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RESEARCH ARTICLE

Method validation and evaluation of household processing on reduction of pesticide residues in tomato

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Abstract
Metalaxyl and chlorpyriphos are widely used pesticides around the world. The purpose of this study was to evaluate validation parameters, matrix effect (ME %), reduction behavior, processing factor (PF) and estimate the behavior of metalaxyl and chlorpyriphos in tomato fruit samples. "Quick, Easy, Cheap, Effective, Rugged, and Safe" (QuEChERS) extraction and gas chromatography coupled to mass spectrometry (GC/MS) were used for the analysis. Results showed successful trends by evaluating validation parameters [selectivity, linearity, limits of detection (LOD), limits of quantification (LOQ) and precision]. The correlation coefficients were > 0.99; the LOD for metalaxyl ranged from 0.01 to 0.003 mg/kg and the LOQ for chlorpyriphos ranged from 0.03 to 0.009 mg/kg. The matrix effect (ME %) of metalaxyl was found to exhibit a medium matrix effect while for chlorpyriphos no matrix effect was seen. Recovery (70–120%) and precision (RSD $< 20\%$) for both pesticides metalaxyl and chlorpyriphos were within the satisfactory ranges recommended by the European Commission. The PF was generally < 1 (ranged between 0.34 and 0.98). Except when using washing solutions, metalaxyl PFs were > 1. The highest reduction rate was achieved by sonication treatments which could effectively remove chlorpyriphos residues spiked in tomato matrices rather than the metalaxyl residues. On the other hand, washing treatments were less efficient in removing metalaxyl residues from tomato samples. Overall, any one of these processes can contribute substantially to reduce consumer exposure to pesticides residues in tomatoes.

Keywords GC/MS · Matrix effect · Pesticides · Processing factor · QuEChERS · Tomato

1 Introduction

Tomatoes are widely consumed in several countries and considered as functional food, because they contain antioxidants such as ascorbic acid, vitamin E, carotenoids, flavonoids, lycopene, and phenolic acids. On the other hand, tomatoes are susceptible to pests, and pesticides are needed in the different phases of cultivation to control pests and diseases that may cause yield reduction; however, the presence of pesticide residues in tomatoes may be harmful to health (Reiler et al. 2015).

Metalaxyl [methyl D, L, N-(2,6-dimethylphenyl)-N-(2-methoxiacetyl) alaninate] is a systemic fungicide of the alaninate group (Worthing and Hance 1991), used to control *Peronosporales* fungi, which cause diseases in several crops, chiefly orange, lemon, potato, tomato, and tobacco (Sujkowski et al. 1995). This fungicide is available in different formulations such as Apron 35 WS (for seed treatment), Ridomil 5 G (for soil treatment), Ridomil 25% WP, Vacomil 35% WP (for foliar sprays) and in a mixture with mancozeb; captan; folpet, carbendazim and copper oxychloride. Metalaxyl is registered for use in many countries worldwide. Zadra et al. (2002) and Li et al. (2013) reported that metalaxyl is stable to hydrolysis under normal environmental pH values. It is also photolytically stable in water and soil when exposed to natural sunlight. Chlorpyriphos [O, O, -diethyl-O-(3, 5, 6-trichloro-

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2pyridyl) phosphonothioate] is an organophosphorus broad-spectrum insecticide registered for application to more than 40 different food crops. It is non-systemic and fairly persistent, but almost insoluble in water (2 mg L^{-1}). Chlorpyriphos has the potential toxicity in humans (Rani et al. 2013).

Validation parameters such as sensitivity, linearity, specificity, trueness, precision, LOD, LOQ, and matrix effect are commonly evaluated in pesticide residues determination by chromatography techniques (SANTE/11813/2017). It is established that the matrix effect is significant when $> \pm 20\%$. In recent years, it has been essential to use matrix-matched calibration in the routine procedure of pesticide analysis in food by chromatographic methods to avoid an error caused by the presence of matrix effect (Kwon et al. 2012). It is important to highlight that the pesticides contain at least one of these functional groups such as hydroxyl, amino, and phosphate, react with the active surfaces in the GC/MS (injector, column, and detector) system. Therefore, to avoid the matrix effect and ensure reliable results, it is necessary to use matrix match calibration curves.

