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Studies on Dissipation Pattern of Tolfenpyrad and Harvest Time Residues in Cabbage under Field Conditions

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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Original research Article

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ABSTRACT

The use of Tolfenpyrad, a broad-spectrum insecticide in preventing the crop losses, studies on its dissipation pattern and safe waiting period required were studied. Tolfenpyrad 15 EC @ 150 g *a.i.* ha^{-1} at recommended dose under field 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. Tolfenpyrad was sprayed two times at head formation stage and cabbage samples collected

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at regular intervals were analysed for residues. The dissipation pattern of tolfenpyrad 15 EC was studied collecting samples at regular intervals *i.e,* 0, 1, 3, 5, 7, 10,15 and 20 days after last spray and analyzed. The initial deposits of 0.184 mg kg^{-1} tolfenpyrad recorded at 2 hours after last spray dissipated to 0.145, 0.086, 0.021, 0.010 mg kg^{-1} with dissipation percent of 21.19, 53.26, 88.58 and 94.56 at 1,3,5,7 days after final spray. The tolfenpyrad residues dissipated to less than LOQ (<LOQ) of 0.01 mg kg^{-1} after 10 days showing a hundred per cent dissipation. The safe waiting period and half-life for tolfenpyrad were 7.09 and 1.590 days, respectively. The residues of tolfenpyrad in cabbage and soil samples were less than LOQ both field conditions at harvest (20 days after last spray).

Keywords: MRL; initial deposit; dissipation; half-life; safe waiting period; tolfenpyrad; QuEChERS; LC MS/MS.

ABBREVIATIONS

AINP	:	*All India Network Project*
LC/MS/MS	:	*Liquid Chromatograph-Mass Spectrometer*
R^2	:	*Coefficient of determination*
LOQ	:	*Limit of quantitation*
Mg	:	*Milligram*
CRM	:	*Certified Reference Materials*

1. INTRODUCTION

"India produced 9.60 million tonnes of cabbage in 2020-21 from 4.12 lakh ha of land, at an average of 23.27 MT per ha. Cabbage is grown in 820 ha in Telangana, producing 27,780 tonnes per ha with a productivity of 33.71 tonnes per ha" [1]. According to Abhijith et al. [2], "the main pest is the diamondback moth *Plutella xylostella* (Linnaeus), which has a destructive potential between 14 to 84 per cent. Being a very profitable vegetable crop, cabbage requires extensive plant protection methods that involve the application of numerous different insecticides". Rather than being need based these applications are calendar driven. These applications are frequently either unnecessary or untimely. 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 [3,4]. The residues if present in excessive amounts may be a potential health hazard to the consumer and can cause many chronic diseases [5]. The dissipation of an insecticide varies with the nature of insecticide, dose, number of applications, interval between application, crop variety, etc. 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 [6]. 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.

2. MATERIALS AND METHODS

The experiment was conducted at Horticultural Polyhouse; College of Agriculture, Rajendranagar, while the residue work was be taken up at AINP on Pesticide Residues Rajendranagar, PJTSAU, Hyderabad. Dissipation studies of tolfenpyrad were conducted in *Rabi*, 2022 with Plot size (20 sq. m.) by collecting cabbage samples at regular intervals *i.e.,* 0, 1, 3, 5, 7, 10, 15 and 20 days after last spray in polythene bags and brought to the laboratory immediately for further sample processing in the laboratory as detailed here under.

2.1 Chemicals and Reagents

Certified Reference Materials of insecticides (CRMs) (M/s Nichino and TRC) of purity levels {Tolfenpyrad-99.6%, Cyantraniliprole-98.0%} and all the analytical grade solvents and reagents viz., Acetonitrile (HPLC grade), n- Hexane (HPLC grade), sodium chloride (NaCl), anhydrous sodium sulphate (Na2SO4) and anhydrous magnesium sulphate (MgSO4) (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.

2.1.1 Method validation

The residue analysis method was validated following SANTE, 2021 document. The method was validated on LC-MS/MS through linearity, LOD, LOQ, fortification and recovery studies.

2.1.2 Preparation of working standards

The certified reference materials of the selected insecticides and the analytical grade solvents were used for preparing primary, intermediate and working standards. The working standards were prepared in the range of 0.01 ppm to 0.1 ppm in 10 ml calibrated graduated volumetric flasks using methanol as solvent and stored in Sanyo biomedical deep freezer maintained at -20˚C.

2.1.3 Linearity studies

A series of standards i.e., 10, 20, 50, 100, 200 and 500 µg l-1 (ppb) were prepared by diluting the working standard (1 µg ml-1) with methanol in calibrating volumetric flasks. 1 µl of each concentration was injected three times in LC-MS/MS SHIMADZU 8040 Model for linearity studies.

