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

Reena Chauhan
Department of Chemistry,
Chaudhary Charan Singh
Haryana Agricultural University
Hisar, Haryana, India

Corresponding Author:
Reena Chauhan
Department of Chemistry,
Chaudhary Charan Singh
Haryana Agricultural University
Hisar, Haryana, India

Persistence of quinalphos and triazophos residues in capsicum

Sushil Ahlawat and Reena Chauhan

Abstract
In the present study quinalphos and triazophos was applied twice @ 500 and 250 g a.i.ha^{-1} separately on capsicum field to assess the dissipation behavior of two insecticides. Samples were collected periodically as per set schedule for residue analysis. Residues of these two insecticides were estimated on GC-MS/MS. The limit of quantification (LOQ) of quinalphos and triazophos was found to be 0.01 and 0.05 mg kg^{-1}. Residues of quinalphos and triazophos reached below LOQ on 5th and 7th day after last spray. Dissipation behavior follows the first order kinetics with half-life ($t_{1/2}$) 0.86 days and 1.43 days for quinalphos and triazophos, respectively.

Keywords: Capsicum, dissipation, insecticides, residues, half-life

Introduction
Capsicum (sweet pepper) is an important tropical and sub tropical crop from solanaceae family. Its cultivation is gaining popularity because it's higher and superior quality fruits, off season production and easy access to urban markets. It is grown in both irrigated and rainfed conditions. In open field conditions its yields ranges from 20 to 40 tonnes/ ha, whereas in green house the yield is about 100-200 tonnes/ha [1]. Suitable climate, high plant density, monocropping of susceptible genotype, make the crop prone to pest predominate among which are mites, thrips, powdery mildew, whiteflies and nematodes. Thrips (*Scirtothrips dorsalis* Hood), is an important pest of capsicum [2]. India by causing substantial economic losses due to widespread cultivation of high-yielding susceptible varieties with a narrow genetic base, heavy dependency on inorganic fertilizers, and apparent change in climate [3-6]. The crop is susceptible to attack by a number of insect pests from the time plant first emerges in the seed bed until harvest [7]. Pesticides help farmers in large way they help in preventing crop loss, increase productivity, cost of production reduced, quality improves and most important increase their income [8]. As a result, application, frequency and dosage of pesticides are substantially higher in the crops. Now a day, the food safety issue induced by food contamination with reference to pesticide residue is becoming more and more important [9]. As, these residues enters inside the living body by various modes *viz*., fruits, vegetables and environment (water and soil) [10]. It will be beneficial if sufficient data are available on the persistence of these frequently used insecticides so that farmers can follow the suggested waiting period between spray and crop harvesting. Keeping this point in view, a study was carried to access the persistence behaviour of quinalphos and triazophos residues in/on capsicum.

Materials and Methods
Chemicals: Reagents used were of analytical grade, florisil and sodium sulphate was obtained from M/s Merck Specialties Private Limited, Mumbai, India. Certified reference material of quinalphos (99.4% purity) and triazophos (98.9% purity) were procured from Sigma Aldrich. All the solvents used were of analytical grade and redistilled in glass apparatus. Suitability of used solvents was ensured by running reagent blank.

Preparation of standard solution
A standard stock solution of quinalphos and triazophos having concentration of 1 mg mL^{-1} was prepared in acetone. The standard solutions required for constructing a calibration curve (2.00, 1.50, 1.00, 0.50, 0.25 and 0.10 µg mL^{-1}) were prepared from stock solution by serial dilution using acetone and were stored at 4ºC.

Field experiment
The experiment was conducted at the Research Farm of Entomology Department, CCS Haryana Agricultural University, Hisar. Each experiment was laid out in randomized block design (RBD) with three replications along with control.

Control plots were sprayed with water only for comparison. Quinalphos (25EC) and triazophos (40 EC) was applied twice at the interval of 10 days at 50% fruit initiation stage in separate plots with the help of knapsack sprayer fitted with hollow cone nozzle.

Sampling procedure

About 1 to 2 kg marketable size capsicum fruit samples were collected randomly from control and treated plots of each treatment at 0 (2 h), 1, 3, 5,7,10 and 15days after last application of the insecticide. The samples from each plot were collected separately, packed in polyethylene bags and brought to the laboratory for processing. Samples were extracted and cleaned up immediately after sampling.

