



Residue Content of Organophosphorus Pesticides and their Toxic Metabolites in Greenhouse-Grown Tomatoes during Pre-Harvest Interval and Post-Harvest Processing: A Kinetic Study

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Abstract

Background: Organophosphorus pesticides (OPPs) have a wide application throughout the world and exert adverse effects on human health. Moreover, these chemical compounds are responsible for thousands of deaths per year worldwide. Kinetic and mathematical models could be used to optimize the application of pesticides on fruits and vegetables and monitor their residues.

Objectives: The present study aimed to model the dissipation of diazinon and chlorpyrifos in different conditions, such as household conditions (e.g., storage at room and refrigerator temperatures, as well as cooking) and field condition for greenhouse tomatoes.

Methods: A multi-residue analysis of diazinon, chlorpyrifos, and their oxon derivatives was established by gas chromatography-tandem mass spectrometry. The limit of quantification (LOQ), recovery, precision, linearity, and the limit of detection (LOD) were evaluated to ensure that the method was able to effectively determine the studied pesticides in the tomato samples. The linear and nonlinear kinetic models were presented for chlorpyrifos and diazinon residues in tomato using zero-order, first-order, and second-order equations.

Results: Based on the best fitting models for diazinon in the case of laboratory treatment at the refrigerator, room, and boiling temperatures, the half-lives were calculated as 18.79 days, 11.41 days, and 45.39 min, respectively. The half-life of diazinon was lower than that of chlorpyrifos in both field and laboratory treatments.

Conclusion: Modeling the removal of the pesticides indicated that the nonlinear first- and second-order models were the best fitted models for the dissipation of both pesticides in field and post-harvest conditions.

Keywords: Chlorpyrifos oxon, Dissipation kinetic, Nonlinear model

1. Background

Organophosphorus pesticides (OPPs) have a wide application across the globe. These compounds inhibit acetylcholine esterase which results in the uncontrolled firing of neurons, the loss of asphyxiation respiratory control, and finally death (1,2). Moreover, they exert other adverse effects on human health due to their immunosuppressive, cytotoxicity, mutagenicity, and endocrine-disrupting properties. They are also associated with decreased average birth weight. These chemical compounds are responsible for thousands of deaths per year worldwide (3,4).

The degradation, transformation, and dissipation of insecticide residues in stored foods considerably depend on light, temperature, food type, and moisture content. OPPs, including diazinon and chlorpyrifos, reach their greatest toxicity by oxidative desulfurization (4,5). Among their metabolite components, chlorpyrifos oxon has been shown to be 100 times more toxic than chlorpyrifos, whereas diazoxon is 10 times more lethal than diazinon (6,7).

As reported by the World Health Organization (WHO), dietary exposure to insecticide residues is almost five times higher, compared to exposure through air or drinking water (8). *Lycopersicon esculentum* (tomato) as one of the widely consumed fruits in the world is among the 10 most pesticide-contaminated fruits and vegetables. The consumption of tomatoes varies across different countries. For instance, the annual tomato consumption per capita in the USA, Sweden, Germany, and Iran were recorded as 9.5, 10, 25, and 62.2 kg, respectively (9,10).

Kinetic and mathematical models could be used to optimize the application of pesticides on fruits and vegetables and monitor their residues. A kinetic model of pesticide dissipation can help predict the half-lives of pesticides for the estimation of their final residue levels in different conditions, including pre- and post-harvesting. 'Half-life' is described as the time it takes to remove 50% of a substance and demonstrates the persistence of a pesticide (11-14). The validation of the methods (including the assessment of the linearity of the analytical curve, accuracy, precision, the limits of detection and quantification, and

recovery) perform a peculiar role in trace analysis. Therefore, a preliminary phase of contamination monitoring in fruits and vegetables should be designed for the validity of the method (15,16).

The previously conducted studies have mainly focused on primary compounds, and only a few of them have addressed their metabolites.

2. Objectives

The present study aimed to model the dissipation of diazinon, chlorpyrifos, and their oxon derivatives in different conditions (including pre-and post-harvest conditions) and assess the interactions among the independent variables.

