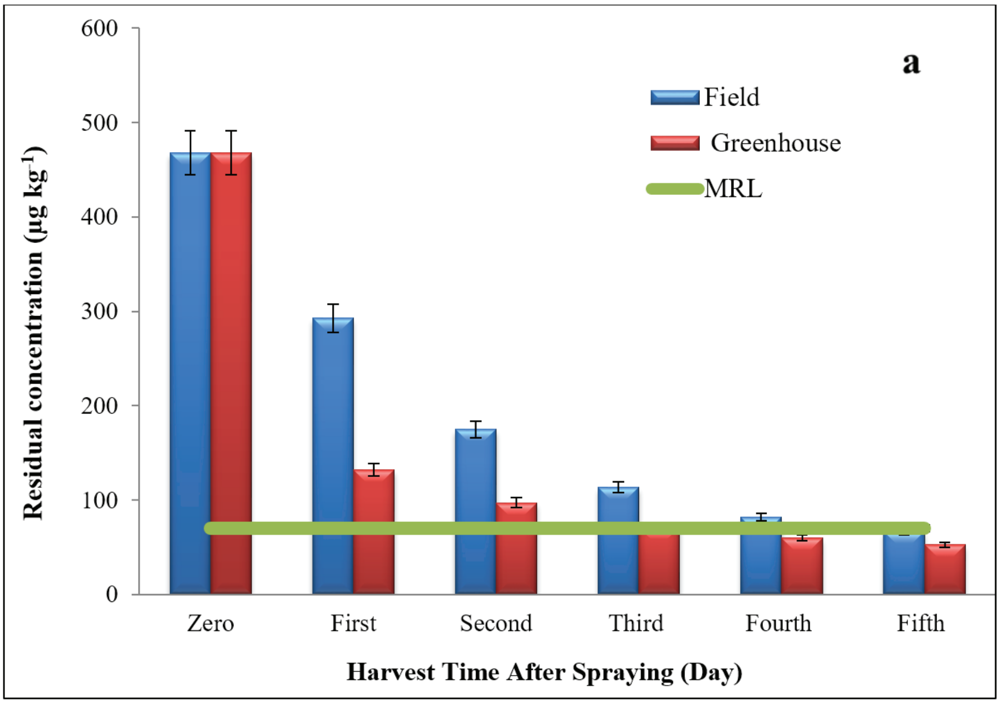
3. Results and discussion

3.1. Deltamethrin

The EU has determined the deltamethrin MRL in tomatoes as 70 µg kg^{-1}. The residual concentration of deltamethrin was reached less than MRL in the field and greenhouse on the fifth and fourth days after spraying, respectively (Fig. 1a). Therefore, considering the PHI period for deltamethrin, which has defined to be three days according to the manufacturer's instrument, its residual concentration met the MRL in both conditions. Residual concentration and reduction percentage of deltamethrin in raw tomato and paste of field- and greenhouse-grown are shown in Table 3. Comparison between the mean residual concentration of deltamethrin at different harvest times from 1 to 5 days with the MRL showed a non-significant difference in the field ($p = 0.14$) and greenhouse ($p = 0.43$). The mean difference of percentage reduction in raw tomato between the field (84.91%) and greenhouse (91.42%) conditions was not significant ($p=0.18$). The residual concentration of deltamethrin in tomato paste made from both field-grown and greenhouse-grown products showed a decreasing trend (Fig.1b). The concentration of deltamethrin in the paste from field products was decreased up to 95% on the fifth day after spraying. While its removal was more than 95% in the greenhouse products (Table 3).

3.2. Abamectin

The comparison of the residual concentration of abamectin in the field and greenhouse-grown tomatoes with the MRL of 90 µg kg^{-1} was shown in Figure 2a. The residual concentration of abamectin was less than MRL on the second day after spraying in both growing conditions (58 µg kg^{-1} and 77 µg kg^{-1}, respectively). The PHI period for abamectin has been defined to be three days based on the manufacturer's instrument. Thus, considering the PHI period for abamectin can reach its residual concentration below the MRL in tomatoes grown in the field and greenhouse. The decreasing trend was observed in the residual concentration of abamectin in the tomato paste made from field-grown and greenhouse-grown products (Fig. 2b). The concentration of abamectin was reduced to more than 89% in the paste made from crops in both conditions after five days (Table 3). The residual concentration of abamectin in the paste can reach below 40 µg kg^{-1} in the field and 46 µg kg^{-1} in the greenhouse, considering the PHI period in tomato (three days).



