The Pharma Innovation Journal 2023; 12(6): 3352-3355

www.ThePharmaJournal.com

The Pharma Innovation

**ISSN (E): 2277-7695**
**ISSN (P): 2349-8242**
**NAAS Rating: 5.23**
TPI 2023; 12(6): 3352-3355

www.thepharmajournal.com
Received: 15-03-2023
Accepted: 30-04-2023

**Pooja**
Department of Chemistry, Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

**Sushil Ahlawat**
Department of Chemistry, Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

**Ashu**
Department of Chemistry, Guru Jambheshwar University of Science and Technology, Hisar-Haryana, India

**Sakshi Goyal**
Department of Biochemistry, Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

**Corresponding Author:**
**Pooja**
Department of Chemistry, Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

# Persistence and dissipation studies of Quinalphos residues in tomato by using GC-MS/MS

**Pooja, Sushil Ahlawat, Ashu and Sakshi Goyal**

**Abstract**
In the present study, the risk assessment, dissipation behavior, persistence, and half-life period of quinalphos have been investigated on Tomato fruit by spraying the pesticide at the fruiting stage followed by another application after a ten-day interval. Gas chromatography-tandem mass spectrometry was used to analyze the residues of quinalphos from the samples after extraction using the quick, easy, cheap, effective, rugged, and safe method. In this paper, we present a novel, accurate, and cost-effective gas chromatography method for determining average tomato deposits of quinalphos. After the application of insecticide, quinalphos deposits were 0.307 mg/kg and the residues dissipated by following the first-order kinetics with a half-life of 2.62 days. At the recommended dosage, quinalphos residues reached below detection limits of quantification (0.05 mg/kg) after 7 days. For risk assessment studies, the 10th day will be safe for consumers to consume tomatoes.

**Keywords:** Quinalphos, QuEChERS, tomato, half-life, dissipation kinetics

## Introduction
Nutrients like phytochemicals, proteins, dietary fibers, vitamins, and minerals are found in vegetables, and these are essential for our health (Harinathareddy *et al*., 2014) [7]. Various chronic diseases can be treated naturally by eating vegetables. One such vegetable is tomato (*Lycopersicon esculentum Mill*.), which is either consumed raw or in a variety of processed forms such as soup, ketchup, puree, paste, or dehydrated powder. Their antioxidant abilities, β-carotene, vitamins, minerals and lycopene, which acts as an anti-prostate cancer agent, make them a wonderful source of nutrients. Tomato plants produce glycoalkaloids dehydrotomatine, esculeoside A, and lycopene, which are bioactive carotenoid pigments that protect them against bacteria, insects, fungi, and viruses (Friedman, 2013) [5]. In Asia, tomato consumption has increased rapidly in recent years. After China, India is the world's second largest tomato producer. Tomato production is limited by several diseases caused by pests. More than 50% of tomato production can be lost to pests (Engindeniz, 2006) [4]. As a result, a variety of natural and synthetic pesticides have been approved for use to control these insects, pests, and pathogens of diverse classes (Godara *et al*., 2022) [6].
Quinalphos (o,o-diethyl-o-quinoxlin-2-yl-phosphorothioate) has been found to be quite effective against pests causing harm to the tomato crop (Battu *et al*., 2008) [2] (Figure 1). However, several agencies are concerned about the amount of pest control chemicals left in food after the crop has been raised with them. Therefore, it is essential that the levels of harvest time residues of quinalphos in tomato fruits are safe for consumers and permissible for domestic and international trade. Despite some scanty literature (Torres *et al*., 1997) [10], the present field trials were conducted to determine whether quinalphos persists in the pulp and rind of tomato fruits under subtropical conditions in Haryana.