3. Methods

3.1. Reagents and materials

Chlorpyrifos (diethoxy-sulfanylidene-(3, 5, 6-trichloropyridin-2-yl) oxy- λ 5-phosphane) and diazinon (diethoxy-(6-methyl-2-propan-2-ylpyrimidin-4-yl) oxy-sulfanylidene- λ 5-phosphane) were purchased from Sigma-Aldrich. Chlorpyrifos oxon (diethyl (3, 5, 6-trichloropyridin-2-yl) phosphate) was provided by Dr. Ehrenstorfer (Augsburg, Germany). Diazoxon (diethyl (6-methyl-2-propan-2-ylpyrimidin-4-yl) phosphate) was obtained from Toronto Research Chemicals (Toronto, Canada). Sodium chloride, trisodium citrate dihydrate, disodium hydrogen citrate, magnesium sulfate, PSA (primary-secondary amine), formic acid, acetonitrile, ethyl acetate, methane, and TPM (Triphenylmethane) were of analytical and HPLC (high-performance liquid chromatography) grade and were acquired from Sigma-Aldrich (Switzerland).

3.2. Standard and working solutions

About 10 mg chlorpyrifos, diazinon, chlorpyrifos oxon, and diazoxon were dissolved with ethyl acetate in a 10 mL volumetric balloon in order to reach the concentration of 1000 mg/L. The stock solution was kept at -20°C. The working solutions were made by diluting 250 μ L of the standard solution with ethyl acetate in a 25 mL volumetric balloon in order to obtain a concentration of 10 ppm. Appropriate dilutions were used to prepare the calibration curves for the gas chromatography-mass spectrometry (GC/MS) analysis.

3.3. Sample collection

The experiments were conducted in Amzajerd greenhouses located in Hamadan from November-December 2018. The field trials were performed on experimental plots of tomato plants. Two treatments with chlorpyrifos (40.8% EC) and diazinon (60% EC) at the recommended dosages of 2/1000 and 1/1000 were applied to determine the dissipation kinetics under laboratory and greenhouse conditions. The

tomato samples were randomly picked 2 hours, as well as 1, 3, 7, 10, and 21 days after pesticide application. After being harvested, the tomato samples were transported to the laboratory for further analyses.

In addition, to investigate the dissipation pattern of the pesticides for the post-harvested tomatoes, the harvested samples were separately collected and stored in the laboratory for different analyses 2 h after spraying. The tomato samples were analyzed for diazinon, chlorpyrifos, and their oxon derivatives at room temperature on days 1, 2, 3, and 5, at refrigerator temperature on days 1, 3, 5, and 7, and at boiling temperature after 5, 30, and 45 min, as well as 1 and 2 h.

3.4. Sample preparation

The extraction of the samples was performed by a modified QuEChERS method (17). The top layers of the samples were transferred to 5 mL centrifuge tubes and were acidified with 10 μ L formic acid (5%). The solution was evaporated to dryness and dissolved with methane to 1 mL. Finally, the methane solution was analyzed by GC-MS/MS.

3.5. Instrumentation

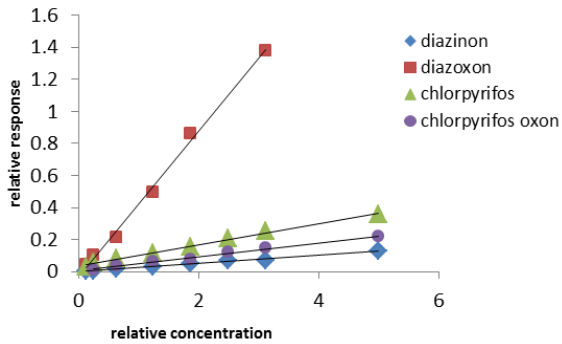
The qualification analyses of both pesticides and their degradation products were performed using a gas chromatograph (Agilent 7890, UK) coupled with a tandem mass spectrometer. An autosampler (Shimadzu, Japan) was utilized to inject the sample solution (1 μ L) in the splitless mode. A silica capillary column coated with diphenyl-methyl polysiloxane was used as the stationary phase for separation in GC. Perfluoro tributylamine (PFTBA) was employed for the calibration of the MS spectrometer. The temperature program of GC was set in the following way: the initial temperature of 75°C was kept for 4 min and increased up to 120°C with the time rate of 25°C/min. Thereafter, it increased up to 300°C with the time rate of 50°C/min and was kept for 7 min. The inlet temperature, the flow gas, and the interface temperature were 250°C, 3 mL/min, and 280°C, respectively. The multi-reaction monitoring mode was applied for all of the compounds (diazinon, chlorpyrifos, and their oxon derivatives).