Extraction and cleanup

The samples were processed and analyzed at Pesticide Residue Analysis Laboratory, Department of Entomology, CCS Haryana Agricultural University, Hisar. The capsicum fruit samples were processed by QuEChERS (Quick, Easy, Cheap, Effective, Rugged and safe) method for determining the residues of quinalphos and triazophos. A sub sample of 15 g was weighed into a 50 mL centrifuge tube and then 30 mL HPLC grade acetonitrile was dispensed into it. The sample was homogenized using high speed homogenizer (Heidolph Silent Crusher-M®) for 2-3 min at 14,000-15,000 rpm. Sodium chloride (NaCl) 10 ± 0.1 g was added to homogenize the sample for phase separation. The contents were centrifuged at 2500-3000 rpm for 3 min. An aliquot of 15 mL HPLC grade acetonitrile layer was transferred over 10 ± 0.1 g sodium sulfate (Na_2SO_4) in a test tube. The HPLC grade acetonitrile extract subjected to cleanup by dispersive solid phase extraction (DSPE). An aliquot of 6 ml acetonitrile was taken in a test tube containing 0.15 ± 0.01 g PSA sorbent, 0.90 ± 0.01 g anhydrous $MgSO_4$ and 0.05 ± 0.01g graphitic carbon black and the contents were thoroughly vortexed on vortex shaker. Again it was centrifuged at 2500-3000 rpm for 1 min. 4 mL aliquot of this HPLC grade acetonitrile was evaporated to dryness using low volume evaporator at 35° C. Volume was made up to 2 mL with hexane.

Estimation by GC-MSMS

The residues of quinalphos and triazophos were estimated on GCMS/MS (Agilent 7890A series) Column: HP-5, column (30 m x 0.32 mm i.d. x 0.25 µm film thickness) containing 5 percent diphenyl / 95 percent dimethyl polysiloxane. Oven temperature ramping was: 70°C (2 min) → @25°C/min → 150°C (0 min) → @15°C/min → 200°C (0 min) →@8°C/min → 280°C (2 min). Detector: Mass 7000 GCMS/MS. Detector parameters were: source temperature = 230°C; emission current = 35 µA; energy = – 70 ev; repeller voltage = 11 v; ion body = 12 v; extractor = – 7.2 v; ion focus = – 7.4 v; quadrupole one (MS^1) temperature =150°C; quadrupole two (MS^2) temperature = 150°C. Gas flow rates: helium (carrier gas) = 1 ml/min. (through column) and 2.25 ml/min. (collision flow/quench flow), nitrogen (collision cell) = 1.15 ml/min. Other parameters: split ratio = 1: 10; vacuum (high pressure) = $2.23x10^{-05}$ torr; rough vacuum = $1.51x10^{+02}$ torr; injection volume = 2 µL. Under these operating conditions the retention time of quinalphos and triazophos was found to be 21.402 and 26.225 minutes, respectively. Residues were estimated by comparison of peak height/peak area of the standard with that of the unknown or spiked samples run under identical conditions. The limit of quantification (LOQ) of quinalphos and triazophos was found to be 0.01 and 0.05 mg kg^{-1}. The half life as well as time required to reach below determination level was calculated by using formula of Hoskins [11].

Results and Discussion

Quality control and quality assurance of analytical method

Capsicum fruit were spiked with quinalphos and triazophos at three concentration levels (0.01, 0.05 and 0.10 mg kg^{-1}) and analyzed as per the methodology described above to estimate the trueness of the method. Per cent recoveries of quinalphos varied from 81.35 to 90.02 and triazophos recoveries ranged from 83.11 to 88.66. Therefore, the results have been presented as such without applying any correction factor (Table 1).

Table 1: Per cent Recoveries of Quinalphos and Triazophos in/on capsicum

Fortification level (mg/kg)	Average* Recovery (%)±SD	
	Quinalphos	Triazophos
0.01	81.35±3.25	83.11±2.95
0.05	84.47± 5.64	85.20±1.52
0.10	90.02±3.49	88.66±4.05

Limit of detection and quantification

In general, residues of quinalphos and triazophos were determined by comparing the peak areas of the reference standards with that of the unknown or spiked samples which is run under identical conditions in instruments as reference standards. For quinalphos and triazophos, half-scale deflection obtained was 0.5 and 1ng, respectively, which could be easily identified from the baseline. As 0.1 ng of the compound produced 10% deflection which can be measured. From final volume (4 ml) when 2 µl (10 mg) of the sample was injected, it did not produce any background interference. Thus, limit of quantification (LOQ) was found to be 0.01 mg kg^{-1} and limit of detection (LOD) 0.003 mg kg^{-1} for quinalphos and 0.05 mg kg^{-1} LOQ and 0.016 mg kg^{-1}, LOD for triazophos. Chromatograms of quinalphos and triazophos are presented in Figs 1 and 2.

