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The effects of heat treatment on the degradation of the organophosphate pesticide chlorpyrifos-ethyl in tomato homogenate

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RESEARCH ARTICLE

Abstract

Tomato is often thermally processed. Chlorpyrifos-ethyl, a broad-spectrum organophosphate pesticide, is widely used on the tomato plants. Therefore, understanding of the fate of the residues during the tomato thermal processing is important for the calculation of dietary exposure. The effects of thermal processing on the reduction of the chlorpyrifos-ethyl residues in tomato homogenates were investigated. Tomato homogenates spiked with chlorpyrifos-ethyl were subjected to thermal processing at the commonly used temperature values (60-90 °C) at various time intervals (10-60 min) in the production of tomato products. A QuEChERS technique for sample preparation and a gas chromatograph-electron capture detector for analysing chlorpyrifos-ethyl residues in tomato homogenate were used. The results were further confirmed by using a gas chromatography-mass spectrometry system. Reduction rate of the chlorpyrifos-ethyl residues was as high as 55.8% at 90 °C for 60 min. Degradation rates could be considered as first order kinetics model. Apparent activation energies (Ea), temperature coefficients (Q_{10}), half time (DT_{50}) and time to reduce to 90% of the initial value (DT_{90}) of chlorpyrifos-ethyl were calculated as kinetic parameters. The results of this study could shed light on the fate of chlorpyrifos-ethyl residues during tomato processing and may also prove invaluable in estimating potential risk from dietary exposure.

Keywords: tomato homogenate, chlorpyrifos-ethyl, thermal degradation

1. Introduction

Tomatoes (*Lycopersicon esculentum* Mill.) are one of the most widely grown and consumed vegetables in many parts of the world. Turkey is one of the leading and most important fresh and industrial type tomato producers and exporters in the world, ranking fourth (after China, US and India) globally in total tomato production. Recent reports showed that the production quantity of tomatoes has been reached at 11,350,000 tonnes in Turkey (http://faostat3.fao.org). The annual fresh tomato consumption in Turkey per capita is over 80 kg. This amount is 3 to 4 times greater than that of the EU and many important tomato producing countries in the world (Keskin *et al.*, 2010).

As a result of its high economic value, as well as the large number of pests that infest tomatoes during the growing season, significant quantities of pesticides are often necessary for the protection of this crop. This may lead to residues on (or in) the fruit at harvest. Although, there are so many kinds of pesticides in tomato production, chlorpyrifos-ethyl is one of the most widely used pesticides to protect tomato crop because of its broad-spectrum efficiency against various pests (US EPA, 2002). This pesticide (IUPAC name: *O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate), a crystalline organophosphate insecticide, acaricide and miticide used to control foliage and soil-borne insect pests on a variety of food and feed crops, is one of the most commonly used nonsystemic contact pesticides in tomato cultivation, especially in open-field production (US EPA, 2002). It has potential for both acute toxicity at larger amounts and neurological effects in foetuses and children even at very small amounts. For acute effects, the Environmental

Protection Agency (EPA) classifies chlorpyrifos as Class II: moderately toxic. Chlorpyrifos is toxic to mammals (LD_{50}=163 mg/kg body weight male rats; US EPA, 1984), and acts as a cholinesterase inhibitor. In addition, chlorpyrifos is a very persistent pesticide, and a half-life range of 30 to 120 days has been reported (Nicholls, 1996). It was reported that recovery of chlorpyrifos was 100% after 6 months and 1 year from tap water and irrigation water treated with different fertilisers (Gilani, 2010).