3.6. Validation study

The European Health and Consumer Guidelines were employed for the validation study (18). The limit of quantification (LOQ), recovery, precision, linearity, the limit of detection (LOD), and specificity of these compounds were evaluated to ensure that the method was able to effectively determine chlorpyrifos, diazinon, and their oxon derivatives in the tomato samples. The absolute recovery and relative standard deviations (RSD) of chlorpyrifos, diazinon, chlorpyrifos oxon, and diazoxon were obtained by investigating the spiked samples at three

Table 1. Limit of quantification, limit of detection, and regression equation for the studied pesticides

Insecticide	LOQ mg/kg	LOD mg/kg	Regression equation	R ²	MRL mg/kg
Chlorpyrifos	0.083	0.0277	$y=47.377x+758.56$	0.9965	0.5
Chlorpyrifos oxon	0.0478	0.015	$y=31.169x+10.198$	0.9955	0.05
Diazinon	0.0103	0.00308	$y=11.626x+70.742$	0.9934	0.05
Diazoxon	0.039	0.01226	$y=244.88x-615.3$	0.9936	0.05

**Figure 1.** Standard calibration curves for the analyses

different levels (75, 100, and 125 $\mu\text{g}/\text{kg}$) on three different days.

The LOD and LOQ were calculated at the lowest concentrations of the analysis and yielded peaks with the signal/noise ratios of 3 and 10, respectively. The LOQ is the lowest concentration and has an acceptable precision ($\text{RSD} \leq 20\%$) and recovery (70%-120%). The LOQs determined for this method were lower than those set by Iranian national standards for the above-mentioned pesticides in tomato (Table 1). The calibration curves of the peak area versus the concentrations of diazinon, chlorpyrifos, diazoxon, and chlorpyrifos-oxon were constructed using eight concentration levels (5, 10, 25, 50, 75, 100, 125, and 200 $\mu\text{g}/\text{kg}$) (Figure 1). The typical chromatograms of these pesticides are displayed in Figure 2.

3.7. Modeling the chlorpyrifos and diazinon residues

3.7.1. Linear kinetic modeling

The linear kinetic models were presented for chlorpyrifos and diazinon residues in tomato using zero-order, first-order, and second-order equations (19).

Zero-order model

The following equation was considered for zero-order kinetic (Equation 1):

$$C_t = C_0 - k_0t \quad (1)$$

where C_t ($\mu\text{g}/\text{kg}$) signifies the residue concentration after the application of pesticide at time t , C_0 ($\mu\text{g}/\text{kg}$) is the initial concentration at time 0 which dissipates through kinetic processes, and k_0 indicates the reaction rate constant (1/day).

The half-life ($t_{1/2}$) for the zero-order model was determined by Equation 2:

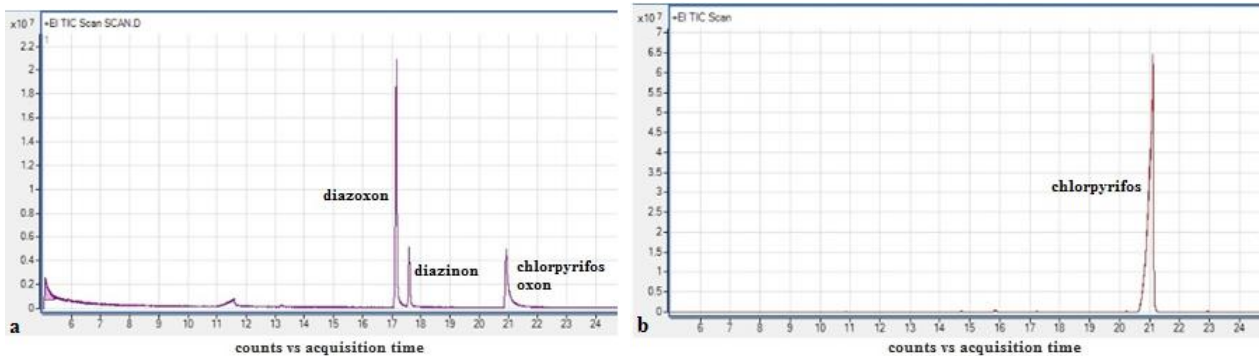
$$t_{1/2} = C_0/2k_0 \quad (2)$$

First-order model

First-order kinetic can be expressed as follows (Equation 3):