Qualitative Analysis Report

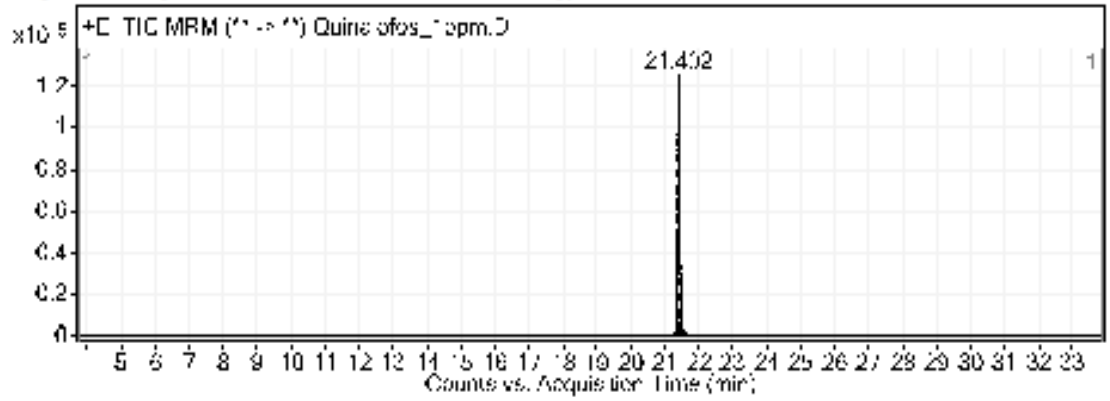
Data Filename	Quinalofos_1ppm.D	**Sample Name**	Quinalofos_1ppm
Sample Type		**Position**	2
Instrument Name	GCMS	**User Name**	DATASYSTEM01\admin
Acq Method	Quinalophos_MRM.M	**Acquired Time**	4/30/2014 11:27:07 AM
IRM Calibration Status	Not Applicable	**DA Method**	test.m
Comment			

Expected Barcode **Sample Amount**

Dual Inj Vol 2 **OperatorName** DATASYSTEM01\admin
RunCompletedFlag True

User Chromatograms

Fragmentor Voltage **Collision Energy** 0 **Ionization Mode** EI

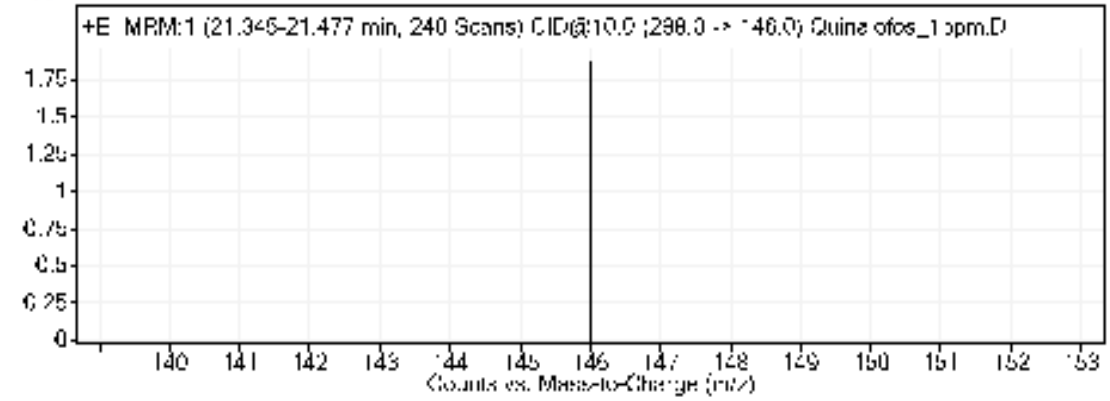


Integration Peak List

Start	RT	End	Height	Area
21.284	21.402	21.573	125275	541755

User Spectra

Spectrum Source **Collision Energy** **Ionization Mode**
Peak (1) in "+ TIC MRM (** -> **)" 10 EI



Spectrum Source **Collision Energy** **Ionization Mode**
Peak (1) in "+ TIC MRM (** -> **)" 15 EI