Pesticides residues in food products are influenced by processing methods between harvesting of raw commodities and consumption of prepared foods (Holland *et al.*, 1994). Commercial and house-hold processing methods such as cooking, blanching and concentrating can reduce residue levels in food, which further reduces the impact on human health (Balinova *et al.*, 2006; Cengiz *et al.*, 2006, 2007; Certel *et al.*, 2012; Kooner *et al.*, 2010; Satpathy *et al.*, 2011). When residues are present in raw agricultural commodities generally consumed only after processing at either industrial or homemade scale, it may be necessary to investigate the pesticide residue levels in the processed commodities. In addition, understanding of the fate of the residues during the processing may be important for the calculation of dietary exposure.

Although, so far there is no report on the kinetic evaluation of chlorpyrifos-ethyl residues in tomato homogenates during thermal treatments, there are many studies about removal of chlorpyrifos residue from vegetables during home preparation and commercial processing (Byrne and Pinkerton, 2004; Han *et al.*, 2013; Ling *et al.*, 2011; Randhawa *et al.*, 2007).

Tomatoes are frequently subjected to thermal treatments such as evaporation, blanching, sterilising and canning before being consumed as juice, paste, ketchup, or canned products. About 90% of the tomatoes processed in the industry in Turkey are used in tomato paste production and the rest are used in the production of other tomato products such as canned tomato, dried tomato and pickle (Keskin *et al.*, 2010). Therefore, determination of kinetic properties of the chlorpyrifos-ethyl residues during the thermal processing of tomato products is important for the reduction of dietary exposure to the residues which pose a serious threat to human health.

The objective of this research was to evaluate the kinetic parameters of chlorpyrifos-ethyl degradation in tomato homogenates under the thermal processing. The results obtained from the present study may increase our understanding of the effective management of chlorpyrifos-ethyl usage in tomato production.

2. Materials and methods

Chemicals and standards

Chlorpyrifos-ethyl analytical standard was supplied with purity certifications by Dr. Ehrenstorfer GmbH (Augsburg, Germany). Acetonitrile was purchased from Sigma-Aldrich (St. Louis, MS, USA). All the chemicals used were of analytical grade, except acetonitrile which were GC grade. QuEChERS extraction bags with 6 g $MgSO_4$ and 1.5 g NaOAc, and bags with 4 g $MgSO_4$, 1 g primary secondary amine (PSA) were purchased from Agilent (Agilent Technologies, Palo Alto, CA, USA). The water was produced by an ultrapure (18.2 MΩ cm at 25 °C) purification system from Millipore (Bedford, MA, USA). Organically grown tomatoes were purchased from the local market. All samples were stored in a refrigerator at 4 °C before analysis.

Preparation of standard solutions

A stock standard solution of chlorpyrifos-ethyl was prepared in acetonitrile at a concentration of 100 mg/l and stored at -18 °C in a refrigerator. Intermediate (10 μg/l) and working standard solutions (31.25-2,000 μg/l) were daily prepared with appropriate dilutions of the stock standard solution.

Preparation for analysis

All glassware, filter papers and auxiliary equipment (such as knife) were cleaned and rinsed with extra-pure acetone prior to the residue analyses and recovery studies. In this way, interference caused by materials which contaminate the analyte from this apparatus was avoided.

Spiking procedure

A spiking procedure was used to determine the variations of chlorpyrifos-ethyl residues in tomato homogenates during the thermal treatment. It is reported that the spiking is only acceptable if the raw agricultural commodity residues can be shown to consist only of surface residues (Timme and Walz-Tylla, 2004). Chlorpyrifos-ethyl as nonsystemic pesticide consists entirely of surface residues, and as expected no conjugates have been found in the interior of plants (EXTOXNET, 1993). It has also been noted that the behaviour of residues in spiked samples does not differ from the behaviour of field incurred residues when the latter are in a free unconjugated form (US EPA, 1996). Therefore, the study of residue reduction of chlorpyrifos-ethyl in tomatoes was planned to incorporate spiking of tomato homogenates.