$$\ln C_t = -k_1t + \ln C_0 \quad (3)$$

where k_1 is the rate constant (1/day), and C_t and C_0 ($\mu\text{g}/\text{kg}$) are the residue concentration at time t and the initial concentration at time 0, respectively. Equation 4 was used to determine half-life ($t_{1/2}$)

**Figure 2.** Chromatographic profiles of spiked tomato samples with the target analyses under established GC/MS2 conditions. The retention time of every insecticide is as follows: (a) diazoxon: 17.1 min, diazinon: 17.53 min, chlorpyrifos oxon: 21.048 min; (b) chlorpyrifos: 21.04 min

for the first-order model

$$t_{1/2} = C_0/2k_0 \quad (4)$$

The half-life ($t_{1/2}$) for the zero-order model was determined from the equation $t_{1/2} = \text{Ln}2/k_1$.

Second-order model

The second-order form of the linear kinetic model is as follows (Equation 5):

$$1/C_t = 1/C_0 + k_2 t \quad (5)$$

Where k_2 is the rate constant (1/day), and C_t and C_0 ($\mu\text{g}/\text{kg}$) are the residue concentration after the application of pesticide at time t and the initial concentration at time 0, respectively.

The half-life ($t_{1/2}$) for the second-order model was calculated using Equation 6:

$$t_{1/2} = 1/k_2 C_0 \quad (6)$$

3.7.2. Nonlinear kinetic modeling

The nonlinear chi-square test is a statistical tool obtained by dividing the sum squared difference by its corresponding value. The Solver Add-in as part of Microsoft Excel was employed for fitting the nonlinear first- and second-order equations to the experimental data and determining the kinetic parameters, such as the rate constant (1) and $t_{1/2}$ (20,21).

4. Results

4.1. The dissipation dynamics of chlorpyrifos and diazinon and the production of oxon derivatives

The chlorpyrifos and diazinon residues in the

greenhouse were reduced from 2.01-0.09 $\mu\text{g}/\text{g}$ and from 1.92-0.01 $\mu\text{g}/\text{g}$, respectively. In field conditions, the 5-day residual values of chlorpyrifos were less than the maximum residue levels of the Iranian national and the European Union standards (0.1 $\mu\text{g}/\text{g}$), whereas the required time for diazinon to reach the maximum residue limit (MRL) accepted by the European Union (EU) (0.01 $\mu\text{g}/\text{g}$) was 10 days.

At room and refrigerator temperatures, the final residual concentrations of both diazinon and chlorpyrifos were higher than the MRL after 5 days. In room conditions, the reductions of chlorpyrifos and diazinon were 27.17% and 32.8%, respectively, whereas in refrigerator conditions, they were calculated at 23.11% and 17.29%, respectively.

At boiling temperature, the residue levels of chlorpyrifos and diazinon decreased from 2.77- 1.21 $\mu\text{g}/\text{g}$ and from 2.92-0.19 $\mu\text{g}/\text{g}$ within 2 h, respectively, and the dissipation rates were obtained at 56.3% and 93.4%, respectively.

In the present study, the residue of the oxon derivative of chlorpyrifos (chlorpyrifos oxon) was positive after the application of chlorpyrifos (40.8% EC) at the recommended dosages of 2/1000. On the contrary, diazinon oxon was found to be below the detection limit in all of the analyzed samples. The residue levels of chlorpyrifos oxon fluctuated during field conditions and reached a maximum of 7 days after spraying. At boiling temperature for 2 h, chlorpyrifos oxon varied from 224.8-170.59 $\mu\text{g}/\text{kg}$, while at room and refrigerator temperatures, it ranged from 147.9-180.34 $\mu\text{g}/\text{kg}$ and 53.07-202.6 $\mu\text{g}/\text{kg}$, respectively (Figure 3).