Fig 1: Chromatogram of Quinalphos

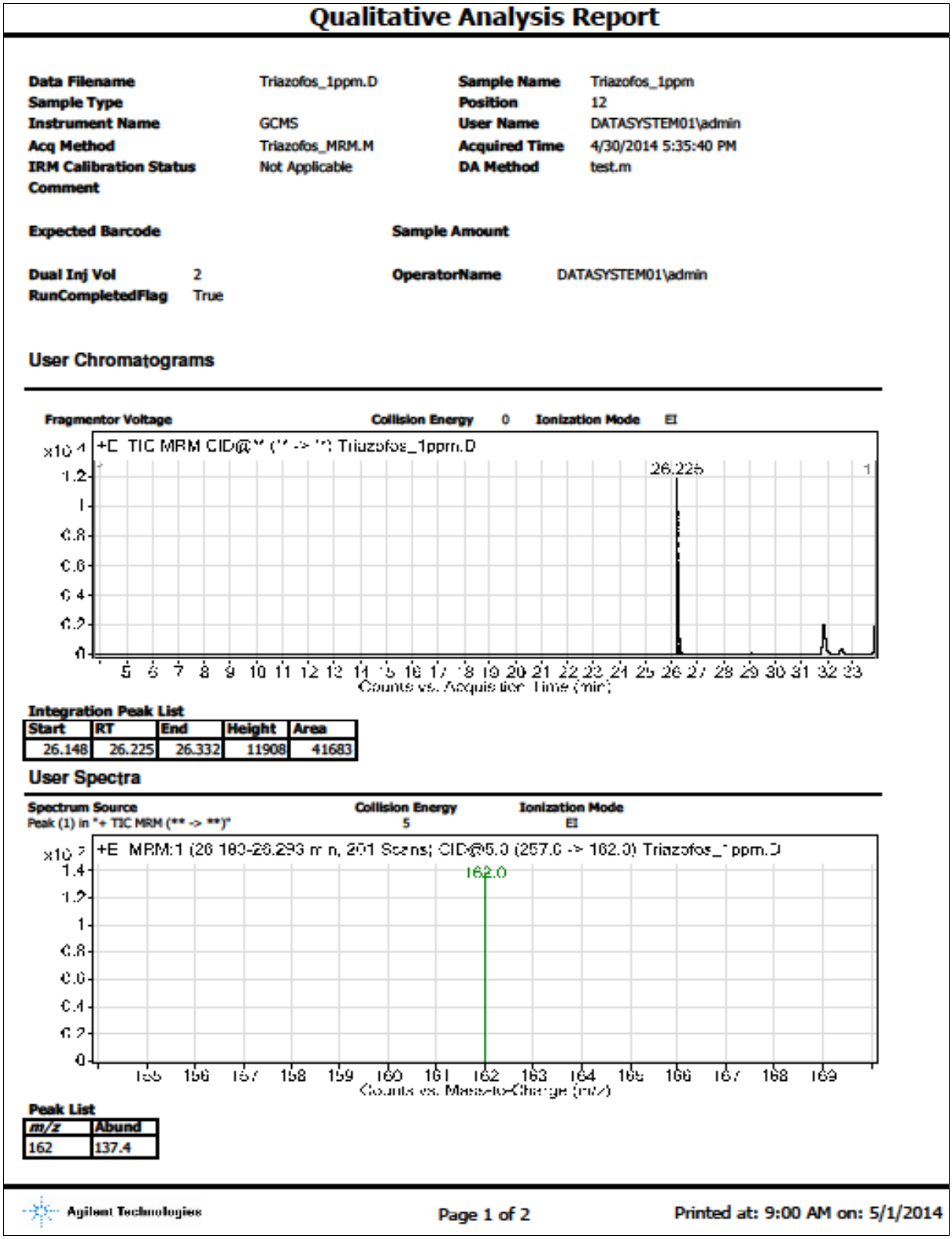


Fig 2: Chromatogram of Triazophos

Persistence of quinalphos and triazophos in capsicum

Analysis of capsicum fruits after two applications of quinalphos (500 g a.i. ha^{-1}) and triazophos (250 g a.i. ha^{-1}) are presented in Table 2. Samples were collected after 2nd application shows the mean initial deposits of 0.085 mg kg^{-1} for quinalphos. These deposits were dissipated to 0.038 and 0.018 mg kg^{-1} on 1 and 3day after last application, respectively thereby showing the loss of about 55.29 and 78.82 per cent. These residues reached below LOQ (0.01 mg kg^{-1}) in 5 days. The mean initial deposits of triazophos were observed to be 0.470 mg kg^{-1} on the capsicum fruits after 2nd application. These deposits dissipated to 0.244, 0.110 and 0.058 mg kg^{-1} after 1, 3 and 5 days respectively, thereby showing a loss of about 48.08, 76.59 and 87.65 per cent. Residues of triazophos dissipated below LOQ (0.05 mg kg^{-1}) on 7 day after last application. Sushil *et al*., 2018 [12] applied selected pesticides (chlorpyriphos, ethion, quinalphos and spiromesifen) on chilli at their recommended dose and found that spiromesifen dissipated fast as compare to others. Ahlawat *et al*., 2017 [13] studied three organophosphates in tomato and green pea and results are in agreement with us. Kumari and Chauhan (2015) [14] studied the dissipation