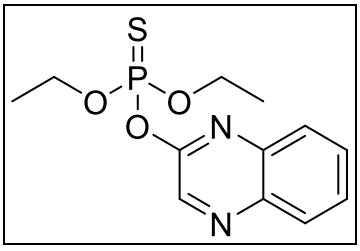


**Fig 1:** Chemical structure of Quinalphos

## Material Method

### Chemicals and Reagents

The certified reference materials of Quinalphos with a purity of 96% was acquired from Sigma Aldrich, Pvt, Limited. All the analytical organic solvents and reagents such as acetonitrile, acetone, sodium chloride, magnesium sulphate, and anhydrous sodium sulphate, were purchased from Merck (Darmstadt, Germany). Primary secondary amine (PSA) was supplied by Agilent Technologies Private Limited, Bangalore, India. Each of the chemicals used for the analysis was first subjected to glass distillation and then ran as reagent blank.

### Field Application and Sampling

Tomato (*Lycopersicon esculentum* Mill.) variety "HS-102" was raised following recommended agronomic practices at the Research Farm of Chaudhary Charan Singh Haryana Agricultural University, Hisar (29.14°N, 75.70°E). Quinalphos 25 EC formulation was sprayed only once at the time of 50% fruiting stage with the dosage of 250 g.a.i. $ha^{-1}$on selected experimental plots with the knapsack sprayer. Additionally, one of the experimental fields was left untreated to serve as a control. The samples in triplicate were collected randomly at 0 (2 h), 1, 3, 5, 7, 10, and 15 days after application (DAA). Samples were transported to the laboratory for the residue analysis.

### Sample Preparation

Tomato samples were processed using the QuEChERS method proposed by Sharma, (2007) [9]. A representative sample of 15 g macerated tomato fruits was combined with 30 mL acetonitrile and homogenized using a low-volume homogenizer (Heidolph) for 3-4 minutes at 14,000 rpm. To separate the water (tomato) and acetonitrile phases of the aforementioned representative sample, 3.3 g of sodium chloride (NaCl) is added to the extract and vortexed for 2 minutes. Following the 3 min centrifugation of the extract at 2500 rpm, the upper 18 mL acetonitrile layer was deposited over sodium sulphate to eliminate any remaining moisture traces. The dispersive solid phase extraction (d-SPE) technique was used for the cleanup of the extract with primary secondary amine (PSA) 0.4 g and 1.15 g magnesium sulphate ($MgSO_4$) as adsorbent. Then, the extract was recomposed to a volume of 3 mL in n-hexane and filtered through a 0.2-micron filter before GC–MS/MS analysis.

### GC-MS/MS Analysis

Pesticide analytes in samples were determined by GC-MS/MS (Shimadzu GC-MS TQ 8040) equipped with a capillary column (SH-Rxi-Sil MS column of 0.25 µm thick film having 30 m length and 0.25 mm internal diameter) using helium gas as the carrier gas at a constant flow rate of 1.5 mL $min^{-1}$. Samples were injected (1 µl) with an autosampler (20iAOC) in splitless injection mode. Temperature of the injection port was 250 °C and programming of the oven temperature was done to optimize the working conditions. The oven temperature programming began from 80 °C and remained at this temperature for 2 min, then start to increasing up to 180 °C at 20 °C/min ramp rate and attain the temperature of 300 °C, at rate of 5 °C/min and remains for 10 min. Pesticide residues could be confirmed and quantified by using GC-MS/MS in Multiple Reaction Monitoring (MRM) with a ESI(+) source of ionization throughout a scanning mass range of 40-1000 m/z,. Peaks in the total ion chromatogram of the sample recorded in MRM mode were detected based on their particular retention time ($R_T$) and their characteristic ion peaks in the mass chromatogram. The retention time on of quinalphos was found to be 16.432 min (Figure 2). The analysis was carried out in a completely air-conditioned laboratory with a temperature of less than 22 °C and a relative humidity of less than 60%.

### Dissipation Studies

The data on the residues over days were analysed using first-order kinetics with the equation (1) as follows:

$$C_t = C_o e^{-K_1 t} \quad (1)$$

Where, $C_0$ represents the initial concentration (mg $kg^{-1}$); $C_t$ concentration of the pesticide residue (mg $kg^{-1}$) at time t (in days), and $K_1$ denotes the rate constant ($day^{-1}$). A regression coefficient ($R^2$) was used to depict the link between residue data and time by plotting the log [residues (mg $kg^{-1}$) x $10^3$] on the y-axis and days after application on the x-axis. The half-life ($t_{1/2}$) of residues was calculated according to Hoskins formula (Hoskins, 1961).