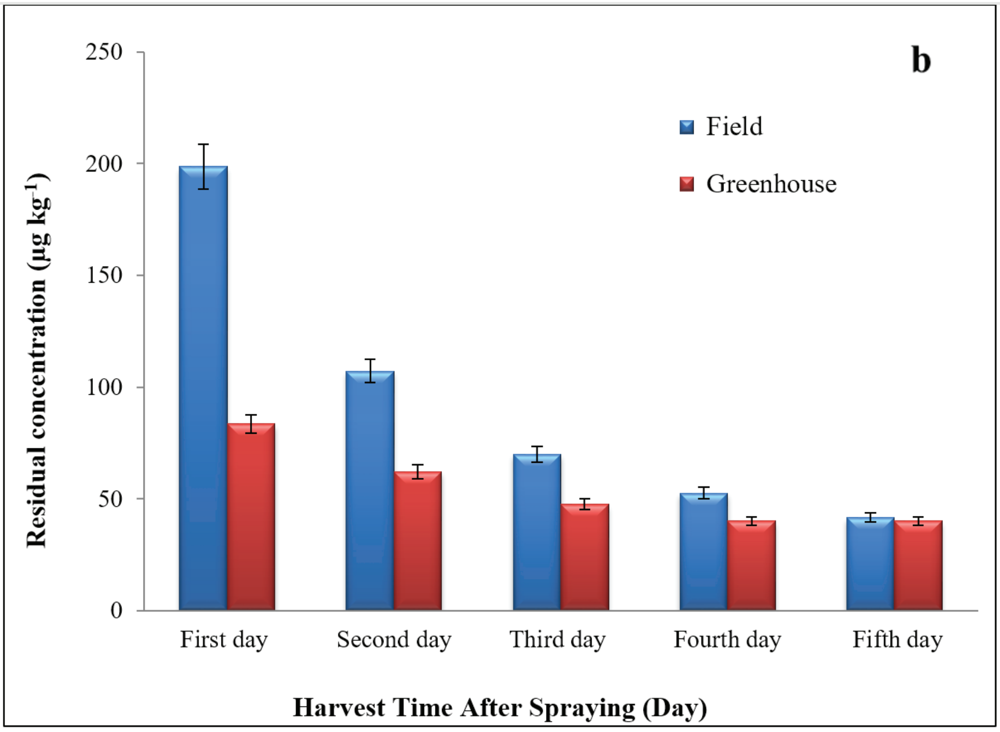


Fig. 1. The comparison of the mean residual concentrations of deltamethrin in field-grown and greenhouse-grown tomatoes (a) and paste (b)

