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Dissipation study of spiromesifen on capsicum and soil using GC-MS

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Abstract
This investigation was carried out to study persistence of spiromesifen (Oberon 22.9% SC) in the soil and capsicum after being applied twice at the 50% fruiting stage with interval of 10 days. Gas chromatography-tandem mass spectrometry was used to examine spiromesifen traces in samples extracted using the liquid-liquid partitioning technique. This study presents a novel, precise, and cost-effective gas chromatography method for quantifying spiromesifen levels in capsicum plants and soil samples. The initial deposits of spiromesifen were measured to be 0.86 mg/kg, and their dissipation followed first-order kinetics with a half-life of 1.96 days. Following a treatment period of 10 days, the residual levels were found to have decreased to a point below the detection limit of 0.05 mg/kg. It is advisable to observe a waiting time of 24 hours for the safe use of capsicum.

Keywords: QuEChERS, spiromesifen, dissipation kinetics, half-life

Introduction
Capsicum (*Capsicum annuum* L.) is one of the most well-liked and lucrative annual herbaceous vegetable crops. Insect pests are one biotic component that lowers crop quality; even a little imperfection may significantly lower a product's worth. However, the mite Polyphagotarsonemus latus banks is the most destructive pest in field and poly house conditions [1, 2], with over 20 insect species having been documented on chiles (Capsicum spp.) in India by Butani (1976) [3]. According to Reddy and Kumar (2006), without insecticidal treatment, capsicum yields might drop by 40-60 t/ha [4].
Spiromesifen(3-(2,4,6-trimethylphenyl)-4(3,3-dimethylbutyl-carbonyloxy)-5-(spirocyclopentyl)-3-dihydrofuran-2), a chemical with insecticidal and acaricidal properties, is recommended for the control of a wide variety of insect pests, including whiteflies (*Bemisia* and *Trialeuroides* spp.) and mites (*Tetranychus* and *Panonychus* spp.) on vegetables [5]. To prevent the development of pesticide resistance, it is used in conjunction with neonicotinoids and diafenthiuron in various vegetable cropping systems. Since then, farmers have been irresponsibly spraying chemicals to lower mite numbers and boost yields. Since capsicum is often ingested fresh, the current study aimed to investigate the dissipation behavior, risk assessment, and safe waiting duration of spiromesifen.

Material and Method
Spiromesifen certified reference materials with a 96% purity were purchased from Sigma Aldrich, Pvt, Limited. Acetonitrile (ACN), sodium chloride, acetone, magnesium sulfate, and anhydrous sodium sulfate were all acquired from Merck (Darmstadt, Germany) for use in analytical procedures. Agilent Technologies Private Limited, Bangalore, India, provided the primary secondary amine (PSA). Each of the compounds used in the analysis was glass distillated before being run as a reagent blank.

Field application and sampling
Capsicum (*Capsicum annuum* L.) variety "Capsicum/KT1" was grown at the Chaudhary Charan Singh Haryana Agricultural University's Research Farm in Hisar using suggested agronomic procedures. Spiromesifen (Oberon 22.9 SC formulation) was sprayed twice with a 10-day interval at the 50% fruiting stage using a knapsack sprayer at a dose of 92 g.a.i. ha^{-1} on chosen experimental plots, and one of the experimental fields was treated with water as a control. The triplicate samples were taken in a random manner at certain time points, namely 0 (2 hours), 1, 3, 5, 7, 10, and 15 days following the application. The samples were brought to the laboratory in order to conduct residue analysis.

Extraction and clean-up

A representative sample of 25 g chopped and macerated capsicum fruits was dipped separately overnight in an Erlenmeyer flask and kept for 24hr. Following acetone rinsing, the extract was filtered into a 1L separatory funnel. 600 mL of brine solution was added to the filter, and then it was partitioned twice with 100 and 50 mL of DCM. After passing over a bed of sodium sulfate, the organic layer was collected in a 500 mL reagent bottle. Two more n-hexane (50, 100 mL) partitions were performed on the aqueous layer, and the resulting organic layer was collected in the reagent bottle. In addition, 25 mL of n-hexane was used to wash the sodium sulphate layer. After filtering through Whatman's filter No. 1, the extract was treated with 300 mg of activated charcoal powder for around 1 hour to clarify the solution. The resulting extract was concentrated in a rotating vacuum evaporator at less than 30 °C. Before GC-MS analysis, the extract was reconstituted to 3 mL in n-hexane and filtered through a 0.2-micron filter.