behavior of chlorpyriphos in chilli and reported that residues below LOQ (0.01 mgkg^{-1}) on 30th day after application at recommended (160 g a.i ha^{-1}) and double the recommended dose (320 g a.i ha^{-1}). Results are in agreement with Samriti *et al*. 2011 [15].

The dissipation of residues of quinalphos and triazophos from capsicum fruits followed first order kinetics. The correlation coefficient varied from - 0.9776 to -0.9906 (Table 3). The Half-life ($t_{1/2}$) of quinalphos on capsicum was observed to be 0.86 days and of triazophos to be 1.43 days (Table 2; Fig. 3 and 4). Half-life of chlorantaniliprole in capsicum was 1.18 and 2.05 days when applied at recommended (30 g a.i ha^{-1}) and doubles the recommended dose (60 g a.i ha^{-1}) Ahlawat *et al*., 2019 [16]. Saini *et al*., 2015 [17] reported almost similar regression equation and correlation coefficient in fipronil when applied on chilli.

Table 2: Residues (mg kg^{-1})* of Quinalphos and Triazophos in/on Capsicum

Days after treatment	Quinalphos (25EC) Dose 500g a.i. ha^{-1}		Triazophos (40EC) Dose 250g a.i. ha^{-1}	
	Average Residues ±SD	Dissipation (%)	Average Residues ±SD	Dissipation (%)
0	0.085±0.008	-	0.470±0.003	-
1	0.038±0.002	55.29	0.244±0.035	48.08
3	0.018±0.003	78.82	0.110±0.001	76.59
5	BDL	-	0.058±0.004	87.65
7	BDL		BDL	-

* Average of three replicates
Below the determination limit (BDL): 0.01 mg kg^{-1} for quinalphos 0.05 mg kg^{-1} for triazophos
Half Life Period ($t_{1/2}$): 0.86 for quinalphos:1.43days for triazophos

Table 3: Theoretical dissipation models and half-life period of quinalphos and triazophos on capsicum

Insecticides	Treatment Level (g a.i. ha^{-1})	Correlation coefficient (r)	Half-life (days)	Regression equation(y=a+bx)
Quinalphos	500	-0.9776	0.86	y=1.8757-0.2158x
Triazophos	250	-0.9906	1.43	y=2.6150-0.1773x

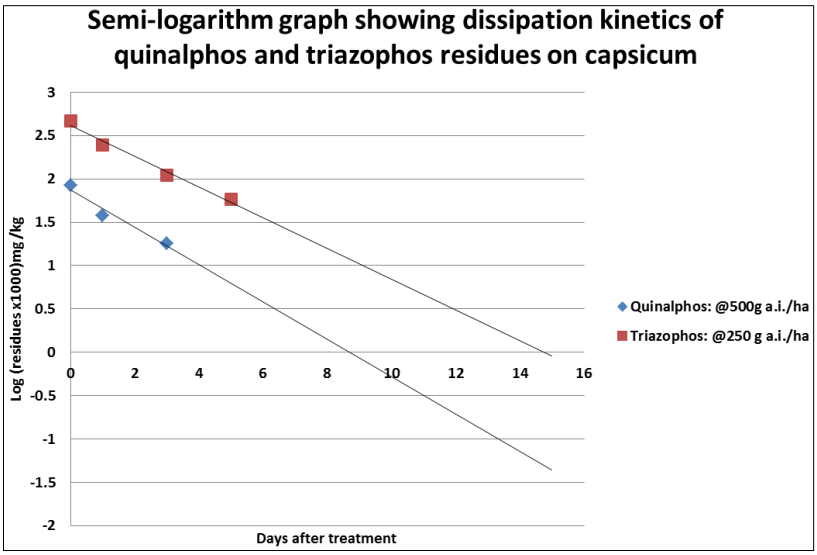


Fig 3: Dissipation kinetics of quinalphos and triazophos

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