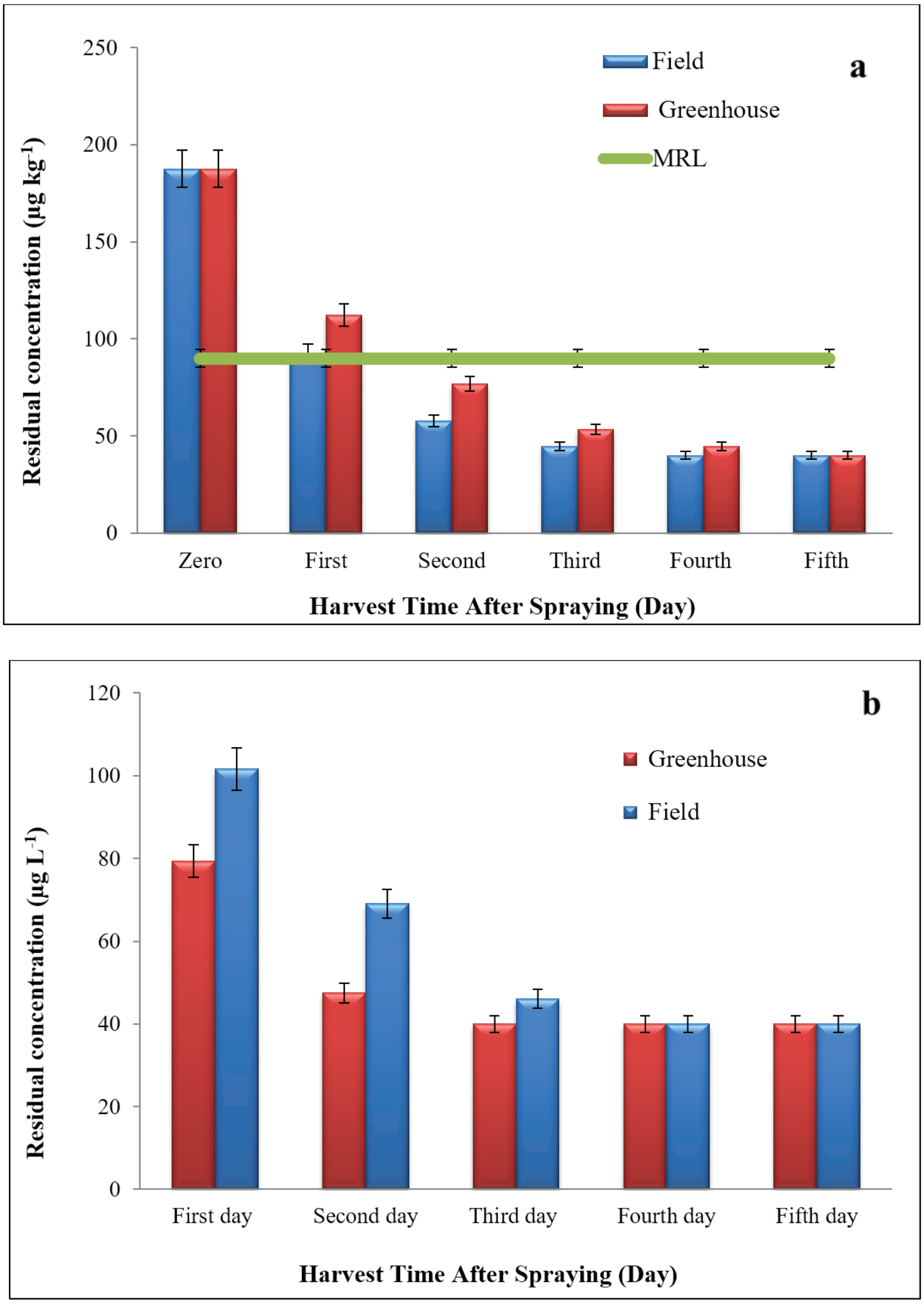


Fig. 2. The comparison of the mean residual concentrations of abamectin in field-grown and greenhouse-grown tomatoes (a) and paste (b) and the EU maximum residue limits

Table 3. Residual concentration and reduction percentage of deltamethrin, abamectin, and acetamiprid in raw tomato and paste of field-grown and greenhouse-grown

