The Pharma Innovation Journal 2021; SP-10(12): 1083-1086

www.ThePharmaJournal.com

The Pharma Innovation

ISSN (E): 2277- 7695
ISSN (P): 2349-8242
NAAS Rating: 5.23
TPI 2021; SP-10(12): 1083-1086
© 2021 TPI
www.thepharmajournal.com
Received: 07-10-2021
Accepted: 09-11-2021

Anugu Anil Reddy
Assistant Professor, Department of Entomology, Agricultural Polytechnic, PJTSAU, Kamareddy, Telangana, India

Narendra Reddy C
Associate Dean, College of Agriculture, PJTSAU, Rajendranagar, Hyderabad, Telangana, India

Srinivasa Reddy S
Assistant Professor, Department of Entomology, Agricultural College, PJTSAU, Telangana, India

Manohar Rao A
Professor and Univ. Head (Rtd.), Department of Horticulture, College of Agriculture, PJTSAU, Rajendranagar, Hyderabad, Telangana, India

Narendar Reddy S
Associate Dean, Agriculture College, PJTSAU, Jagtial, Telangana, India

Corresponding Author
Anugu Anil Reddy
Assistant Professor, Department of Entomology, Agricultural Polytechnic, PJTSAU, Kamareddy, Telangana, India

Dissipation pattern of fipronil on chilli (*Capsicum annum* L)

Anugu Anil Reddy, Narendra Reddy C, Srinivasa Reddy S, Manohar Rao A and Narendar Reddy S

Abstract
An experiment was conducted during *kharif*, 2015 to evaluate the efficacy of seven insecticides *viz.*, fipronil 5% SC @ 500 g a.i ha^{-1}, spinosad 45% SC @ 125 g a.i ha^{-1}, chlorantraniliprole 20% SC @ 30 g a.i ha^{-1}, profenophos 50% EC @ 400 g a.i ha^{-1}, lambda cyhalothrin 5% SC @ 15.63 g a.i ha^{-1}, imidacloprid + beta cyfluthrin 300% OD @ 30 g a.i ha^{-1} and dimethoate 30 % EC @ 300 g a.i ha^{-1} against chilli thrips. The dissipation pattern of fipronil 5% SC @ 500 g a.i ha^{-1} was studied collecting samples at regular intervals *i.e.* 0, 1, 3, 5, 7, 10 and 15 days after last spray and analyzed. The initial deposits of 1.47 mg kg^{-1} were dissipated to below detectable levels (BDL) by 15th day after third spray on chilli. The residues of 0.97, 0.52, 0.41, 0.36, and 0.16 mg kg^{-1} were recorded at 1, 3, 5, 7 and 10 days after last spray, respectively.

Keywords: insecticides, thrips, initial deposit, fipronil, efficacy and dissipation

1. Introduction
Chilli (*Capsicum annum* L.), is an important vegetable and condiment crop grown throughout the world and it has immense commercial, dietary and therapeutiuc values. It is a rich source of A, C, E and P and an alkaloid capsacin, which has high medicinal value and is used in many pharmaceutical preparations. India is the world leader in chilli production followed by China and Pakistan. The major chilli exporting countries with their percentage share in world exports are India (25%), China (24%), Spain (17%), Mexico (8%), Pakistan (7.2%), Morocco (7%) and Turkey (4.5%). The bulk share of chilli production in the world is held by Asian countries. In India chilli is cultivated in an area of 774.9 lakh ha with an annual production of 1492.1 lakh tones (Horticultural Statistics, India 2015) [3]. Important chilli growing states in India are Andhra Pradesh, Telangana, Karnataka, Maharashtra and Tamilnadu which constitute nearly 75 per cent of the total area under chilli. Area under chilli crop in Andhra Pradesh and Telangana is around 1.72 lakh ha which is about 25.12 per cent of the total area in India. In Telangana State it is grown in 73,000 hectares with 2,53,000 tonnes production from major chilli growing areas such as Khammam, Warangal, Mahabubnagar and Ranga Reddy districts (*WWW. Indiastat.com*) [8].
Although the crop has great export potential besides huge domestic requirement, a number of limiting factors contribute for its low productivity. Among these various biotic stresses, ravages caused by insect pests are significant. The pest spectrum in chilli is complex with more than 293 insects and mites species debilitating the crop in field as well as in storage (Butani, 1976) [1]. Among these, chilli thrips, *Scirtothrips dorsalis* Hood has become the most notorious and pernicious pest on chilli. The overall reduction in fruit yield of chilli due to thrips and mites damage was up to 34 per cent (Thania *et al.*, 2011) [6]. These pests not only cause reduction in yield, but also act as vectors for several viral diseases and cause complete failure of crop and various biotic (pest and diseases), abiotic (rainfall, temperature, relative humidity and light intensity) and phenological factors (flower and fruit drop) limits the yield and quality of the chilli. A number of pesticides are being frequently used, to combat these pests. However, some of these insecticides leave residues on pods and these residues may persist up to harvest. Presence of pesticide residues in the harvested chillies was posing problem at the time of export and in recent times importing countries have rejected few consignments. Pesticide use has increased rapidly over the last two decades at the rate of 12 per cent per year. The extensive and irrational use of pesticides resulted in the presence of residues of insecticides on chilli is likely to be associated with severe effects on human health.

