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DISSIPATION DYNAMICS OF TOLFENPYRAD IN CABBAGE (*BRASSICA OLERACEA* VAR. *CAPITATA*) UNDER POLY HOUSE CONDITIONS

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ABSTRACT

Studies were undertaken to establish the dissipation pattern of tolfenpyrad 15 EC @ 150 g *a.i.* ha^{-1} at recommended dose under poly house conditions to assess the differences in rate of dissipation and also to recommend safe waiting periods and half-life period based on MRLs established by FSSAI by using QuEChERS method. Spray of tolfenpyrad at recommended dose resulted in 0.519 mg kg^{-1} initial deposit recorded at 2 hours after spray, which dissipated below the limit of quantitation (LOQ) of 0.01 mg kg^{-1} by at 20th day in poly house. However, safe waiting period and half-life for tolfenpyrad were 17 days and 2.93 days, respectively.

Key words : Initial deposit, QuEChERS, LC MS/MS, Certified reference materials (CRMs), Residues, Fortification studies.

Introduction

Cabbage originated in the Mediterranean region and was brought to India during the Mughal era (Das, 1992; Khalid, 2006). According to Abhijith *et al*. (2019), the main pest is the diamondback moth *Plutella xylostella* (Linnaeus), which has a destructive potential between 14 to 84 per cent. According to reports, most farmers spray between 10 and 20 times with between 29 and 33 different types of pesticides from 13 distinct groups during a single growing season of cabbage (Gangaraju *et al*., 2020 and Biradar *et al*., 2020). The residues if present in excessive amounts may be a potential health hazard to the consumer and can cause many chronic diseases (Dhaliwal and Singh, 2000). Food products become safe for consumption only if a safe waiting period is observed. Hence, it is necessary that pesticides should be effective against a pest along with toxicologically acceptable residues on food commodities (Singh *et al*., 2007). With a novel mode of action, Tolfenpyrad, an insecticide from the pyrazole class, was created in Japan and received its initial approval in 2002. It works by preventing complex I from functioning in the mitochondria's respiratory electron-transfer chain. Hemipteran, coleopteran, dipteran, lepidopteran, thysanopteran, and acarine pests are all commonly controlled using it. Hence studies were conducted to establish the dissipation pattern of tolfenpyrad to fit in pest management strategy.

Materials and Methods

During the *rabi* season of 2022-23, protected cultivation of cabbage (variety "Indu Seminis") was conducted at the Horticultural Polyhouse, College of Agriculture, Rajendranagar. The experimental site, located at 542.3 m altitude, experiences a semi-arid tropical climate with coordinates of 17.3850° N latitude and 78.4867° E longitude. Healthy seedlings, sown in nursery and transplanted after one month into poly house conditions, received two applications of tolfenpyrad 15 EC at 150 g *a.i.* ha^{-1}, spaced 10 days apart during head

Table 1 : Recovery of tolfenpyrad from fortified cabbage head samples.

Treatments	Fortified level			
	0.01 mg/kg		0.1 mg/kg	
	Mean recovery level (mg kg^{-1})	Recovery %	Mean recovery level (mg kg^{-1})	Recovery %
Tolfenpyrad	0.010	96.15	0.09	87.98

formation. Samples for residue analysis were systematically collected from cabbage plants at intervals of 0, 1, 3, 5, 7, 10, 15 and 20 days after the final spray. These samples were promptly sealed in polythene bags and transported to the Pesticide Residues Laboratory, AINP on Pesticide Residues, PJTSAU, Rajendranagar, Hyderabad. At the laboratory, the QuEChERS method was employed for sample processing, with preparation of Working Standards and linearity studies using Certified Reference Materials (CRMs) of Tolfenpyrad insecticide. Fortification and Recovery studies were conducted following the guidelines outlined in the SANTE document (11312/2021).

Chemicals and Reagents

Certified Reference Materials of insecticides (CRMs) (M/s Nichino and TRC) of purity levels {Tolfenpyrad-99.6%} and all the analytical grade solvents and reagents *viz*., Acetonitrile (HPLC grade), n- Hexane (HPLC grade), sodium chloride (NaCl), anhydrous sodium sulphate (Na_2SO_4) and anhydrous magnesium sulphate ($MgSO_4$) (Merck India Pvt Ltd.,), primary secondary amine (59.6 µm particle size) (PSA-Ethylene diamine N-propyl bonding with silica gel base) (Agilent Technologies) and LC-MS/MS grade Methanol, Acetonitrile and Water (JT Baker) were used for extraction, clean up and detection of pesticide residues

Table 2 : Details of parameters of LC-MS/MS for the analysis of selected insecticides.

LC-MS/MS	SHIMADZU LC-MS/MS – 8040.	
Detector	Mass Spectrophotometer	
Column	KINETEX C18 column, 2.6 µ particle size 100 mm length, 3 mm ID	
Columnoven temperature	40°C	
Nebulizing gas	Nitrogen	
Nebulizing gas flow	2.0 litres/min	
Capillary Voltage	6 kV	
Pump mode/ flow	Gradient	
Mobile phase	A: 5 mM Ammonium Formate in 80:20 H_20: MeOH+0.1% FA B: 5 mM Ammonium Formate in 90:10 MeOH: H_20 +0.1% FA	
Flow rate	0.4 mL/min	
Total Time Programme	Time	% B
	0.01	60
	1.00	95
	4.00	85
	8.00	60
	8.20	60
	8.21	Stop
Injection volume	1 µl	
DL Temperature	250°C	
Heat BlockTemperature	300°C	
MRM transitions		Tolfenpyrad
	Precursor ion	384.3
	Quantifier ion	197.05
	Qualifier ion	145.00
Retention time		5.8 min
Software used	Shimadzu - Lab solutions	

(Table 2).