The effect of food processing on pesticide residues have been reviewed comprehensively over the last decade. Processing factors (PFs) are the ratio of residue concentrations after processing the raw commodity. PF values > 1 indicate an increase in pesticide residue concentrations after processing; PF values < 1 indicate a decreases in pesticide residues. PF depends on both the crop and the physicochemical properties of pesticides. Peeling and storage are important processing procedures that can remarkably reduce non-systemic pesticide residues in some fruits and vegetables (Ramezani and Shahriari 2015).

Hanafi et al. (2016) investigated the effect of various treatments to reduce high-risk pesticide residues like indoxacarb, fenarimol, acetamiprid and chlorfenapyr in okra fruits by washing, boiling or steaming in different time intervals, followed by a cooking treatment. The results showed that after washing, the reduction of residues was not correlated to water solubility. Chlorfenapyr (non-systemic pesticide) was decreased by 90% and acetamiprid (systemic pesticide) by 48%. The pesticide residues were washed off by removing the loosely attached pesticides on the okra fruit surface.

Lozowicka et al. (2016) determined PFs for 16 pesticide residues in raw strawberries, where washing with ozonized water was more effective than washing with tap water (36.1 to 75.1% vs. 19.8 to 68.1%, respectively). Boiling decreased the residues of the most compounds, with reductions ranging from 42.8 to 92.9%. Ultrasonic cleaning lowered residues for all analyzed pesticides with removal of up to 91.2%. The data indicated that ultrasonic cleaning and boiling were the most effective treatments for the reduction of 16 pesticide residues in raw strawberries, resulting in a lower health risk exposure. The level of pesticide residues is affected by washing, preparatory steps, heating or cooking, processing during product manufacturing and post-harvest handling and storage. Washing raw materials is the simplest way to reduce the pesticide residue in the final product (Bajwa and Sandhu 2014).

The British Crop Protection Council (2014) and Devine et al. (1993) reported that washing and peeling of tomatoes efficiently removed almost all chlorpyriphos and ethyl-parathion. This was expected, as these 2 organophosphates have log Kow values of 4.7 and 3.84, respectively, making them immobile in plant tissue and therefore located on the outer surface of the peel.

According to Celik et al. (1995) organophosphorus residues were reduced by 9–40% by washing tomatoes and peppers, depending on the type of crops and pesticide. Holland et al. (1994) reported an appreciable reduction of pesticide residues in different commodities by using different processing methods.

Andrade et al. (2015) reported that washing tomato samples with 10% sodium bicarbonate solution efficiently reduces dimethoate residues, while washing with 10% vinegar solution was recommended for reduction of acetamiprid and procymidone. Washing with 10% bicarbonate and vinegar solution were efficient to reduce imidacloprid and thiamethoxam, washing with water showed the lowest residue concentration for diflubenzuron; and washing with water and vinegar, did not differ significantly for azoxystrobin. Washing did not effect fipronil residues.

This study was conducted to evaluate validation parameters and processing factors of metalaxyl and chlorpyriphos in Egyptian tomato samples.

2 Materials and methods

2.1 Tomato samples

Organic tomato fruits were bought from a local food market (ISIS), supplied with a certification label (blank values were not higher than 30% of the limit of quantification, LOQ).

2.2 Commercial pesticides

Ridomil 72% contains 8% of metalaxyl active ingredient, and commercial Helban 48% contains 48% of the Chlorpyrifos active ingredient, were obtained from the local market.

2.3 Certified reference material (CRM)

Metalaxyl (1000 ug/ml) dissolved in acetone were supplied from SPEXCertiPrep, New Jersey, USA. Chlorpyrifos 1000 µg/mL in methanol, were supplied from Restek, Pennsylvania, USA. Acetonitrile (HPLC grade, assay 99.9%) were obtained from Merck KGaA, Darmstadt, Germany. Hydrogen peroxide solution 31% (Ultrapure), anhydrous Sodium bicarbonate and acetic acid were purchased from Sigma-Aldrich, St. Louis, USA. The QuEChERS kit consisted of extraction packets and dispersive SPE kit suited to the tomato matrix, were purchased from Agilent Technologies, California, USA.