Pesticide		Raw tomatoes				Tomato paste			
		Field		Greenhouse		Field		Greenhouse	
	Day	RC (µg kg^{-1})	PR (%)	RC (µg kg^{-1})	PR (%)	RC (µg kg^{-1})	PR (%)	RC (µg kg^{-1})	PR (%)
Deltamethrin	1	292.62	69.74	131.91	86.36	198.70	79.45	83.50	91.36
	2	174.80	81.92	97.30	89.93	107.20	88.91	62.10	93.57
	3	113.40	88.27	71.61	92.51	69.91	92.77	47.90	95.08
	4	81.91	91.53	59.82	93.80	52.50	94.57	<40	>95.86
	5	66.60	93.11	52.52	94.50	41.60	95.69	<40	>95.86
Mean		145.87	84.91	82.63	91.42	93.98	90.28	-	-
MRL		70	-	70	-	-	-	-	-
p-value		0.14*	0.18**	0.43*	-	-	-	-	-
Abamectin	1	92.60	75.58	112.34	70.38	79.40	79.06	101.60	73.21
	2	57.80	84.75	76.80	79.74	47.50	87.47	69.11	81.77
	3	44.81	88.18	53.50	85.89	<40	>89.45	46.12	87.84
	4	<40	>89.45	44.70	88.21	<40	>89.45	<40	>89.45
	5	<40	>89.45	<40	>89.45	<40	>89.45	<40	>89.45
Mean		-	-	-	-	-	-	-	-
MRL		90	-	-	-	-	-	-	-
p-value		-	-	-	-	-	-	-	-
Acetamipride	3	835.61	77.76	538.41	85.67	476.33	87.32	328.11	91.27
	5	577.622	84.63	418.91	88.85	340.71	90.93	242.91	93.53
	7	462.33	87.69	359.71	90.42	277.40	92.61	215.81	94.25
	9	371.61	90.11	301.62	91.97	234.11	93.77	193.21	94.85
	11	319.52	91.49	259.81	93.08	210.61	94.39	172.51	95.41
Mean		513.34	86.34	375.69	90.00	307.83	91.80	230.51	93.86
MRL		500	-	500	-	-	-	-	-
p-value		0.89*	0.22**	0.06*	-	-	0.19**	-	-

*Comparison between mean concentration and maximum residue limit (MRL),
**Comparison between percentage reduction in field and greenhouse
RC: Residual concentration
PR: Percentage reduction

3.3. Acetamiprid

The EU defined the concentration of 500 μg kg^{-1} as the MRL level for acetamiprid. The mean residual concentration of acetamiprid in the field, greenhouse, and MRL level is compared in Figure 3a. The results showed that the residual concentration of acetamiprid in raw tomato in the field from the seventh day (462 μg kg^{-1}) and in the greenhouse from the fifth day (419 μg kg^{-1}) reached below the MRL by LC-MS. The manufacturer has not defined the PHI period for acetamiprid. Therefore, the acetamiprid PHI period of 7 days for the field-grown and 5 days for the greenhouse-grown tomato can be suggested based on the results of the current study. The difference in the mean reduction percentage of acetamiprid in the field-grown (86.34%) and greenhouse-grown (90.00%) samples were not significant (p=0.22). Comparing the mean residual concentration of acetamiprid in raw tomato and the MRL (500 μg kg^{-1}) showed a non-significant difference in the field (p=0.89) and greenhouse (p=0.06). The residual concentration of the acetamiprid in the tomato paste after spraying field-grown and greenhouse-grown products followed a decreasing trend (Fig. 3b). The concentration of acetamiprid was approximately reduced to 95% in the paste made from crops in both conditions after 11 days (Table 3). The mean percentage reduction of acetamiprid in the paste from greenhouse crops (93.86%) was insignificantly (p = 0.19) more than field crops (91.80%).

Elbashir et al. measured the residual concentrations of fenpropathrin, λ-cyhalothrin, and deltamethrin in field-grown tomatoes for 30 days. The results showed that the pesticide residues of fenpropathrin after 27 days, λ-cyhalothrin after 18 days, and deltamethrin after three days immediately after washing reached below the MRL defined by the Codex and the EU [18]. In Salghi's study on evaluating residual pesticides' organochlorine, pyrothyroid, and dicarboximide in greenhouse-grown tomatoes, the residual concentration of deltamethrin was reported in the range of 1-0.01 mg kg^{-1}. The residual concentration of pesticides in the two studied samples was higher than the MRL [19]. Due to the Rafiei's study, the results of deltamethrin in greenhouse-grown cucumber showed that the residual concentration of pesticide reached the allowable limit (0.2 mg kg^{-1}) on the fifth day after spraying and was not measurable on the seventh day after it [20]. In Abdelfatah's study on the residual concentrations of abamectin, acetamiprid, spinosad, diniconazole, penconazole, and fipronil in the field-grown tomatoes, residual concentrations of abamectin and acetamiprid were reported one hour after spraying as 5.80 and 1.10 mg kg^{-1}, respectively. The results of this study showed that ten days after spraying with abamectin and one day after spraying with acetamiprid, the residual pesticides reached below the EU MRL [21]. The study of Fujita et al on the residual amount of acetamiprid, azoxystrobin, permethrin, and dinotefuran in field-grown and greenhouse-grown lettuce showed that the residual concentrations of pesticides in the greenhouse crop were approximately the same as in the field, but for dinotefuran, the residual pesticides in the greenhouse crop were higher than that in the field [22]. According to Badawy et al.'s study, the residual concentrations of acetamiprid and imidacloprid in greenhouse-grown tomatoes reached below the Europe MRL within three days and five days after spraying, respectively [8]. The results of Chen et al.'s study on the residual concentration of propamocarb in greenhouse-grown and field-grown vegetables showed that the residual of propamocarb in the greenhouse crop was higher than the field crop [23].