Results and Discussion

The linearity studies yielded a high correlation coefficient (R^2 = 0.993), indicating excellent agreement between the measured and expected concentrations. Fortification studies conducted at the limit of quantitation (LOQ) level of 0.01 mg/kg and at 10 times LOQ demonstrated satisfactory recovery rates of 96.15% and 87.98%, respectively. These results fell well within the acceptable range as stipulated by SANTE guidelines in 2021 (Table 1 and Fig. 1).

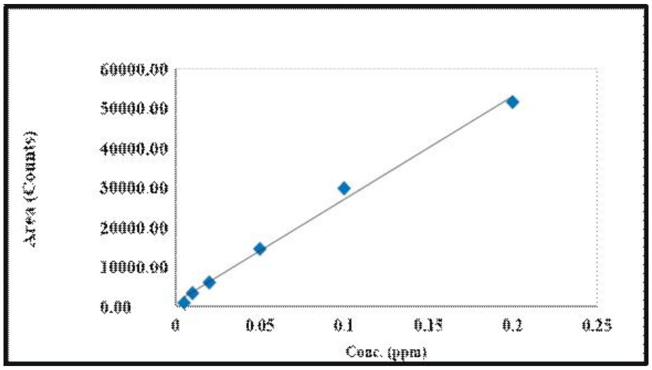

Fig. 1 : Linearity curve for Tolfenpyrad.

Table 3 : Dissipation of tolfenpyrad in cabbage heads after final spray under poly house conditions.

Days after last spray of Cabbage heads	Residues of tolfenpyrad (mg kg^{-1})				Dissipation (%)
	R1	R2	R3	Average	
0	0.513	0.525	0.519	**0.519**	-
1	0.348	0.373	0.356	**0.359**	**30.82**
3	0.320	0.330	0.336	**0.329**	**36.60**
5	0.202	0.238	0.227	**0.222**	**57.22**
7	0.114	0.110	0.102	**0.108**	**79.19**
10	0.044	0.043	0.033	**0.040**	**92.29**
15	0.017	0.017	0.018	**0.017**	**96.72**
20	<LOQ	<LOQ	<LOQ	<LOQ	
Soil	<LOQ	<LOQ	<LOQ	<LOQ	
Regression equation	Y=-0.1025x+2.7431				
R^2	0.9767				
Half-life (days)	2.93				
T_{tol} (days)	17				
	0.01* (FSSAI MRL)				

In Poly house situation, the dissipation pattern of tolfenpyrad was investigated; revealing an initial residue level of 0.519 mg kg^{-1} detected 2 hours after the final spray. Over the course of 20 days, these residues diminished to below the limit of quantitation (<LOQ, 0.01 mg kg^{-1}) (Table 3). The calculated half-life and recommended waiting period were determined to be 2.93 days and 17 days, respectively. Notably, soil samples collected at harvest showed no detectable residues of tolfenpyrad. Thus, initial deposits of 0.519 mg kg^{-1} in the polyhouse environment decreased to <LOQ within 20 days.

These findings of present investigation are agreement with the results of Pathipati *et al.* (2017), who reported initial deposits of chlorantraniliprole of 0.36 mg kg^{-1} and 1.31 mg kg^{-1} in open field and polyhouse, respectively when chlorantraniliprole 20 SC @ 60 ml *a.i.* ha^{-1} was sprayed three times. The calculated waiting periods for safe harvest were 7.0 and 15.0 days in poly house conditions. It was reported that dissipation is slow in poly house conditions as compared to open fields due to various factors. Similarly, Tang *et al.* (2021) reported that the residues of imidaclothiz and pyridaben dissipated faster in greenhouse-grown *Brassica campestris* spp. samples than in open field samples. Lan *et al.* (2022) investigated the distribution of tolfenpyrad residues and dietary risk in four leafy green vegetables, *Brassica bara* L., *Spinacia oleracea* L., *Lactuca sativa* L and *Brassica chinensis* L. The residue levels of tolfenpyrad in leafy green vegetables collected 21 days following the previous treatment were judged safe for consumers. Wu *et al.* (2023) findings revealed that when tolfenpyrad 15% SC was applied once at double the permissible dosages (225 ghm^{-2}) in open field, the half-life of tolfenpyrad in broccolini was 3.35 days. Final residue testing revealed a positive correlation between application dose and spraying frequency and the risk of residue in the harvested broccolini. Also, Liu *et al.* (2022) reported that the final residues of the four pesticides spirotetramat, flonicamid, thiamethoxam and tolfenpyrad in eggplant after the final applications at 7 and 10 days were 0.01-0.21, 0.085-0.26, 0.05-0.078 and 0.01-0.21 mg/kg, respectively with half-lives ranging from 3.4 to 14.5 days.

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Ethical approval

This article does not contain any studies with human participants or animals performed by any of the authors

Conflict of interest

None declared

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