GC-MS analysis

The analysis of spiromesifen residue was conducted using gas chromatography-mass spectrometry (GC-MS) with a Shimadzu 2010 instrument. A capillary column with a thickness of 0.25 µm, a length of 30 m, and an internal diameter of 0.32 mm (HP-1 column) was used. Helium gas was used as the carrier gas, flowing at a constant rate of 1.5 mL min^{-1}. The injection of samples (1 µL) was conducted using an autosampler (20iAOC) operating in split-less injection mode. The temperature of the injection port was recorded as 260 °C, whereas the oven temperature was measured at 175 °C. In the present experimental settings, the observed retention time for spiromesifen was determined to be 12.85 minutes, as seen in Figure 1. Residues were estimated by comparison of peak height / peak area of the standard with those of unknown or spiked samples performed under similar circumstances. The study was conducted inside a laboratory environment that was fully equipped with air conditioning, maintaining a temperature below 22 °C and a relative humidity below 60%. The determined limit of quantification for spiromesifen was shown to be 0.05 mg/kg.

Dissipation Studies

The analysis of the data pertaining to the residues seen over a period of days was conducted using a mathematical model based on first-order kinetics. The equation (1) used in this analysis is shown below:

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

Where, C_0 represents the initial concentration (mg/kg); C_t concentration of the pesticide residue (mg/kg) at time t (in days), and k denotes the rate constant (day^{-1}). The relationship between residue data and time was analyzed using a regression coefficient (R^2). The log-transformed values of residues (mg/kg) multiplied by 10^3 were shown on the y-axis, while the days following application were plotted on the x-axis. The calculation of the half-life ($t_{1/2}$) of residues was performed using the formula proposed by Hoskins (1961) [6].

Data analysis

The data is expressed in the form of mean±standard deviation (SD). An analysis of variance (ANOVA) was conducted to examine the relationships between various treatments and the number of days after application for each parameter involved in the dissipation processes. There are variations in the statistical significance of the means was established at a p-value of 0.05. All the figures were created by utilizing the software Origin Pro 9.0 (Origin Lab Corporation, Northampton, MA, USA).

Result and Discussion

The present study included the implementation of recovery trials at varying levels, namely 0.05 mg/kg and 0.10 mg/kg, in order to evaluate the repeatability and precision of the analytical methodology and to gauge its efficacy. As a result, the control capsicum samples were spiromesifen-spiked at 0.05 mg/kg and 0.10 mg/kg. The concentrations described before were then subjected to testing in line with recognized methods. Table 1 indicates that there was a consistent recovery rate over 85%. Spiromesifen had a limit of quantification (LOQ) of 0.05 mg/kg and a limit of detection (LOD) of 0.01 mg/kg.

The results shown in Table 2 (Fig. 3) demonstrate the residue levels and percentage dissipation of spiromesifen (22.9% SC). These findings suggest that when spiromesifen (22.9% SC) is applied to capsicum fruits at the authorized dosage of 96 ga.i./ha under field conditions, an initial residue of 0.86 mg/kg is seen. After one day of treatment, the pesticide exhibited a dissipation rate of around 48.84%. Subsequently, a gradual decline in the concentration of residues deposited as a result of T_1 treatment in capsicum fruits was seen, with dissipation rates of 80.35%, 88.14%, and 91.86% for the time periods of 3, 5, and 7 days following the application, respectively (see Figure 3). On day 10, the residues were recorded as being below the 0.05 mg/kg quantification threshold. Therefore, the dissipation might be characterized as expeditious and almost exhaustive. The high temperature is believed to have been a contributing element in the dispersion of spiromesifen. The findings of Sharma *et al.* (2005) [7], who investigated the persistence of spiromesifen on apple after application of Spiromesifen 22.9% SC at 96 ga.i./ha at various places, are in accord with these results. No any residue of spiromesifen were reported in the soil. Similar to this, no residues were found in the cotton or chilli crop soil during harvest [8]. In soil samples (0–15 cm) taken from an apple orchard 40 days after spraying, no spiromesifen residues were found [7].

The dissipation kinetics of spiromesifen were seen to follow a first-order decay model, with a half-life of 1.96 days. In accordance with the European Union Maximum Residue Limit (EU MRL) of 0.5 mg/kg, it is suggested to wait for a period of 1 day before consuming capsicum to ensure safety.