4.2. Modeling pesticide dissipation in tomatoes

The kinetic parameters, including the half-lives

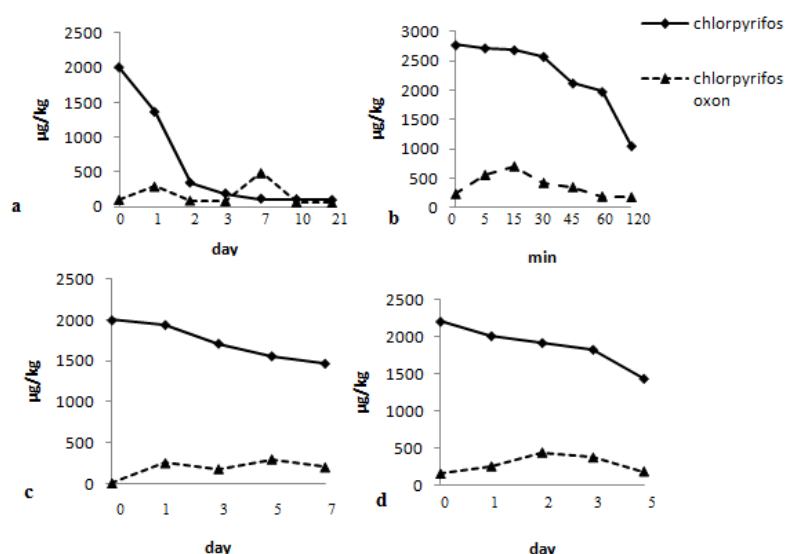


Figure 3. Dissipation of chlorpyrifos and its metabolite chlorpyrifos oxon in the tomato samples in: (a) greenhouse, (b) boiling, (c) refrigerator, and (d) room conditions

Table 2. Regression equation, correlation coefficient, and half-life of diazinon in tomato

Condition	Model	Dynamic equation	k	t _{1/2} (day)	R ²
Greenhouse	Zero-order model	c _t = -316.11t + 1791.9	316.11	2.83	0.9287
	First-order model	ln c _t = -0.6017t + 7.7929	0.6017	1.15	0.981
	Second-order model	1/ct = 0.0029t - 0.002	0.0029	0.68	0.8384
	Nonlinear first-order model	c _t = 1919.7e ^{-0.465t}	0.465	1.48	0.990
	Nonlinear second-order model	1/ct = 5.2E-04 + 2E-04t	2E-04	2.70	0.932
Refrigerator	Zero-order model	c _t = -74.299t + 2047.8	74.299	13.78	0.9664
	First-order model	ln c _t = -0.0397t + 7.6258	0.0397	17.45	0.971
	Second-order model	1/ct = 2E-05t + 0.0005	2E-05	19.01	0.9752
	Nonlinear first-order model	c _t = 2056.8e ^{-0.058t}	0.058	11.84	0.976
	Nonlinear second-order model	1/ct = 4.8E-04 + 2.58E-05t	2.58E-05	18.79	0.979
Room	Zero-order model	c _t = -168.79t + 2375.9	168.79	7.03	0.9487
	First-order model	ln c _t = -0.0863t + 7.7789	0.0863	8.03	0.9564
	Second-order model	1/ct = 4E-05t + 0.0004	4E-05	10	0.9641
	Nonlinear first-order model	c _t = 2371.3e ^{-0.078t}	0.078	8.88	0.960
	Nonlinear second-order model	1/ct = 4.2E-04 + 3.69E-05t	3.69E-05	11.41	0.965
Boiling	Zero-order model	c _t = -0.0292t + 2.6626	0.0292	45.59 (min)	0.9365
	First-order model	ln c _t = -0.0162t + 7.9145	0.0162	42.786	0.914
	Second-order model	1/ct = 0.0107t + 0.3316	0.0107	30.99	0.967
	Nonlinear first-order model	c _t = 2920.5e ^{-0.016t}	0.016	43.32	0.964
	Nonlinear second-order model	1/ct = 3.4E-04 + 7.54E-06t	7.54E-06	45.39	0.975