Tomato samples free from chlorpyrifos-ethyl were used in the current study. The absence of the compound in blank tomato samples was also confirmed by residue analysis. To prepare the samples for spiking procedure, about 200 g of tomatoes were manually washed in distilled water and homogenised using a Waring blender (Waring Commercial, Torrington, CT, USA) for 2 min at high speed. A representative 50±0.1 g portion of tomato homogenate previously homogenised was weighted and transferred to 250 ml bottles. The homogenate was fortified homogenously with appropriate standard solution to a final concentration of 1 mg/kg.

Thermal treatments

Prepared bottles were placed in a constant temperature thermo reactor at 60, 75 and 90 (±0.1 °C). After appropriate time intervals (10, 20, 40 and 60 min), the bottles were removed from the reactor. The levels of decreasing chlorpyrifos-ethyl residues were analysed as soon as the temperature of the homogenate reached room temperature (about 20 °C). The experiments were repeated two times. Control samples, spiked with chlorpyrifos-ethyl standard but not subjected to thermal treatment, were analysed in parallel within each sample group. The level of decreasing chlorpyrifos-ethyl after each thermal treatment was calculated by comparing the level of chlorpyrifos-ethyl which was determined in the control sample. The initial °Brix of the tomato homogenates was 4.6° and remained constant during the thermal treatments. No visible change in the colour of the tomato homogenates was observed when samples were heated.

Sample extraction and clean-up

A 15-g homogenised sample was weighed accurately into a 50 ml centrifuge tube. 15 ml extraction solvent of acetonitrile/acetic acid (99:1, v/v) was rapidly added into the sample using a pipettor (Eppendorf, Hamburg, Germany). Then, the mixture was gently shaken for several seconds by hand followed by vortex mixing to ensure homogenous sample. Then QuEChERS extraction bag with 6 g anhydrous $MgSO_4$ and 1.5 g NaOAc was added and the tube was vortexed for 1 min immediately. Then the mixed solution was extracted by centrifugation at 4,000 rpm for 5 min. During the clean-up step, 6 ml upper acetonitrile layer was transferred into a 10 ml Teflon centrifuge tube, then cleaned up using 1.2 g of 3:1 $MgSO_4$:PSA (w/w). The tube was vortexed for 1 min and centrifuged for 5 min at 4,000 rpm. Afterwards the supernatant was filtered through the 0.45 μm nylon syringe filter and loaded into sample vials for gas chromatography (GC) analysis. 1 μl was injected into the GC system.

Gas chromatography-electron capture detector conditions

Analyses were carried out on a Shimadzu QP2010 Plus gas chromatograph (Shimadzu, Kyoto, Japan) equipped with an electron capture detector (ECD), an autosampler and an injector. Chlorpyrifos-ethyl was separated through a TR-5 (30 m × 25 mm × 0.25 μm) capillary column. Injector and detector temperatures were held at 280 and 300 °C respectively. Oven temperature was programmed as follows: initial temperature 90 °C for 2 min, raised to 180 °C (10 °C/min) for 1 min, and raised to 270 °C (10 °C/min) for 20 min. High-purity (over purity 99.99%) nitrogen was used as the carrier gas with a gas flow at 27.5 cm/s linear velocity and the pressure maintained at 90 kPa. Column flow was 1.0 ml/min. Labsolution software was used for instrument control and data analysis (Shimadzu Corporation, Kyoto, Japan). Quantification of the chlorpyrifos-ethyl was performed using the external standard method based on the detected and integrated peak area. A series of standards for chlorpyrifos-ethyl was prepared and injected into the GC system under the conditions stated above and the retention times and areas were recorded. Calibration curves were prepared for these concentrations.