2.1.4 Determination of LOD (Limit of Detection) and LOQ (Limit of Quantification)

LOD was calculated from the linearity calibration graph using the formula:
LOD= 3 x (Standard Deviation/Slope)
LOQ was calculated from the linearity calibration graph using the formula:
LOQ= 10 x (Standard Deviation/Slope)

2.2 Fortification and Recovery Studies

Prior to pesticide application and field sample analysis, the residue analysis method was validated following the SANTE document (11312/2021). For recovery studies, cabbage samples from control plots were fortified at two fortification levels *viz.,* LOQ level (0.01 µg ml^{-1}) and 10 x LOQ (0.1 µg ml^{-1}) to know the suitability of the method to detect and quantify pesticides in cabbage below Maximum Residue Limits (MRLs) of Codex Alimentarius Commission (CAC).

2.2.1 Estimation of insecticides by LC-MS/MS analysis

The equipment used was Shimadzu LC-MS/MS 8040 mass spectrometer for quantification of insecticides. The method parameters adopted are given in Table 1.

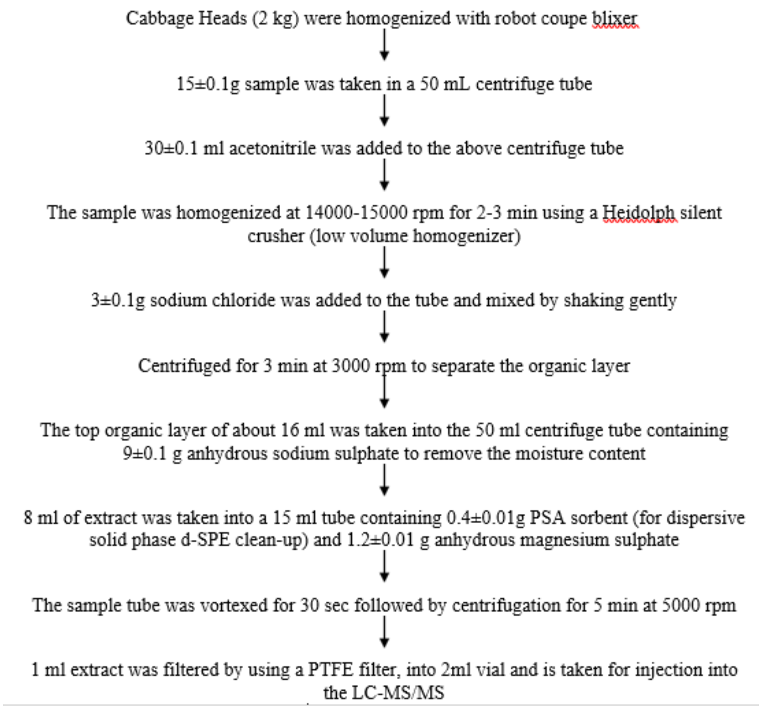

Chart 1. Flow chart of QuEChERS method

Table 1. 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		
Column oven 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_2$0: MeOH+0.1% FA B: 5 mM Ammonium Formate in 90:10 MeOH: $H_2$0 +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 Block Temperature	300 °C		
MRM transitions		**Tolfenpyrad**	**Cyantraniliprole**
	Precursor ion	384.3	472.9
	Quantifier ion	197.05	283.9
	Qualifier ion	145.00	177.0
Retention time		5.8 min	1.45 min
Software used	Shimadzu - Lab solutions		

3. RESULTS AND DISCUSSION

The linearity curve of tolfenpyrad is depicted in Fig. 4. The correlation coefficient (R^2) value obtained from the linearity curve was 0.993. The recovery of tolfenpyrad in the cabbage head sample fortified at 0.01 mg/kg was 96.15 while at 0.1 mg/kg it was 87.98. (Fig. 1 & Table 2).

The linearity curve of cyantraniliprole is depicted in Fig. 2. The correlation coefficient (R^2) value obtained from the linearity curve was 0.992. The recovery of cyantraniliprole in the cabbage head sample fortified at 0.01 mg/kg was 92.88 while at 0.1 mg/kg it was 89.66 (Table 3 & Fig. 2). The dissipation pattern of tolfenpyrad under field conditions is presented in Table 4 (Fig. 3 and Fig. 4). The results of tolfenpyrad residues revealed that the mean initial deposits of 0.184 mg kg^{-1} detected at 2 hours after last spray, which dissipated to 0.145, 0.086, 0.021, 0.010 mg kg^{-1} with dissipation percent of 21.19, 53.26, 88.58 and 94.56 at 1,3,5,7 days after final spray. The residues dissipated to <LOQ (Limit of quantification) of 0.01mg kg^{-1} at 10 days. The regression equation was Y= -0.1893x + 2.3424 with R^2 value of 0.9692. The calculated half-life and safe waiting period for tolfenpyrad are 1.590 and 7.09 days, respectively. Residues of tolfenpyrad and cyantraniliprole was found to be below the limit of quantitation in soil samples collected at harvest.