### Data Analysis

Data is represented as mean ± S.D (Standard deviation). For each parameter involved in the dissipation and decontamination processes, analysis of variance (ANOVA) was performed to analyze the interactions among different treatments, and days after the application. Differences in means were determined to be statistically significant at a p-value of 0.05. The software Origin Pro 9.0 (Origin Lab Corporation, Northampton, MA, USA) was used to create all of the figures.

## Results and Discussion

In the present study, recovery experiments were conducted at various levels, i.e., 0.05 mg/kg and 0.10 mg/kg, in order to establish the reliability and validity of the analytical method and to check its efficiency. Accordingly, the control samples of hot pepper were fortified with different insecticides at the above-mentioned concentrations, and then analyzed according to the methodology described above using the fortified control samples. There was consistent recovery of more than 85% of all insecticides in hot pepper (Table 1). There was a limit of quantification (LOQ) of 0.05 mg/kg and a limit of detection (LOD) of 0.01 mg/kg for tomato fruits. At all the days, there was significant reduction in the residues of Quinalphos (p=0.05).

The residue data and percent dissipation of Quinalphos (25 EC) are shown in Table 2 (Fig. 3) indicate that the foliar application of recommended (250 ga.i.$ha^{-1}$($T_1$)), of Quinalphos (25 EC) on Tomato fruits in field conditions shown an initial residue of 0.307 mg/kg at respective dose. The insecticide dissipated to about 3.90 percent after 1 day of application. After then, progressive degradation in the concentration of residues deposited due to $T_1$ application in tomato fruits was observed with dissipation rates of 63.84, 75.89, and 83.38 for 3,5, and 7 days after the application (Figure 4). Further, it was noted that the residues reached below the limit of quantification i.e. 0.05 mg/kg on the $10^{th}$ day. Thus, the dissipation can be considered to be rapid and almost complete. The factor which appeared to have played role in the dissipation of Quinalphos is the high temperature.

The dissipation of Quinalphos followed first order kinetics with half-life value to be 2.62 days.

Quinalphos is used to treat a variety of fruit and vegetable crops. The consumption of Quinalphos alone does not pose any risk to consumers, but the wide range of crops on which Quinalphos is used may contribute significant amounts of Quinalphos intake through the total diet (Bhanti and Taneja, 2007) [3]. According to a study by Kabir *et al*., (2008) [8] on the yard long bean, Quinalphos residues were detected up to 6 days after spraying, and the quantity of residues was above MRL by 4 days. Residue study of Quinalphos in/on okra applied as foliar spray @ 500–1,000 g a.i. $ha^{-1}$ required a pre-harvest interval of 7 days (Aktar *et al*., 2008) [1]. Quinalphos 20 AF applied at the rate of 500 and 1,000 g a.i. $ha^{-1}$ to cabbage crop in consecutive seasons dissipated with a half-life of 1.27–1.38 days and the pre-harvest interval was 5.28–6.7 days (Aktar *et al*., 2010). However, a waiting period of 7 days fould be observed before the fruits are consumed when crop is sprayed with Quinalphos at 250 g a.i. $ha^{-1}$.

**Table 1:** Recovery for Tomato in spiked Tomato samples at different levels

| Substrates | Level of fortification (mg/kg) | % Recovery* (Mean ± S.D) |
|---|---|---|
| Tomato | 0.05 | 87.50 ± 3.20 |
| | 0.01 | 90.20 ± 1.95 |