Gas chromatography-mass spectrometry conditions

A Thermo Scientific ISQ GC-mass spectrometry (MS) (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with a fused capillary column as TR-5MS (30 m × 25 mm × 0.25 μm) was used for the verification of chlorpyrifos-ethyl in analysed samples. The oven temperature programme was as follows: a 90 °C initial temperature was held for 1 min and increased to 150 °C by a rate of 30 °C/min and increased to 190 °C for 2 min by a rate of 10 °C/min and then increased again to 250 °C by a rate of 10 °C/min and finally was held for 10 min at this temperature. The mass conditions were set as follows: ionisation mode with electron impact, ionisation energy of 70 eV. The detector and ion source temperatures were 280 and 230 °C, respectively. High-purity (over 99.999%) helium was selected as the carrier gas at a flow rate of 1 ml/min. Injection volume was 1 μl and identification was determined by SCAN mode from 50 to 550 atomic mass unit.

Method validation

The validation of the analytical method was performed following analytical curves and linearity, limits of detection (LOD) and quantification (LOQ), and recovery. All the analyses were carried out using the same solvent or blank sample of tomato. Linearity was determined by constructing calibration curves with standard solutions, in acetonitrile, containing chlorpyrifos-ethyl in the range of 31.25-2,000 μg/l. Three injections were made at each of the five concentration levels. The LOD was estimated as 3 times the standard deviation, while the LOQ was estimated as 10 times the standard deviation, which was derived from analyses of 8 independent samples at the lowest calibrated level. Recovery studies were carried out by fortified samples with chlorpyrifos-ethyl standards at levels of 1000 μg/l. The fortified samples as well as the unfortified controls were analysed in three replicates. In order to avoid false positive findings, residues were confirmed using GC-MS.

Kinetic study

The degradation kinetics of chlorpyrifos-ethyl in tomato homogenates were studied by isothermal heating at selected temperatures (60, 75 and 90 °C) for a residence time of 0 to 60 min.

First-order kinetic model was used to treat the resulting data of chlorpyrifos-ethyl degradation. Regression analysis was used to calculate the rate constants at different temperatures, from the slopes of the curve.

Equations of this models are (Van Boekel, 1996):

$$\ln (C_t/C_0) = -k_{obs}\, t \text{ or } C_t = C_0 \exp(-k_{obs}\, t) \qquad (1)$$

In these equations, C_t is the concentration of chlorpyrifos-ethyl at various time intervals, C_0 is the initial concentration, t is the time of thermal treatment (min) and k_{obs} is the degradation rate constant.

Dependence of the degradation rate constant on temperature is represented by the Arrhenius equation:

$$\ln k_{obs} = \ln A - (E_a/RT) \qquad (2)$$

Where E_a is activation energy, (kJ/kmol), R is universal gas constant (8.314 kJ/K/kmol), A is the frequency factor (time^{-1}) and T is the absolute temperature (K).

Other kinetic parameters were estimated from the following equations (Reyes and Cisneros-Zevallos, 2007; Sarmah and Rohan, 2011):

$$Q_{10} = \left(\frac{k_{obs2}}{k_{obs1}}\right)^{\left(\frac{10}{T2-T1}\right)} \qquad (3)$$

$$DT_{50} = \frac{\ln(2)}{k_{obs}} \qquad (4)$$

$$DT_{90} = \frac{\ln(10)}{k_{obs}} \qquad (5)$$

3. Results and discussion

Methodological findings

The method used demonstrated acceptable performance for the analysis of chlorpyrifos-ethyl residues in the tested tomato samples. A good linear relationship with high correlation coefficient values was achieved for the compound studied under the chromatographic conditions. The linearity of the assay was checked by calculating the regression line using the least squares method and expressed by the coefficient of determination, $r^2>0.999$. A five-point calibration curve was obtained for chlorpyrifos-ethyl in the range of 31.25-2,000 μg/l by plotting the recorded peak area versus the corresponding analyte concentrations. The regression equation for the calibration curve was $y = 0.6727x + 44.00$. The linear range mathematical equation was used for all the samples since the chlorpyrifos-ethyl levels for them were in the linear range of the calibration curve.