2.4 Instruments

Qualitative and quantitative determination of pesticide residues were performed on a 7890B gas chromatograph coupled to an Agilent 5977A mass detector (Agilent Technologies, Wilmington, USA), the chromatographic separation was achieved by using an analytical column Zebron ZB-5MS Crossbond (30 m, 0.25 mm internal diameter, 0.25 mm film thickness) from Phenomenex, Torrance, CA, USA. To provide excellent surface inertness for trace pesticide analysis (Zhao, and Mao 2011, Zhao 2013). An Agilent ultra-inert splitlesss single taper liner with glass wool (p/n 5190-2293) was used. A laboratory Blender (Waring, Stamford, USA), an analytical balance, model ME 104 (Mettler Toledo, Greifensee, Switzerland), a Vortex-mixer, (VELP scientific, Usmate Velate, Italy), centrifuge (BOECO, Hamburg, Germany), and Ultrasonic Tabletop Cleaner, model P 230 (CREST Ultrasonics, Penang, Malaysia).

2.5 GC-MS analysis

The column temperature was raised from 60 °C (hold 1 min) to 170 °C at 20 °C/min, then to 285 °C at 5 °C/min. The inlet temperature was maintained at 250 °C, injection of 2µl at splitless mode, purge flow 50 ml/min at 0.75 min, Helium with purity grade 6 for 9 s, was used as the carrier gas at constant flow 1 ml /min. The mass detector was operated in electron impact (EI) ionization mode at 70 eV. The temperatures of the transfer line, ion source and quadrupole were set at 285, 250 and 150 °C, respectively. Mass spectra in the full-scan mode were collected at the rate of 1.5 scans/s over the mass range (m/z) of 40–550 after acquisition of the total ion chromatogram for stock standard solutions in scan mode, metalaxyl and Chlorpyrifos peaks were identified by their retention time (RT) and mass spectra. Selected ion monitoring (SIM) mode was used for the quantitative purpose.

2.6 Extraction and clean-up

The samples were treated according to the QuEChERS methodology (European Standard 1566).

2.7 Method validation and matrix effect

The method was validated for linearity, LOD, LOQ, recovery, precision, and matrix effect as recommended by the European Commission (SANTE/11813/2017). A linear calibration curve was prepared by plotting peak area of each pesticide against pesticide concentration. The linear range of the method was evaluated by calculating the regression coefficients (r^2). LOD and LOQ calculations were based on the standard deviation of the response and the slope. The method precision was expressed as the relative standard deviation (RSDr) for repeatability which calculated as relative standard deviation (RSDr) of 5 replicates of spiked blank tomato samples (raw, juice, and pulp) at 2 concentration levels of 0.03 and 0.5 mg/ kg for metalaxyl, 0.01 and 0.5 mg/ kg for chloropyrifos. The percentage recoveries (R %) for chlorpyrifos and metalaxyl were calculated. Matrix effect (ME %) was estimated by comparing the slopes of solvent calibration curves and matrix matched calibration curves. ME % was calculated according to Guedes et al. (2015).

2.8 Preparation of contaminated samples

Tomato samples were contaminated by immersion into the pesticide solution. Organic tomatoes were manually washed in distilled water and dried with filter paper, then dipped into a solution contain 0.5 g Ridomil 72% and 2 ml of Helban 48% per liter of deionized water. To obtain a sufficient quantity of suspension, the samples where immersed for 1 h until the pesticide residue levels did not increase. The contaminated tomatoes were air dried for 24 hrs at room temperature before processing (Cengiz et al. 2017).

2.9 Processing treatments

The following treatments were assessed to evaluate the removal of pesticides residues:

1. Juicing and pulping of raw tomatoes
2. Washing: tomatoes were divided into 4 groups
    - Group 1: tomatoes were washed by immersing in tap water entirely for 10 min, then air-dried at room temperature for 25 min,
    - Group 2: tomatoes were washed with 1% sodium bicarbonate solution for 10 min,

- Group 3: tomatoes were washed with 4% acetic acid solution for 10 min,
- Group 4: tomatoes were washed with 1% H_2O_2.