*Mean ± S.D of three replicates

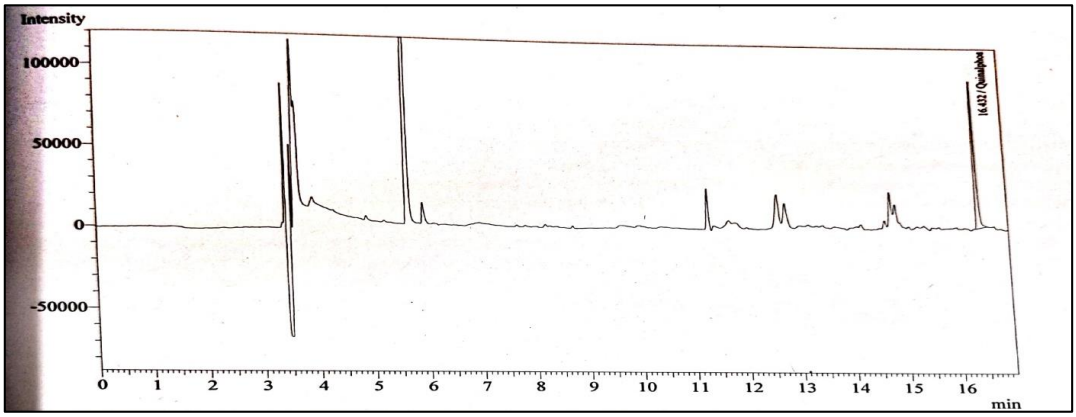


**Fig 2:** Chromatogram of GC-MS/MS showing retention time of quinalphos.

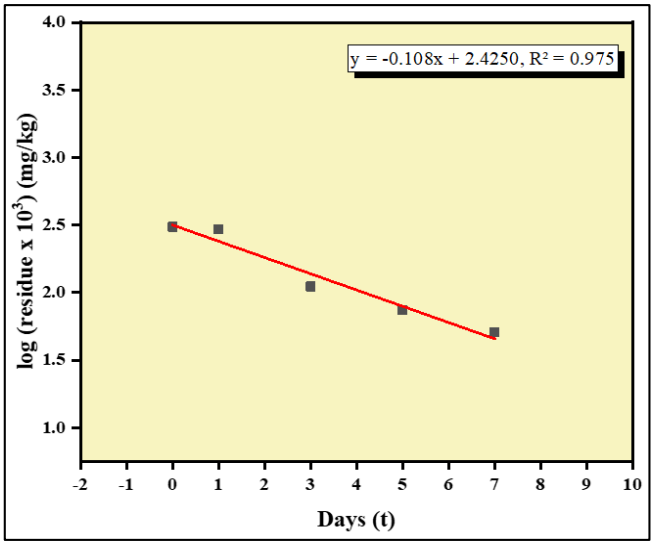


**Fig 3:** Plot of log [residues (mg/g) x $10^3$] of Quinalphos in Tomato fruits v/s days

**Table 2:** Residues of Quinalphos (mg/kg) in tomato fruits after the application of $T_1$ dose

| Days after the treatment | Dose ($T_1$= 500 g a.i.$ha^{-1}$) | | | | |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Average residues*±SD (mg/kg) | % Dissipation |
| 0 (2h) | 0.290 | 0.271 | 0.360 | 0.307 ± 0.046 | - |
| 1 | 0.181 | 0.170 | 0.232 | 0.295 ± 0.033 | 3.91 |
| 3 | 0.090 | 0.101 | 0.142 | 0.111 ± 0.027 | 63.84 |
| 5 | 0.072 | 0.060 | 0.090 | 0.074 ± 0.015 | 75.90 |
| 7 | 0.050 | 0.054 | 0.051 | 0.051 ± 0.005 | 83.39 |
| 10 | <LOQ | <LOQ | <LOQ | - | - |
| 15 | <LOQ | <LOQ | <LOQ | - | - |

LOQ = 0.05 mg/kg LOD = 0.01 mg/kg
*Average residues of three replicates
SD = Standard Deviation

**Table 3:** Dissipation parameters of Fenpropathrin residues in okra fruits

| Dissipation parameters | Dose ($T_1$= 500 g a.i.ha$^{-1}$) |
|---|---|
| **Regression equation** | y = -0.108x + 2.4250 |
| $R^2$ | 0.975 |
| $K_1$ | 0.264 |
| $C_o$ | 0.307 |
| $t_{1/2}$ | 2.62 |