The method was also studied for LOD, LOQ and recovery studies before the determination of chlorpyrifos-ethyl levels in the tomato samples. These methodological parameters were optimised by using tomato samples that did not contain any chlorpyrifos-ethyl residue. Thus, the LOD and LOQ were estimated to be 7.36 and 24.55 μg/kg (% relative standard deviation = 3.80), respectively. For the recovery test, the minimal risk level of chlorpyrifos-ethyl standards (1000 μg/kg) was fortified to the tomato sample during the homogenisation step. A blank value was determined prior to the recovery study. The same extraction procedures and GC-ECD conditions as applied for sample analyses were used for recovery studies. In this way, average recovery ranges of chlorpyrifos-ethyl from tomato samples was 101.51±4.91%.

Detection may be complicated by false-positive results using conventional GC detectors. Mass spectrometry has shown to be a valuable method for the definite identification of contaminants in food (Careri *et al.*, 1996). Residues of chlorpyrifos-ethyl in tomato samples were confirmed through GC-MS in selective ion monitoring (SIM) mode using with three mass fractions. For this reason, the chlorpyrifos-ethyl standard was injected to the GC-MS in SCAN mode in order to determine the mass fragmentations of chlorpyrifos-ethyl. Obtained fragmentations were compared with the NIST library. After setting the optimum MS parameters, chlorpyrifos-ethyl residues were found to be similar to the results obtained from GC-ECD.

Thermal degradation of chlorpyrifos-ethyl

Percentage reduction of chlorpyrifos-ethyl residues in the samples at various temperatures and duration are presented in Figure 1.

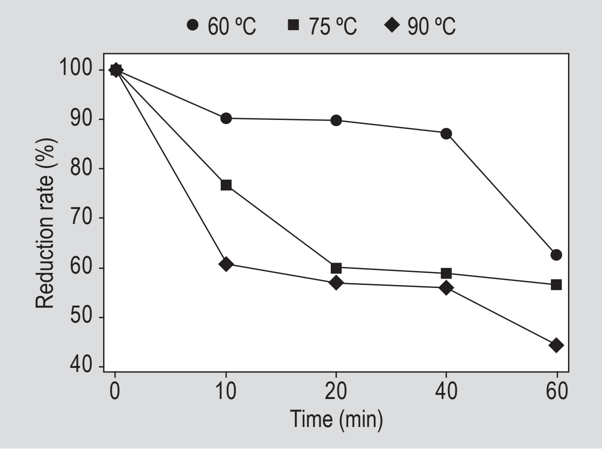

Figure 1. Reduction of chlorpyrifos-ethyl residues in tomato homogenates.

The results showed that thermal treatments resulted in considerable reduction of chlorpyrifos-ethyl depending on temperature and time. The minimum and maximum reductions of residues were observed at 60 and 90 °C, respectively. These findings are consistent with the results of Ling *et al.* (2011) who investigated the effects of washing and cooking on chlorpyrifos in vegetables. They reported that the cooking was the most effective treatment among the various kinds of household processing methods for the reduction of chlorpyrifos residues on tomatoes. According to their study, chlorpyrifos residues in tomato were reduced 75.9% by boiling (100 g samples were boiled for 5 min in 1 l water), 67.2% by microwave heating and 10.3% by frying (Ling *et al.*, 2011).

However, the findings of the current study differ from the study of Randhawa *et al.* (2007) who researched the reductions of chlorpyrifos-ethyl residues in different vegetables during boiling process. They reported that the reduction rates ranged from 12 to 48% depending on the vegetable types. In that study, the various kinds of sliced vegetables were cooked by placing ¾ cup of water in the sauce pan and adding ½ teaspoon of salt and, prepared vegetables were boiled in water for 10-12 min. According to their findings, the boiling process effected to spinach at the reduction rate of 38% and followed by cauliflower with a rate of 29%. The authors also reported that the reduction rate was found to be 32% in tomato samples under the same temperature and time conditions (Randhawa *et al.*, 2007). This difference from our results can be attributed to the sample preparation technique prior to thermal treatments. The determined residue levels of chlorpyrifos-ethyl in the samples after the thermal treatments are illustrated in Table 1.