3. Sonication: Tomatoes were divided into 3 groups and cleaned in an ultrasonic cleaner (45 kHz) filled with distilled water in ultrasonic bath experiment (UB):
   - Group 1: the contaminated tomatoes were soaked in distilled water and cleaned in an ultrasonic cleaner (45 kHz) for sonication for 15 min (UB1),
   - Group 2: sonication for 30 min. (UB2) and
   - Group 3: sonication for 60 min. (UB3).

Three representative replicates were taken from each treatment for residue analysis. After each experiment, the samples were extracted and analyzed and the percentages of reduction were calculated and compared with control.

2.10 Processing factors

The PF values of < 1 indicate a reduction in residues in a processed commodity, whereas values of > 1 indicate concentration effects from the processing procedures. PFs were calculated with following equation (Timme and Walz 2004):

$$PF = \frac{\text{Residues in processed product (mg/Kg)}}{\textit{Residues in raw agricultural commodity } (mg/Kg)}$$

3 Results and discussion

3.1 Evaluation of method validation and matrix effect

The (SIM) mode was used; the monitored ions were 105, 142, 192 for metalaxyl and 197, 199, 314, 316 for chlorpyrifos. The identification procedure for the pesticide residues was the retention time of metalaxyl (13.59 min.) and of chlorpyrifos (14.63 min.). The LOD and LOQ obtained for metalaxyl and chlorpyriphos was based on matrix matched calibration data at low levels of concentrations (supplementary data) which illustrates complete raw data of calculation as we spike blank tomato matrix with pesticides at conc. levels 5, 10, 25, 50, 100 ug/kg each in 5 replicates. Subjected to all the method preparation and injection steps, we found the detector response correlating to its concentration (peak area), calculating the average using data analysis function to calculate LOQ and LOD. The LOD and LOQ for metalaxyl were 0.01 mg/ kg, and 0.03 mg/ kg respectively, while LOD and LOQ for chlorpyrifos were 0.003 mg/ kg, and 0.009 mg/ kg, respectively. Before pesticide residue analysis, recovery experiments were carried out on tomato fruit, tomato juice and tomato pulp. Recovery and precision data are shown in Table 1. The percentage of recovery for metalaxyl in tomato fruit at 0.03 and 0.5 mg/ kg fortification levels were 99.4% and 95.3% with RSD 7.2 and 10, respectively. Whereas in tomato juice recoveries were 90.8% and 100.9% with RSD 12 and 15, respectively. In tomato pulps, the recovery percentage was 98.7 and 92 with RSD 10 and 11.9, respectively. For chlorpyrifos, the recovery percentages were 101.7% and 98.0% in tomato fruits with RSD 11.3 and 6.9, respectively. While in tomato juice recoveries were 91.4% and 96.2% with RSD 12.6 and 10.5, respectively. In tomato pulps the recovery percentage was 97.5% and 96.7% with RSD 7.7 and 8.33 at fortification levels 0.01 and 0.50 mg/ kg, respectively. Recoveries percentage and precision (RSD) within the satisfactory limits recommended by the European Commission and meet the requirements of SANCO guidelines (SANTE/ 11813/2017). The presented linearity with the analytical signal (Table 2), indicated by the values of regression coefficient (r^2) was > 0.99 for both compounds in solvent, and in the matrix (De Sousa et al 2012; Domínguez et al 2014). The ME % (suppression or enhancement) is the signal increase or loss of an analyte in matrix-amended standard solution compared to a matrix-free one. For metalaxyl, ME % was −24.17, categorized as a medium matrix effect. While the ME % of chlorpyrifos was -12.29, categorized as no matrix effect (Table 2). These results were in agreement with the findings reported by Ferrer et al. (2011). The matrix effect of metalaxyl in tomato may be due to its acidic nature (Chawla et al. 2017).