Table 1: Recovery of spiromesifen from spiked capsicum

Substrates	Level of fortification (mg/kg)	% Recovery* (Mean±SD)
Capsicum fruits	0.05	85.40±0.59
	0.10	89.35±0.73

* Mean±SD of three replicates

Table 2: Spiromesifen residue in capsicum treated at single dose

Days after treatment	Dose 96 ga.i./ha				
	R_1	R_2	R_3	Average residues ± SD	Dissipation (%)
0	0.468	1.285	0.855	0.860±0.027	-
1	0.424	0.446	0.453	0.440±0.357	48.84
3	0.148	0.191	0.168	0.169±0.185	80.35
5	0.101	0.104	0.102	0.102±0.136	88.14
7	0.062	0.086	0.07	0.070±0.044	91.86
10	BDL	BDL	BDL	BDL	BDL
Soil (Harvest time)	BDL	BDL	BDL	BDL	BDL

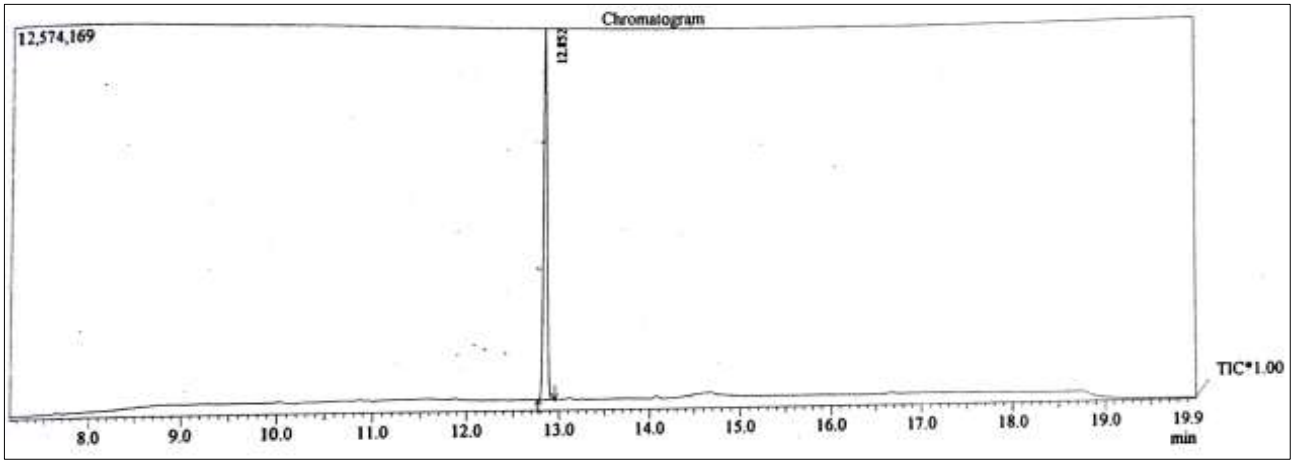

Fig 1: Chromatogram of spiromesifen (1ppm)