Table 3. Regression equation, correlation coefficient, and half-life of chlorpyrifos in tomato

Condition	Model	Dynamic equation	k	t _{1/2} (day)	R ²
Greenhouse	Zero-order model	c _t = -839.33x + 2082.1	839.33	1.24	0.884
	First-order model	ln c _t = -0.8885t + 7.7768	0.88	0.78	0.905
	Second-order model	1/ct = 0.0012t + 0.0002	0.001	0.41	0.822
	Nonlinear first-order model	c _t = 2020.3e ^{-0.4583t}	0.458	1.51	0.914
	Nonlinear second-order model	1/ct = 4.9E-04 + 2.4E-04t	2.4E-04	2.04	0.809
Room	Zero-order model	c _t = -111.37t + 2029.4	111.37	9.11	0.949
	First-order model	ln c _t = -0.0646t + 7.6215	0.064	10.72	0.982
	Second-order model	1/ct = 4E-05t + 0.0005	4E-05	10	0.971
	Nonlinear first-order model	c _t = 2001.9e ^{-0.0557t}	0.055	12.44	0.986
	Nonlinear second-order model	1/ct = 5E-04 + 2.98E-05t	2.98E-05	16.77	0.875
Refrigerator	Zero-order model	c _t = -78.451t + 2141.2	78.451	13.64	0.846
	First-order model	ln c _t = -0.0396t + 7.6687	0.0396	17.50	0.859
	Second-order model	1/ct = 2E-05t + 0.0005	2E-05	20	0.870
	Nonlinear first-order model	c _t = 2211.07e ^{-0.0469t}	0.0469	14.77	0.866
	Nonlinear second-order model	1/ct = 4.5E-04 + 2.29 E-05 t	2.29 E-05	19.739	0.887
Boiling	Zero-order model	c _t = -17.291t + 2730	17.291	78.94 (min)	0.939
	First-order model	ln c _t = -0.0075t + 7.9178	0.0075	92.41	0.940
	Second-order model	1/ct = 3E-06t + 0.0004	3E-06	100	0.940
	Nonlinear first-order model	c _t = 2689.3e ^{-0.0064t}	0.0064	108.3	0.945
	Nonlinear second-order model	1/ct = 3.7E-04 + 2.56E-06t	2.56E-06	145.3	0.945

and the rate constants of the pesticides, were calculated by modeling pesticide removal from tomatoes with four procedures (laboratory (e.g., boiling, refrigerator, and room temperatures) and field treatments).

The nonlinear first-order model gave more accurate fits to the field data (greenhouse) for both diazinon and chlorpyrifos, compared to other models and yielded the correlation coefficient (R²) values of 0.990 and 0.914, respectively (tables 2 and 3). On the contrary, the nonlinear second-order model provided a better pattern of dissipation at the refrigerator, room, and boiling temperatures, except for chlorpyrifos at room temperature whose variation was best described by the nonlinear first-order model (tables 2 and 3). Figures 4 and 5 display the best fitting models for the kinetic behaviors of chlorpyrifos and diazinon in all conditions. The half-lives of diazinon and chlorpyrifos were estimated

from the best fitting models.

Based on the best fitting models for diazinon in the case of laboratory treatment at the refrigerator, room, and boiling temperatures, the half-lives were calculated as 18.79 days, 11.41 days, and 45.39 min, respectively, while the half-life of chlorpyrifos was estimated at 12.44 days-145.3 min.

5. Discussion

In the current research, a significant reduction was detected in chlorpyrifos and diazinon residues in field conditions during various time periods. The dissipation rates of chlorpyrifos and diazinon in field conditions were obtained at 95.5% and 99.4%, respectively. In one study, 3 days after the application of pesticides on cucumbers, the decline of chlorpyrifos residues exceeded 70% and reached 98.67% after 10 days (22). As illustrated by another study, 21 days