3.2 Effect of various household processes

Figure 1 shows the reduction of the first treatment (raw tomato, tomato juice, and tomato pulp) on both metalaxyl and chlorpyrifos residues. The juicing process was the most effective process in removing both pesticides; metalaxyl residues were reduced by 66% in tomato juice and 49% in tomato pulp, while chlorpyrifos residues were reduced by 98% in tomato juice and 81% in tomato pulp. Figure 2 shows the reduction after treatment 2 (washing) showing the less efficient removal of both pesticide residues: The residues of metalaxyl after washing with running water were reduced by 19%. Washing with 1% H_2O_2 solution reduced metalaxyl residues by 2%, and there was no reduction seen after washing with 10% baking soda and 4% acetic acid. The reduction levels for chlorpyrifos were 45% with 1% H_2O_2; 41% with 10% baking soda; 39% with 4% acetic acid, and 34% with tap water, respectively.

Figure 3 shows the effect of treatment 3 (sonication in the ultrasonic bath) for 15, 30, and 60 min. Sonication completely removed chlorpyrifos residues after 60 min. (the percentage of reduction reached 94% after 30min.), while 23% of metalaxyl residues were eliminated after 60 min. sonication. The less efficient removal of metalaxyl

Table 1 Validation parameters for metalaxyl and chlorpyrifos

Pesticide	LOD[a]	LOQ[b]	Recovery and precision (*n = 5)						
			FL [c]	Tomato*		Tomato juice*		Tomato pulp*	
				R%[d]	RSD%[e]	R%	RSD%	R%	RSD%
Metalaxyl	0.01	0.03	0.03	99.4	7.2	90.8	12	98.7	10
			0.5	95.3	10	100.9	15	92.0	11.9
Chlorpyrifos	0.003	0.009	0.01	101.7	11.3	91.4	12.6	97.5	7.7
			0.5	98.0	6.9	96.2	10.5	96.7	8.33

*n: no. of replicates

[a]Limit of detection (mg/kg)

[b]Limit of quantification (mg/kg)

[c]Fortification level

[d]R%: Percentage recovery = CE/CM× 100; CE: the experimental concentration, CM: the spiked concentration

[e]Relative standard deviation

Table 2 ME and linearity parameters in solvent extraction and tomato matrix for metalaxyl and chlorpyrifos

Pesticide	Linear range (mg/ kg)	Solvent extraction		Matrix match tomato		ME %
		Slope	r^2	Slope	r^2	
Metalaxyl	0.03: 2	342610	0. 9981	275931	0.9977	−24.17
Chlorpyrifos	0.01: 2	432881	0.9994	385514	0.9987	−12.29