3.4. Comparison of different condition

In comparison between mean reduction percentages of pesticides in tomato grown in different condition in the present study, it can be stated that residual concentration of both deltametrin (91.42%) and acetamiprid (90.00%) in the greenhouse was decreased more than field (84.91 and 86.34%, respectively) by LC-MS. Abamectin reached below the MRL in a shorter time after spraying (2 days) compared to other pesticides. The extent of pesticide residues in the agricultural products depends on several factors such as the properties of pesticide, its formulation and applied concentration, light, temperature, plant morphology and plant growth factors [24].

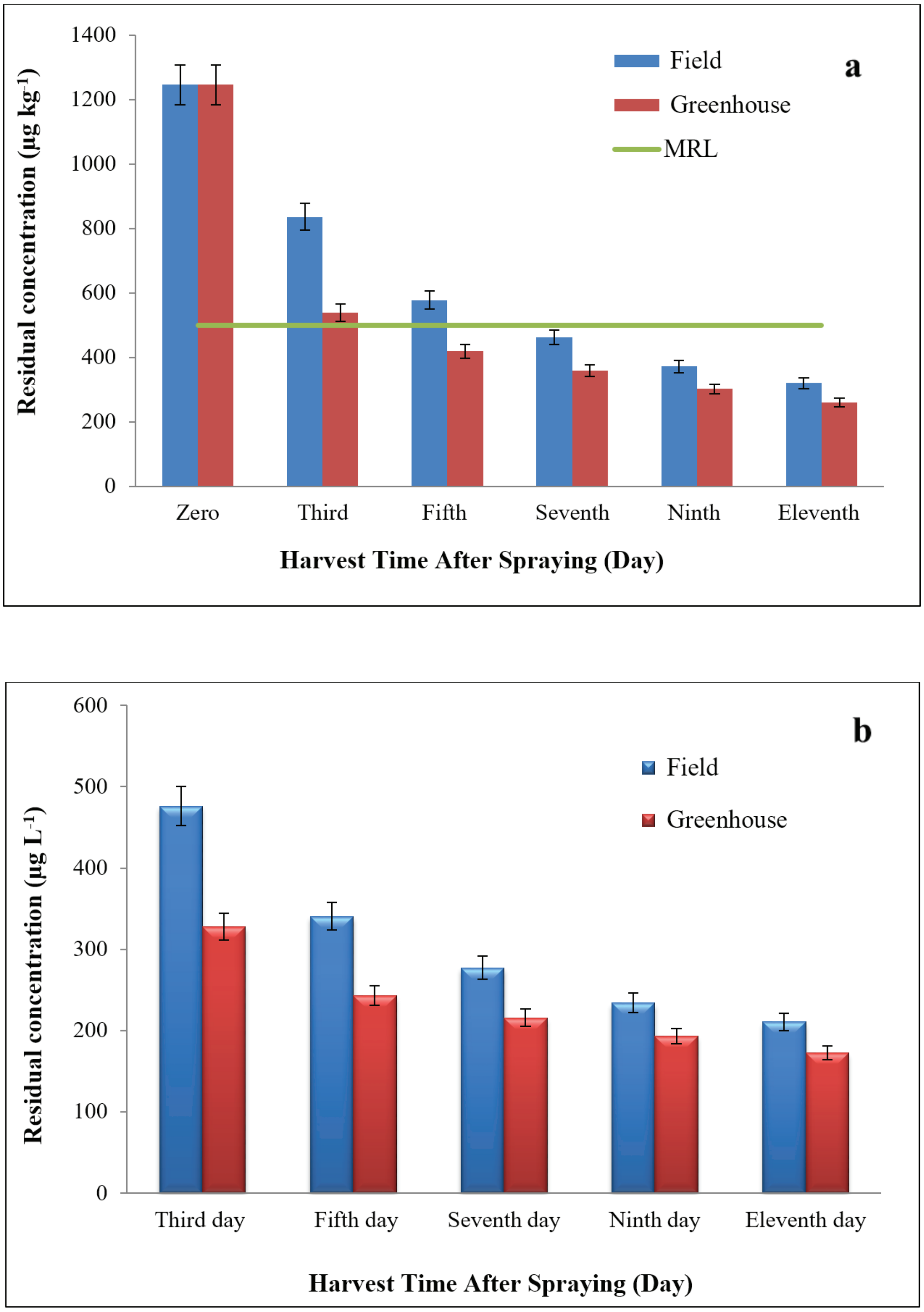


Fig. 3. The comparison of the mean residual concentrations of acetamiprid in field-grown and greenhouse-grown tomatoes (a) and paste (b)

In comparison between raw tomato and tomato paste in both grow condition, it was found that processing of the raw tomato through cooking could decrease the concentration of pesticides in all experiments by LC-MS. Difference of residual concentration of pesticides in the raw and processed products was found to be in the range of 0-10%, and a significant reduction was not observed with the processing product. In Medina et al.'s study evaluating the effect of cooking on the residual pesticides deltamethrin, penconazole, cresoxime methyl, cyproconazole, epoxiconazole, and azoxystrobin in rice, the results reported the reduction of pesticides as 20.73% to 57.72% for home cooking, 32.74% to 70.39% for washing with excess water, and 68.87% to 87.50% for soaking rice before cooking, respectively [25]. The results of Romeh's study examining the processing process on the residual acetamiprid in field-grown eggplant showed that washing 24.73%, boiling 56%, grilling 99%, and frying 46.24% affected the reduction of its residual one day after spraying with the recommended dose [26]. In 2016, Hanafi et al. examined the reduction of non-systemic and low-systemic (indoxacarb, chlorfenapyr, and fenarimol) and systemic (acetamiprid) pesticides in okra after the cooking process. The residual acetamiprid was reduced up to 90% using cooking methods, indicating that the tissues of the okra disintegrated during cooking, so the internal remnants of acetamiprid were exposed to water dissolution and thermal decomposition [27]. The reduction percentage of pesticides in washed and unwashed tomato samples was compared. The significant effect of reducing the residual pesticides of abamectin, deltamethrin, and acetamiprid was observed after washing with tap water. Rinsing with tap water reduced the residual concentrations of