Kinetics of chlorpyrifos-ethyl degradation

A first-order kinetic model was adapted to analyse the chlorpyrifos-ethyl degradation data. We found a high linear relationship between the residence time and the logarithm of the remaining chlorpyrifos-ethyl ($\ln C_t/C_0$). According to the first-order rate equation, k_{obs} values were calculated at various temperatures for chlorpyrifos-ethyl degradation in tomato homogenate (Table 2).

The k_{obs} values of chlorpyrifos-ethyl degradation and the initial chlorpyrifos-ethyl concentration were found to have good linear relationships (R^2>0.7*)*. The values increased with increasing temperature (Table 2). Based on these findings, it can be concluded that thermal treatments at higher temperatures result in faster reductions of chlorpyrifos-ethyl residues. The dependence of rate constants from temperature was found to be well described (R^2=0.99) by the Arrhenius equation. The regression line of the Arrhenius

Table 1. Summary of chlorpyrifos-ethyl residues in the tomato samples after thermal treatments.

Temperature (°C)	Duration (min)	Calculated residue (µg/kg)	Standard deviation	%RSD
60	10	901.47	7.63	0.85
	20	897.43	5.02	0.56
	40	872.32	7.83	0.90
	60	626.11	48.57	7.76
75	10	768.05	65.21	8.49
	20	599.87	14.88	2.48
	40	587.99	48.93	8.32
	60	565.57	2.95	0.52
90	10	606.60	2.33	0.38
	20	569.38	2.63	0.46
	40	558.84	23.61	4.22
	60	442.01	4.97	1.12

%RSD = % relative standard deviation.

Table 2. Degradation rate constants of chlorpyrifos-ethyl at different temperatures.

	Temperature (°C)		
	60	75	90
k_{obs}	0.006691	0.008415	0.01057
R^2	81.8	70.3	71.9

k_{obs} = degradation rate constant; R^2 = coefficient of determination of the linear regression.

Table 3. Kinetics data for chlorpyrifos-ethyl degradation in tomato homogenates.

Temperature (°C)	Q_{10}	DT_{50} (min)	DT_{90} (min)
60	1.257	103.59	344.13
75	1.256	82.37	273.63
90	–	65.58	217.84

Q_{10} = temperature coefficients; DT_{50} = half time; DT_{90} = time to reduce to 90% of the initial value.

plot allows the determination of the reaction rate at any temperature. The Arrhenius plots of the chlorpyrifos-ethyl degradation are illustrated in Figure 2. The straight lines in this figure are the linear fit for each temperature.

The apparent activation energy is obtained from the slope of the Arrhenius plot and Equation 2. Therefore, based on kinetic modelling, the apparent activation energy (E_a) was calculated to be activation energy -15.306 kJ/mol. The E_a value demonstrates the influence of temperature on degradation of chlorpyrifos-ethyl. The greater the E_a value, the more the reaction is dependent on temperature. On the basis of the estimated Arrhenius parameters, predictions about the amount of chlorpyrifos-ethyl degraded under various thermal treatments can be made. In addition, the other kinetic parameters such as temperature coefficients (Q_{10}), half time (DT_{50}) and time to reduce to 90% of the initial value (DT_{90}) were given in Table 3.

The dissipation time for chlorpyrifos-ethyl in tomato homogenate is calculated by reduction to 50% (DT_{50}) and 90% (DT_{90}) of the initial concentration. These values of the compounds obtained in the current study can be used by regulatory authorities for risk assessment purposes and as input parameters in many fate models. Furthermore, selection of appropriate kinetic models was reported to play a key role in the derivation of DT_{50}/DT_{90} values for organic chemicals. Outputs of many predictive models were also very sensitive to the chosen DT_{50}/DT_{90} values used as inputs in fate and risk assessment models (Sarmah and Rohan, 2011).