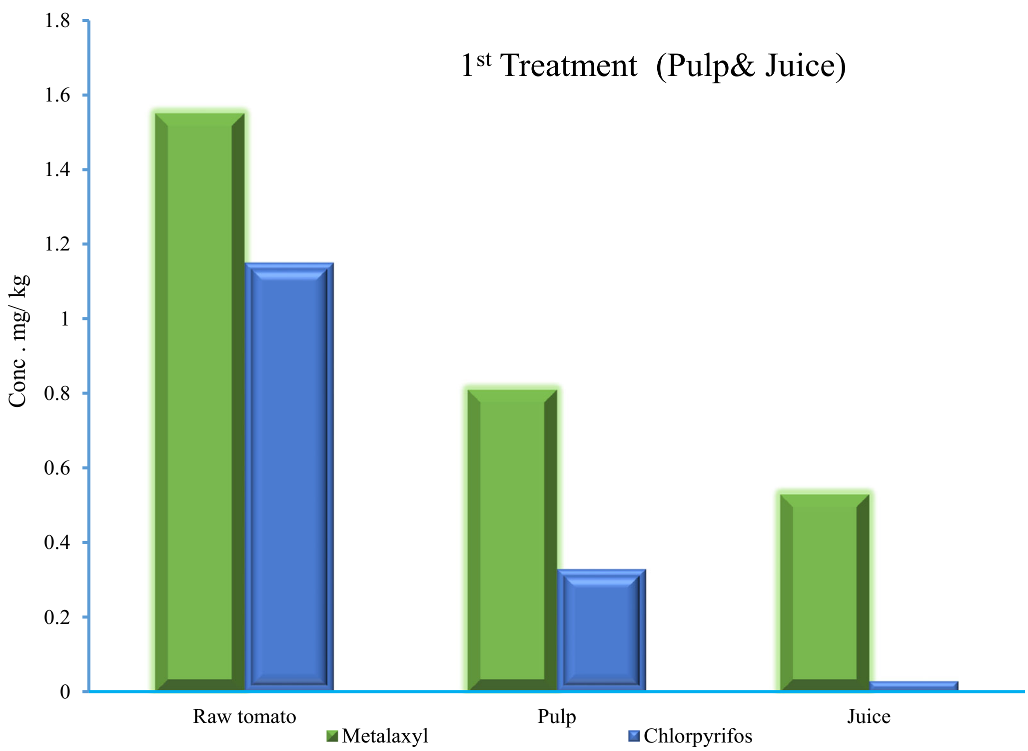

Fig. 1 Effect of various household processes on the reduction of metalaxyl and chlorpyrifos. Treatment 1: tomato juice, and tomato pulp

residues from tomatoes by washing may be due to the distinct nature of tomato peels, the high log Kow values of metalaxyl, and its behavior as a systemic pesticide, penetrating through the peel into the flesh. On the other hand, chlorpyrifos residues were eliminated more successfully. This may be due to the characteristic of

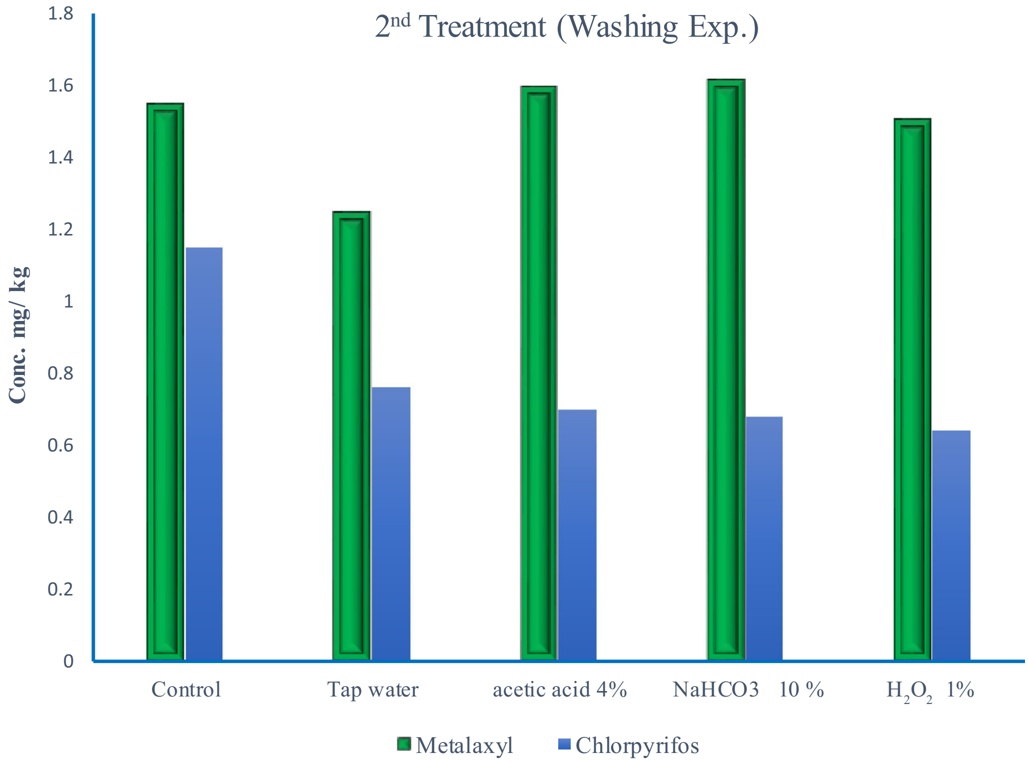

Fig. 2 Effect of various washing solution on the reduction of metalaxyl and chlorpyrifos. Treatment 2: Washing in 1% H_2O_2, 10% baking soda, 4% acetic acid or tap water