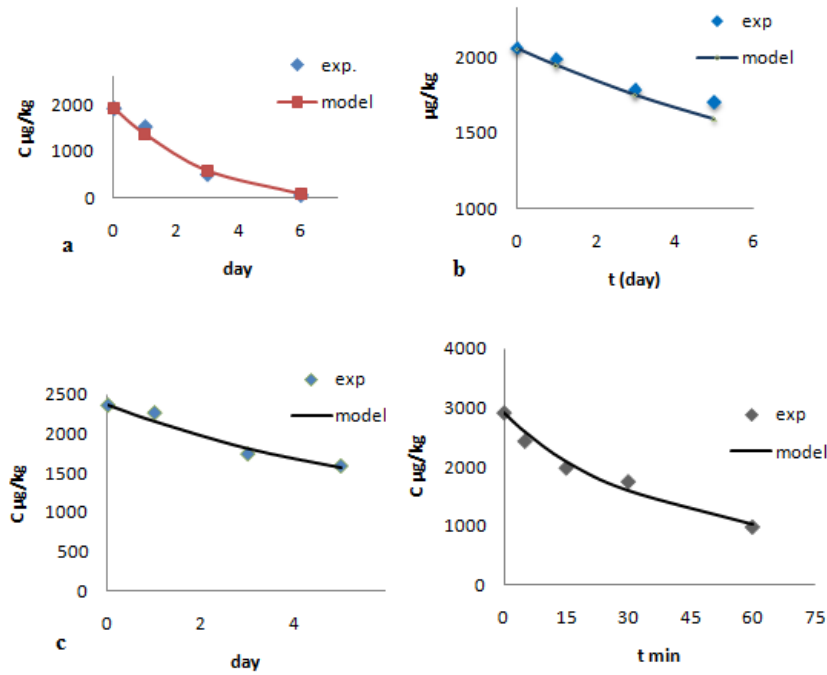


Figure 4. Best-fitting models for the kinetic behaviors of diazinon during field treatment and household conditions (e.g., storage at refrigerator and room temperatures, as well as boiling)

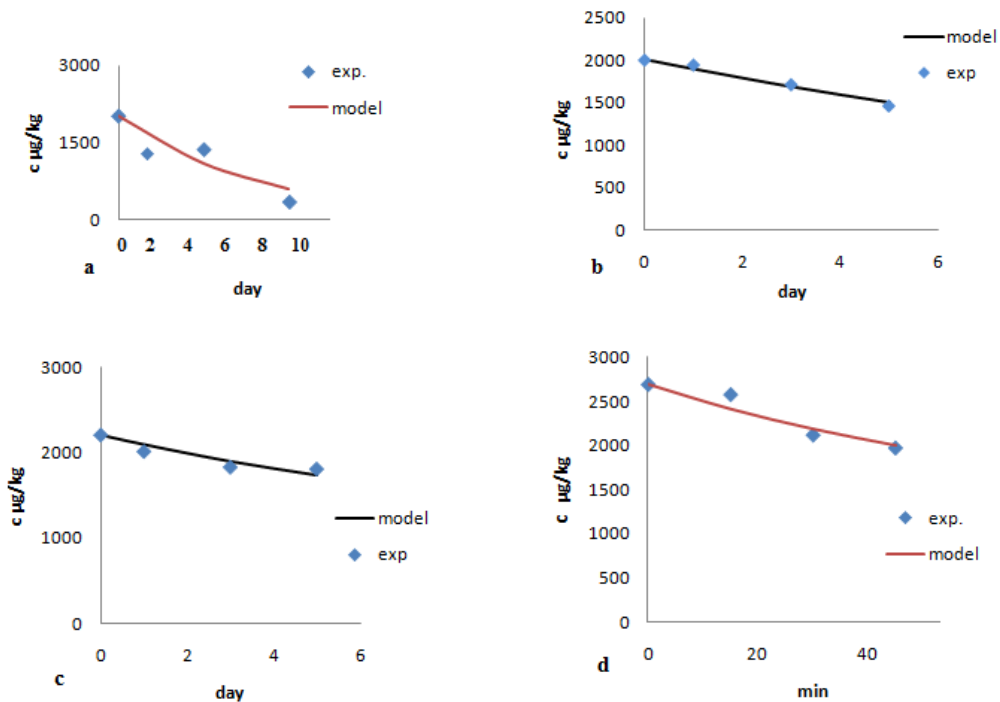


Figure 5. Best-fitting models for the kinetic behaviors of chlorpyrifos during field treatment and household conditions (e.g., storage at room and refrigerator temperatures, as well as boiling)

after spraying at the recommended dose, 98% of chlorpyrifos residues in the sweet corn samples and 91.2% of chlorpyrifos residues in the soil samples were removed. All final residues were lower than the

MRL (0.1 µg/g), and the half-life of chlorpyrifos degradation was calculated at 4.02 days (6).