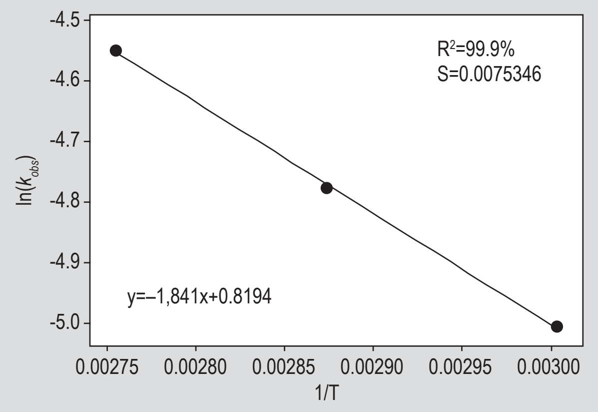

Figure 2. Arrhenius plots for chlorpyrifos-ethyl degradation in tomato homogenates. k_{obs} = degradation rate constant; R^2 = coefficient of determination of the linear regression.

The DT_{50} value (expressed as $t_{1/2}$) was calculated using Equation 4. This value corresponds to a period of time at which the chlorpyrifos-ethyl concentration is equal to half of the initial concentration. The obtained $t_{1/2}$ (min) values for the temperature range from 60 to 90 °C indicate that the $t_{1/2}$ (min) value of chlorpyrifos-ethyl at 60 °C was ca. 2 fold higher than that at 90 °C. Additionally, the temperature coefficient (Q_{10}) values increased with increasing temperature. Q_{10} value is the ratio of the rate constant of a reaction to that of the same reaction at a temperature lower by 10 °C (see also Equation 3).

Although there was no literature available about the kinetic evaluation of chlorpyrifos-ethyl residues in tomato homogenates, there have been some studies on the some kinetic parameters of the residues on tomatoes grown in greenhouse and open fields. Angioni *et al.* (2011), who evaluate the kinetic of disappearance in tomatoes grown in field and treated with chlorpyrifos, reported that the treatments showed the kinetic of disappearance characterised by biphasic behaviour with an almost negligible initial slope, followed by a drop in the third week. In addition, the half-life time calculated in 28 days experiment, as pseudo first order kinetic were reported as 6.9, 9.1 and 7.7 days for emulsifiable concentrates, wettable granules, and microencapsulates, respectively. Temperature range was between 15.7 and 33.7 °C during the treatment in their study. The mathematical dissipation model used was not appropriate to chlorpyrifos behaviour in tomatoes due to obtained low correlation coefficients (Angioni *et al.*, 2011). In another study, half-lives of 4.28, 0.58 and 1.35 days were reported for the dissipation of chlorpyrifos from rice plants, water and soil respectively under paddy field conditions (Zhang *et al.*, 2012). The half-lives of chlorpyrifos-ethyl in tomato homogenates were found as 103.59, 82.37 and 65.58 min for 60, 75 and 90 °C, respectively, in the current study. Based on the findings, it can be concluded that temperature plays an important role in the degradation of chlorpyrifos-ethyl.

4. Conclusions

Although, pesticide residues in/on raw agricultural commodities have been strictly monitored by governments, those in processed commodities such as juice, paste, ketchup, or canned products have mostly ignored. Therefore, the present study undertook the effects of the thermal treatments on chlorpyrifos-ethyl residues in tomato homogenates. The degree and duration of thermal treatments were found to be effective on the chlorpyrifos residue. In lower temperatures and/or short thermal treatment durations, the residues may persist at high level. Therefore, monitoring of residues must be mandatory not only for raw materials but also for processed foods. Further research is recommended in the following areas: formation of toxic degradation products in foods by various processing techniques and practices for minimising pesticide residues during food processing.

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Conflict of interest

The authors declare that they have no conflict of interest.

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