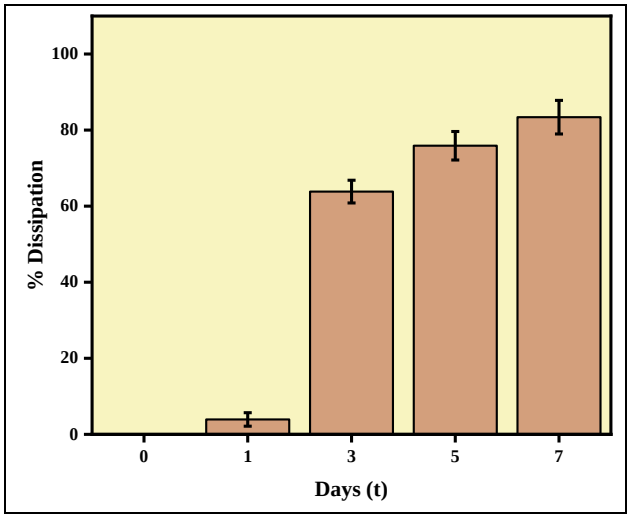


**Fig 4:** Chart showing dissipation pattern of Quinalphos in Tomato at $T_1$ dose

## Conclusion

The dissipation of Quinalphos in tomato fruits followed first order kinetics. Half-life values for Quinalphos on tomato at the recommended dosage were observed to be 2.62 days. A waiting period of 7 days is suggested to reduce the risk before consumption of tomato. The residues of Quinalphos were found to be completely eliminated after 10 days. Therefore, it is recommended to wait for 10 days before harvesting and consuming tomato after the application of Quinalphos.

## Acknowledgement

The authors appreciate the assistance received from the head of the Department of Entomology and Chemistry at CCS, Haryana Agricultural University, Hisar, and the Department of Chemistry at Guru Jambheshwar University of Science and Technology, Hisar, for their contributions to this study by providing the necessary laboratory equipment and staff.

## Conflict of Interest

The authors state that they have no known competing financial interests or personal ties that might seem to have influenced the research reported in this paper.

## Declaration of Funding Information

During this investigation, no grant was supplied by an external funding source.

## References

1. Aktar MW, Sengupta D, Chowdhury A. Degradation dynamics and persistence of quinolphos and methomyl in/on okra (*Ablemoschus esculentus*) fruits and cropped soil. Bulletin of Environmental Contamination and Toxicology. 2008;80:74-77.
2. Battu RS, Singh B, Arora PK, Sahoo SK. Dissipation of quinalphos in kinnow mandarin fruits under subtropical conditions of Punjab, India. Bulletin of Environmental Contamination and Toxicology. 2008;80:395-398.
3. Bhanti M, Taneja A. Contamination of vegetables of different seasons with organ phosphorous pesticides and related health risk assessment in northern India. Chemosphere. 2007;69(1):63-68.
4. Engindeniz S. Economic analysis of pesticide use on processing tomato growing: A case study for Turkey. Crop Protection. 2006;25(6):534-541.
5. Friedman M. Anticarcinogenic, cardioprotective, and other health benefits of tomato compounds lycopene, $α$-tomatine, and tomatidine in pure form and in fresh and processed tomatoes. Journal of Agricultural and Food Chemistry. 2013;61(40):9534-9550.
6. Godara R, Ahlawat S, Chauhan R, Dhanker P. Persistence of azoxystrobin and difenoconazole in tomato fruits following application of ready mix formulation and decontamination by household processing. Pesticide Research Journal. 2022;34(2):183-189.
7. Harinathareddy A, Prasad NBL, Devi KL. Effect of household processing methods on the removal of pesticide residues in tomato vegetable. Journal of Environmental Research and Development, 2014;9(1):50.
8. Kabir KH, Rahman MA, Ahmed MS, Prodhan MDH, Akon MW. Determination of residue of diazinon and Carbosulfan in Brinjal and quinalphos in yard long bean under supervised field trial. Bangladesh Journal of Agricultural Research. 2008;33(3):503-513.
9. Sharma KK. Pesticide residue analysis manual. Directorate of Information and Publications of Agriculture, Indian Council; c2007.
10. Torres CM, Picó Y, Marin R, Mañes J. Evaluation of organ phosphorus pesticide residues in citrus fruits from the Valencian community (Spain). Journal of AOAC International. 1997;80(5):1122-1128.