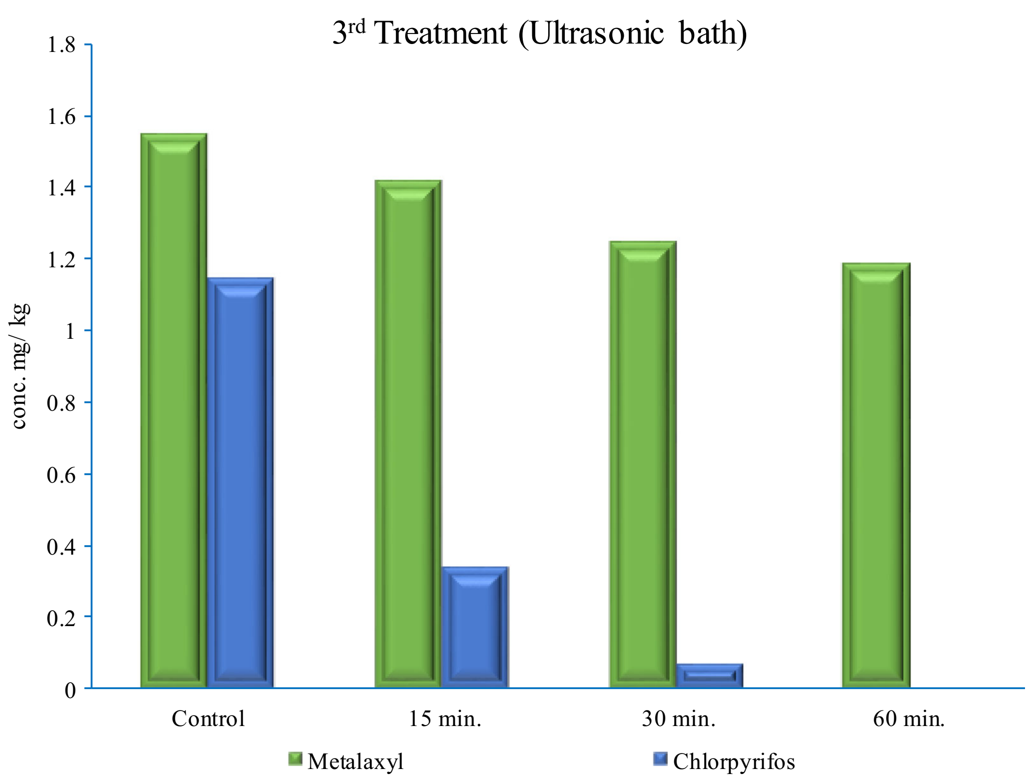

Fig. 3 Effect of sonication in ultrasonic bath on the reduction of metalaxyl and chlorpyrifos. Treatment 3: Ultrasonic bath (UB) for 15, 30, and 60 min