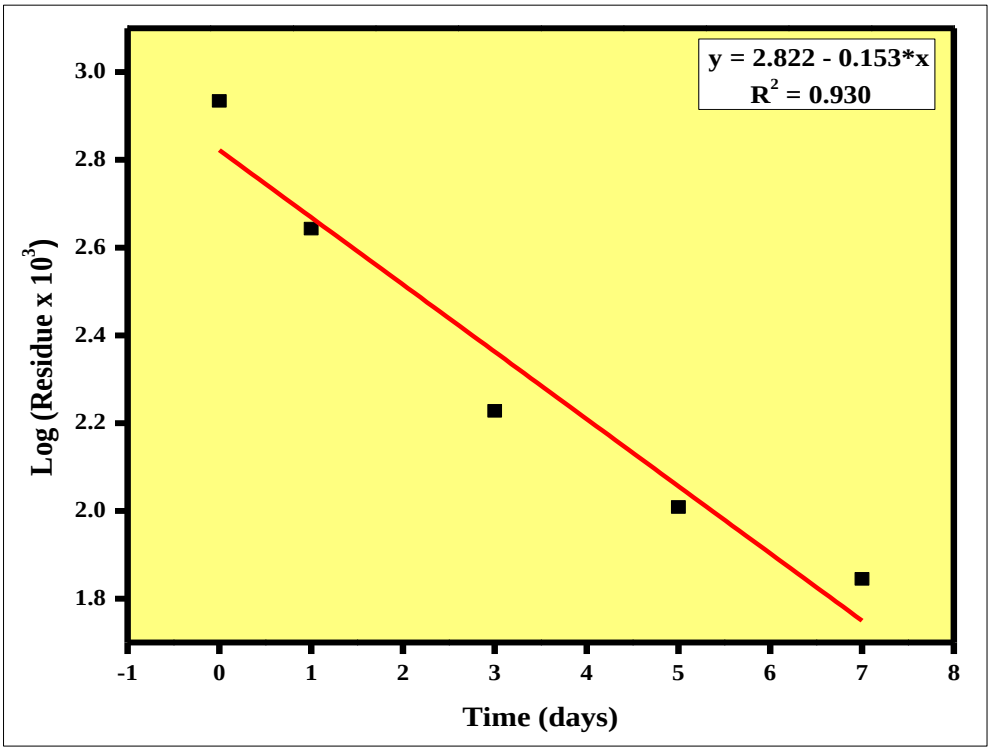

Fig 2: Plot of log (Residue x 10^3) vs days

Table 3: Dissipation parameters of spiromesifen in capsicum

Dissipation parameters	Dose (96 ga.i./ha)
Regression Equation	y = 2.822 – 0.153*x
C_o	0.86 mg/kg
k	0.352 day^{-1}
Half life	1.96 days

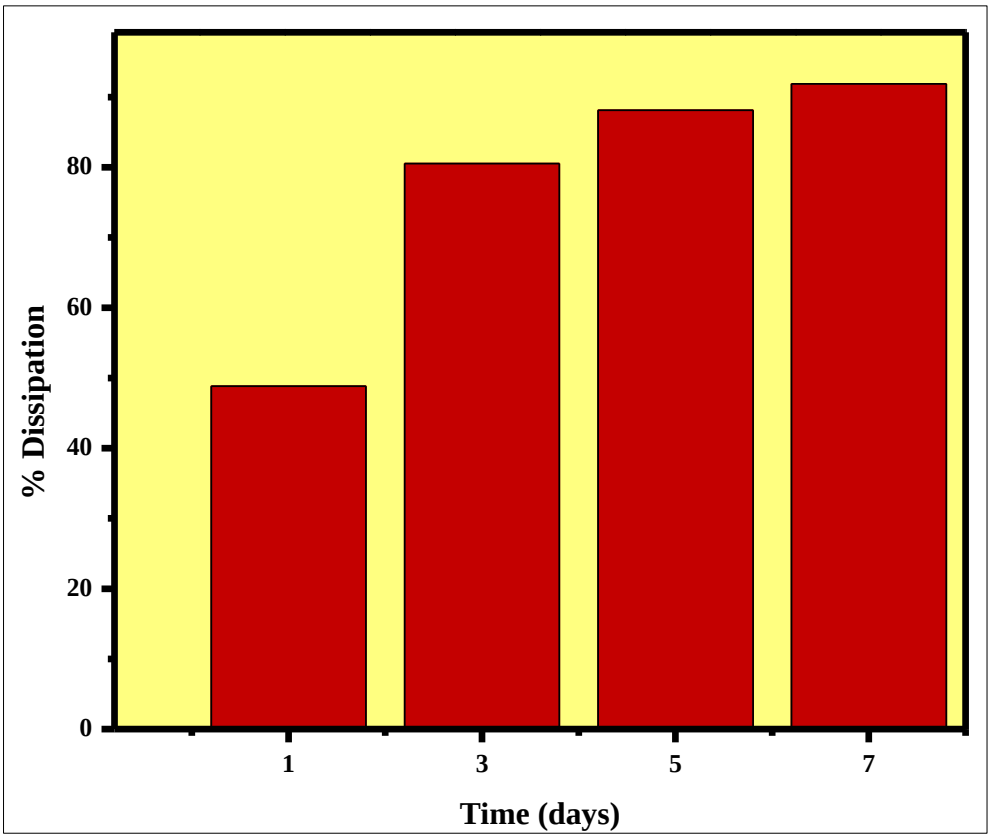

Fig 3: Percent dissipation pattern of spiromesifen in capsicum

Conclusion

The dissipation of spiromesifen, when administered at a single dosage in capsicum, follows first-order kinetics with a half-life of 1.96 days. the spiromesifen residue was found to be below the detection limit after a period of 10 days. There was no detectable presence of spiromesifen residue in the soil. The recommendation for a waiting time of one day is based on the European Union Maximum Residue Limit (EU MRL) of 0.5 mg/kg. It is recommended, from a safety perspective, to wait for one day before to taking capsicum.

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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.

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