acetamiprid, abamectin, and deltamethrin in the crops harvested during one hour after spraying up to 66.85%, 51.62%, and 50.52%, respectively (Table 4). Acetamiprid, as a systemic pesticide, with the highest solubility in water (4250 mg L^{-1}), had the highest reduction percentage after washing compared to the other pesticides. Washing is the first step in the food preparation process and processing methods. Many residual pesticides can be removed by washing them with tap water. Various factors affect the residual pesticides after washing, including the location of the pesticide in the crop (on the surface or in the tissue), washing method, soaking time, physicochemical properties of the plant and pesticide, and the type of pesticide. Pesticides with high water solubility can be more easily eliminated, probably due to their reduced tendency to enter the inner layers [24, 28, 29]. Ajeep et al.'s study on the effect of washing with tap water and washing with an acetic acid solution on the residual amount of five insecticides (dimethoate, carbaryl, chlorpyrifos, cypermethrin, and fenvalerate) and one herbicide (2, 4-dichloro phenoxy acetic acid) in tomato showed that both washing methods reduced the concentration of pesticides by a maximum of 63.08% [30]. In Shalaby's study, it was reported that washing with tap water and acetic acid (1%) could decrease the residual concentrations of abamectin and buprofezin in eggplant and pepper plants two hours after spraying up to 21.86% for washing with water and 41.68% with acetic acid [31]. In Hanafi et al.'s study on okra, the initial residual concentration for chlorfenapyr and acetamiprid was reported to be 7.5 mg kg^{-1} and 0.8 mg kg^{-1}, respectively, which after washing the okra with water, the residual reduction percentage was reported to be 90% for chlorfenapyr and 48% for acetamiprid. This finding is contrary to the water solubility of two studied pesticides [27]. In Elbashir et al.'s study, the residual concentrations of fenpropathrin, λ-Si haloterine, and deltamethrin in outdoor-grown tomatoes were measured over 30 days. The results showed that the residual pesticides fenpropathrin after 27 days, λ-Si haloterine, after 18 days, and deltamethrin after three days in unwashed samples reached below the MRL set by the Codex and the EU. This amount immediately after washing reached below the MRL in the washed samples [18]. Moreover, some methods such as ultrasound-assisted dispersive micro solid-phase extraction, micro-column solid-phase extraction, adsorption (silver nanoparticles, Sulfide Nanoparticles) were used for extraction process [33-38]. The results of similar studies were compared with proposed methods in Table 5.