In the current study, the residues of tolfenpyrad under field conditions dissipated to <LOQ by 10^{th} day with a half-life and safe waiting periods of 1.590 and 7.09 days in field conditions. These findings are consistent with Lan et al. [7] 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. [8] 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. [9] 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". Biswajit [10] tested "three dosages of tolfenpyrad 15% EC (100, 125, and 150 g *a.i.* ha^{-1}) against DBM and aphid-infested cabbage. The lowest mean population of aphid and DBM was seen with tolfenpyrad application at 150 g *a.i.* ha-1, which also produced the highest yield (27.78 t ha^{-1})". Dong et al. [11] studied the dissipations and residues of four pesticides (novaluron, pyriproxyfen, thiocloprid and tolfenpyrad) in citrus fruits under field conditions. The half-life ranged from 13.3 to 28.9 days with a pre-harvest period of 14 days. Guru and Patil [12] investigated the dissipation pattern of triazophos in polyhouse grown capsicum after applying insecticide at the fruit initiation stage at two dosages (500 and 1000 g *a.i.* ha^{-1}). The initial residues deposit of 3.17 and 6.13 mg kg^{-1}, respectively reached to Below Quantification Limit (BQL) at 20 and 25 days with half-life of 2.95 and 2.63 days at recommended and double the recommended doses, respectively. Pre-Harvest Interval (PHI) of twenty days for triazophos can be recommended for safe eating of capsicum fruits cultivated in polyhouses, while taking into account the LOQ of 0.05 mg kg^{-1}. Jing et al. [13] revealed that emamectin benzoate had a half-life of 0.11-0.49 days, while tolfenpyrad had a half-life of 1.12-1.85 days. Emamectin benzoate and tolfenpyrad residues were found to have processing factors (dry weights) of 0.23 to 0.98 and 0.18 to 0.67, respectively, with loss rates of 1.6% to 76.7% and 32.7% to 82.1% in the tea crop [14].

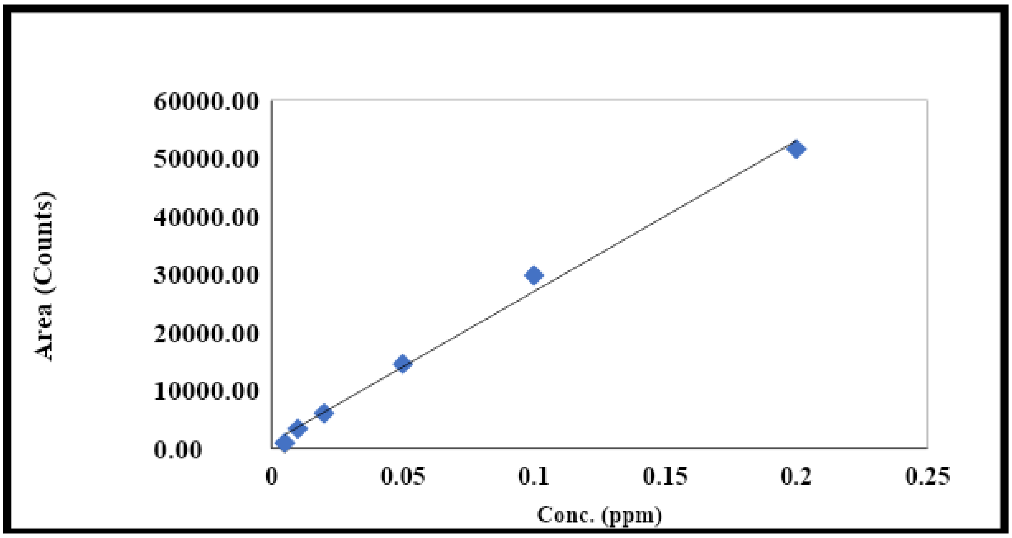

Fig. 1. Linearity curve for Tolfenpyrad

Table. 2. 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

Table. 3. Dissipation of tolfenpyad in cabbage heads after final spray in open field

Days after last spray	**Residues of tolfenpyrad (mg kg^{-1})**				**Dissipation (%)**
	R1	**R2**	**R3**	**Average**	
0	0.192	0.173	0.186	**0.184**	**-**
1	0.142	0.149	0.143	**0.145**	**21.19**
3	0.079	0.090	0.090	**0.086**	**53.26**