Chlorpyrifos and diazinon were less persistent in field conditions, including room and refrigerator

temperatures, compared to laboratory conditions. It can be ascribed to the higher temperature, humidity, and photodecomposition, in the greenhouse, in comparison to other storage conditions, except for the boiling temperature (23). According to the results, temperature plays a crucial role in the degradation of pesticides. In one study, after boiling the samples for 5 min, the reduction percentage of the pesticides ranged from 42.8% (in cyprodinil) to 92.9 (in pyraclostrobin) (24).

The oxon derivatives of chlorpyrifos and diazinon demonstrated a peak at a retention time similar to that of their parent compounds. Therefore, they might not be detected in the samples by conventional methods (GC-MS and HPLC), and their detection is difficult and time-consuming (2). It was observed that the concentration of chlorpyrifos oxon was higher than the MRLs established by the European Union and the national standards. In two previously conducted studies, the formation of chlorpyrifos oxon was detected and increased toxicity after photodegradation and ultrasonic irradiation; nonetheless, the oxidation of diazinon was not the predominant reaction (25,26).

Using the nonlinear first-order model in the case of the field treatment, the half-life was determined at 1.48 days for diazinon and 1.51 days for chlorpyrifos. The half-life of chlorpyrifos was almost the same as that observed by Liang et al. who reported that the decline time of chlorpyrifos in cucumber samples was 1.60 days at the recommended dose (22). The half-lives of both pesticides decreased by increasing the temperature in laboratory studies from 4°C-100°C. Therefore, boiling proved to be more effective in the dissipation of pesticides, compared to storage at refrigerator and room temperatures.

The effective decline of pesticide residues based on the level of heat treatments may be attributed to the increased volatilization and accelerated degradation of these compounds as a result of elevated temperature. These findings were consistent with those suggested by previous studies which indicated that organophosphorus pesticides in foods were effectively decreased by increasing temperature in heat treatments (27,28).

According to the results, it can be observed that the half-life of diazinon was lower than that of chlorpyrifos in both field and lab treatments. It can be ascribed to the physical-chemical characteristics of diazinon, such as its high-pressure volatility, solubility in water, and photolysis, which lead to a more effective dissipation of diazinon residues, compared to chlorpyrifos residues (29,30).

6. Conclusion

In the current research, a significant reduction was observed in chlorpyrifos and diazinon residues in various time periods. The dissipation rates of these

pesticides in field conditions after 5 days were reported as 90.3% and 95.8%, respectively. Modeling the removal of the pesticides indicated that the nonlinear first- and second-order models were the best fitted models for the dissipation of both pesticides in field and post-harvest conditions. The half-life of diazinon was lower than that of chlorpyrifos in both field and laboratory treatments. Moreover, the half-lives of the pesticides significantly decreased in boiling conditions. Chlorpyrifos oxon was found in the samples as an intermediate product of chlorpyrifos, and its concentrations were higher than the recommended MRLs in all household conditions (e.g., at room, refrigerator, and boiling temperatures).

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Footnotes

Authors' Contribution: Study concept and design: R.Sh., M.T.S., S.K. ; analysis and interpretation of data: R.Sh., M.T.S., M.K., A.H., M.L. S.K.; drafting of the manuscript: R.Sh., M.T.S., S.K.; critical revision of the manuscript for important intellectual content: R.Sh., M.T.S., S.K. M.K., A.H., M.L.; statistical analysis: R.Sh., M.T.S., M.K., A.H., M.L. S.K.

Conflict of Interests: The authors declare that they have no conflict of interest regarding the publication of the current study.

Ethical Approval: This research project was approved by the Ethics Committee of Hamadan University of Medical Sciences (IR.UMSHA.REC. 1397.291).

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