Table 4. Comparison of reduction percentage of deltamethrin, abamectin, and acetamiprid in unwashed and washed tomato

Pesticide	Unwashed	Washed	Reduction (%)
Acetamiprid	3758.40	1245.80	66.85
Abamectin	967.10	467.80	51.62
Deltamethrin	379.20	187.60	50.52

Table 5. Comparison of proposed method based on LC-MS technique with the published similar studies

Pesticide	Instrument	Product	Condition	Pesticide Residues	Ref.
Acetamiprid	HPLC	Tomato	Greenhouse	Acetamiprid residues were below the already established European maximum residue limits (EU MRLs) (0.5 mg/kg) 3 days after application.	[8]
Abamectin	HPLC	Tomato	Field	The maximum residues level (MRL) values set by EU for abamectin are 0.02 mg/kg (EU, 2005). Based on these MRL values, PHIs were 7 d.	[21]
Acetamiprid	HPLC	Tomato	Greenhouse	The residual amount of acetamiprid pesticides in tomatoes is decreasing as the PHI approaches.	[32]
Acetamiprid	LC-MS/MS	Lettuce	Field and Greenhouse	No clear difference between the two growing conditions was observed.	[22]
Acetamiprid	LC-MS	Tomato	Field and Greenhouse	The reduction rate of acetamiprid residue in tomato was faster in greenhouse conditions than in the field.	This Work
Deltamethrin				The reduction rate of delthamethrin residue in tomato was faster in greenhouse conditions than in the field.	
Abamectin				The reduction rate of abamectin residue in tomato was faster in the field than in the greenhouse.	

4. Conclusion

The present study aimed to investigate the residual concentrations of pesticides deltamethrin, abamectin and acetamiprid in field-grown and greenhouse-grown tomatoes as raw and processed in the form of homemade tomato paste by LC-MS. The rank of reduction percentage of pesticides at the end of the harvest period in the raw and paste products under both conditions followed as deltamethrin, acetamipride and abamectin. Considering the PHI period for deltamethrin and abamectin (3 days) can reach their residual concentration to the MRL in both conditions. According to results of the current study, the times of 7 days and 5 days can be suggested as PHI period of the acetamiprid for field-grown and greenhouse-grown tomato, respectively. According to the data obtained from the current study and the reduction percentage of the residual amount of pesticide from raw product to processed product under field and greenhouse conditions, it was found that the difference was in the range of 0-10% and significant reduction was not observed with the processing product. The general conclusion that can be inferred from this study was that the highest and most remarkable reduction in the residual amounts of pesticide was related to the washing step, which can reduce the residual pesticide up to 66% which analyzed by LC-MS. It can be suggested to study the initial residues in unwashed, washed, and processed samples, and the residual concentration of pesticides in the soil during the harvest period, and environmental effects in future studies.

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7. Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. This work was supported by the Vice-Chancellor for Research and Technology of Kerman University of Medical Sciences under the code of research ethics certificate IR.KMU.REC.1399.600.

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