Days after last spray	Residues of tolfenpyrad (mg kg^{-1})				Dissipation (%)
	R1	R2	R3	Average	
5	0.023	0.019	0.021	**0.021**	**88.58**
7	0.010	0.009	0.010	**0.010**	**94.56**
10	<LOQ	<LOQ	<LOQ	<LOQ	
SOIL	<LOQ	<LOQ	<LOQ	<LOQ	
Regression equation	Y= -0.1893x +2.3424				
R^2	0.9692				
Half-life (days)	1.590				
T_{tol} (days)	7.09				
MRL (mg/kg)	0.01* (FSSAI MRL)				

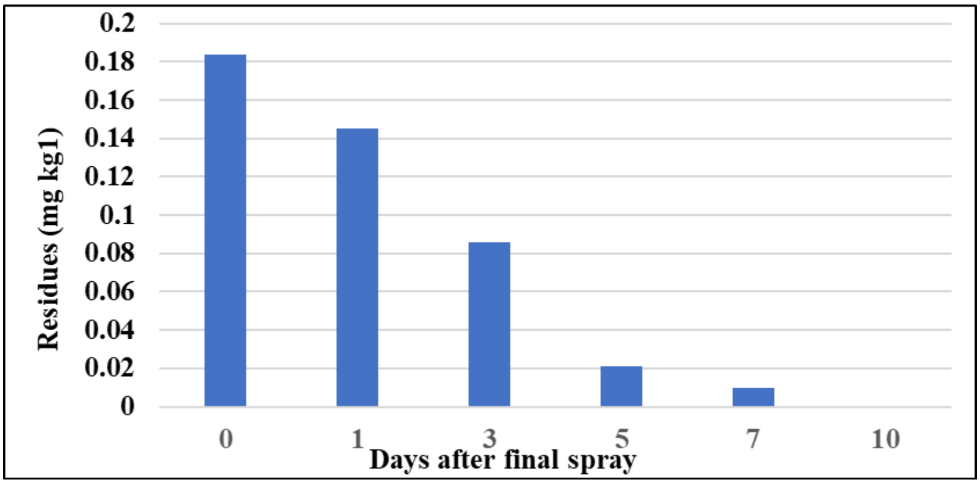

Fig. 2. Dissipation of tolfenpyrad on cabbage in open field

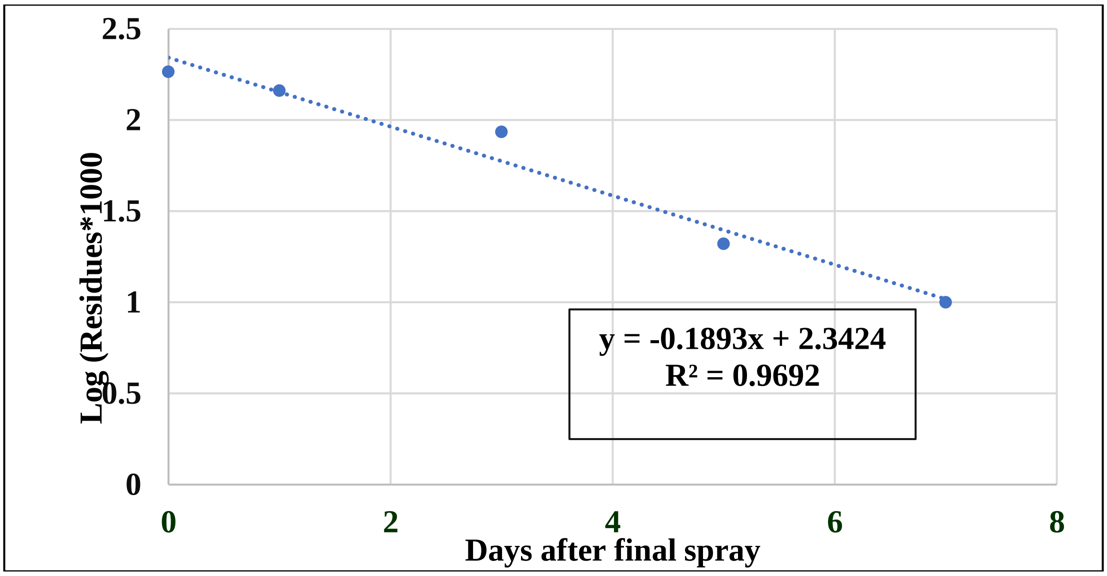

Fig. 3. Semi logarithmic graph depicting dissipation of tolfenpyrad on cabbage in open field

4. CONCLUSION

The studies on dissipation pattern of tolfenpyrad in cabbage heads concluded that residues in open field persisted upto 7 days and reached below the limit of quantitation (<LOQ) of 0.01 mg kg^{-1} by at 10th day. The safe waiting period and half-life for tolfenpyrad were 7.09 days and 1.590 days, respectively. The residues of tolfenpyrad and cyantraniliprole in cabbage and soil samples were less than LOQ both field conditions at harvest (20 days after last spray).

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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