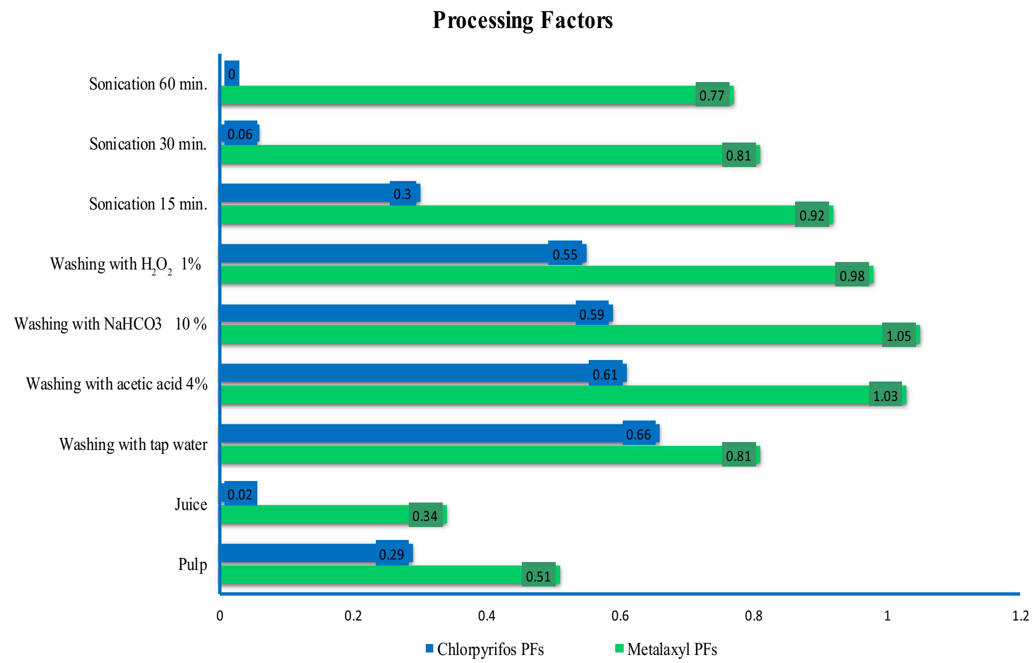

Fig. 4 Processing Factors (PFs) for all processing treatments

chlorpyrifos as a non-systematic pesticide, it may have been physically and chemically removed from the tomato, the minor part of chlorpyrifos residues may be removed physically and the major part removed chemically.

Similar to our study, other investigations have shown that there were differences in efficacy of removing individual pesticides from fruits and vegetables by washing. Rani et al. (2013) reported that by washing of tomatoes with water, chlorpyrifos residues were reduced by 41 to 44% (Duirk and Collette 2006). Wanwimolruk et al. (2017) reported on the effect of washing with running water on pesticide residue removal from tomatoes. Here, both carbofuran and fenobucarb residues were reduced by 58% and 40%, respectively, although without statistical significance ($p > 0.2$). For both cypermethrin and k-cyhalothrin, residues were removed by 27% by washing with running water. However, there was no significant difference ($p > 0.5$) between the mean concentrations of pesticides after washing vs. unwashed samples. In another study, procymidone in cucumber washed with water reduced 24% of the residues and 85% was eliminated with the removal of the peel, even though this pesticide is systemic (Andrade et al. 2015). Chlorpyrifos residue translocated into the internal tissue may not be removed physically and chemically (Pugliese et al. 2004). These disparities in efficacy of washing with water may be due to water solubility of pesticides. Zhang et al. (2012) reported that sonication could effectively remove phorate residues in apple juice with a significant decrease of toxicity caused by phorate.

3.3 Processing factors (PFs)

Figure 4 shows PF values for all treatments. The lowest PF for treatment 1 was juicing followed by pulping (< 1), ranging from 0.34 to 0.51 for metalaxyl, and 0.02 to 0.29 for chlorpyriphos. The PFs for treatment 2 (washing) were generally > 1 for metalaxyl. After washing with tap water, 1% H_2O_2, 10% baking soda or 4% acetic acid, PFs were 0.81, 0.98, 1.05, and 1.03, respectively. On the other hand, the PF for chlorpyrifos was < 1 after washing with tap water, 1%, H_2O_2 10% baking soda or 4% acetic acid (0.66, 0.55, 0.59 and 0.61, respectively).

The PFs after treatment 3 (sonication in the ultrasonic bath) were 0.92, 0.81 and 0.77 after 15, 30 and 60 min. respectively. Chlorpyriphos showed the lowest PFs with 0.3, 0.06, and 0 for the same time intervals, respectively. The results are in agreement with the previously reported results by Ramezani and Shahriari 2015 and Bajwa and Sandhu 2014. We conclude that the status of pesticide residues affect their removal from tomatoes. This is mainly attributed to the difference in the physicochemical properties of the pesticides.

4 Conclusion

In this study, we focused on the development and validation of a GC-MS-based method employing QuEChERS as a sample preparation technique for the determination of chlorpyrifos and metalaxyl residues in tomatoes. All validation parameters have fulfilled the criteria, implying that the method is valid for the determination of chlorpyrifos and metalaxyl residues. The percentage reduction was lower in metalaxyl than in chlorpyrifos. Metalaxyl exhibited a medium matrix effect while chlorpyrifos showed no matrix effect. The PFs of metalaxyl and chlorpyriphos for all treatments were generally < 1, except for metalaxyl after washing with 10% baking soda or 4% acetic acid (PF >1). Sonication treatment effectively removed chlorpyriphos residues in tomato matrices, but not metalaxyl residues. We conclude that our methods can substantially contribute to reduce consumer exposure to pesticides.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

Informed consent This article does not contain any studies with human participants, so no informed consent was necessary for this study.

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