Hence, great significance has to be given to estimate pesticide residues in chilli.

2. Materials and methods

The experiment was laid out in a Randomized Block Design (RBD) with 8 treatments including untreated control replicated thrice with individual plot size of 20 m^2 (5mx4 m) and the insecticides *viz.,* fipronil 5% SC @ 500 g a.i ha^{-1}**,** spinosad 45% SC @ 125 g a.i ha^{-1}**,** chlorantraniliprole 20% SC @ 30 g a.i ha^{-1}**,** profenophos 50% EC @ 400 g a.i ha^{-1}**,** lambda cyhalothrin 5% SC @ 15.63 g a.i ha^{-1}, imidacloprid + beta cyfluthrin 300% OD @ 30 g a.i ha^{-1} and dimethoate 30 % EC @ 300 g a.i ha^{-1} on chilli first at 50% flowering and the second and third spray ten days later to evaluate the efficacy against thrips and the dissipation studies were conducted for the same by collecting cabbage samples at regular intervals *i.e.* 0, 1, 3, 5, 7, 10 and 15 days after last spray in polythene bags and brought to the laboratory immediately for further sample processing in the laboratory as detailed here under.

Chilli fruits (5kg) were homogenized with robot coupe blixer and homogenized

↓

15±0.1g sample was taken in 50 ml centrifuge tube

↓

Required quantity of standard (CRM) added to get desired fortification level

↓

30±0.1 ml acetonitrile was added to the tube

↓

The sample was homogenized at 14000-15000 rpm for 2-3 min using Heidolph silent crusher

↓

3±0.1g sodium chloride was added to tube and mixed by shaking gently

↓

Centrifuged for 3 min at 2500-3000 rpm to separate the organic layer

↓

The top organic layer of about 16 ml was taken into the 50 ml centrifuge tube

↓

9±0.1 g anhydrous sodium sulphate was added to remove the moisture content

↓

8 ml of extract was taken in to 15 ml tube containing 0.4±0.01g PSA sorbent (for dispersive solid phase d-SPE cleanup) and 1.2±0.01 gr anhydrous magnesium sulphate

↓

The sample tube was vertexed for 30 sec followed by centrifugation for 5 min at 2500-3000 rpm

↓

The extract of about 2ml was transferred into test tubes and evaporated to dryness using turbovap with nitrogen gas and reconstituted with 1ml n-Hexane: Acetone (9:1) for GC analysis with ECD for fipronil analysis.

Extraction and clean –up

Gas Chromatograph parameters

Gas Chromatograph	Gas Chromatography- AGILENT- 7890B
Column	VF -5ms Capillary Column 30 m length, 0.25 mm Internal Diameter, 0.25 µm film thickness; 1% methyl siloxane
Column Oven (^{0}C)	Fipronil- Initial 180 ^{0}C - 2 min hold - increase @ 10 ^{0}C/min upto 260 ^{0}C - hold time 5 mins – increase @2 ^{0}C/min upto 280 ^{0}C – hold for 10 mins.
Detectors	Electron Capture Detector (ECD)
Detector Temperature (^{0}C)	300
Injector Temperature (^{0}C)	280
Injector Status	Split Ratio: 1:2
Carrier Gas	Nitrogen, Iolar II, Purity 99.999%
Carrier Gas Flow (ml min^{-1})	2
Make-up Flow (ml min^{-1})	25
Retention time (min)	Fipronil 8.96
Total run time (min)	Fipronil 35

Fortication and Recovery results of fipronil on chilli

Chilli samples fortified with fipronil at 0.01 mg kg^{-1}, 0.05 mg kg^{-1} and 0.1 mg kg^{-1} were analysed and the mean recovery of the residues using the method was 99.18, 92.04 and 91.52 per cent, respectively in green chilli (Table. 1). The results shown that the method was suitable for the analysis of fipronil residues up to 0.01 mg kg^{-1}, and the limit of quantification (LOQ) was 0.01 mg kg^{-1}.

Table 1: Recovery of fipronil from fortified green chilli samples

Details	Recoveries of fipronil from fortified chilli samples					
	Fortified level (mg kg^{-1})					
	0.01 mg kg^{-1}		0.05 mg kg^{-1}		0.1 mg kg^{-1}	
	Residues recovered (mg kg^{-1})	Recovery %	Residues recovered (mg kg^{-1})	Recovery %	Residues recovered (mg kg^{-1})	Recovery %
R1	0.0098	98.11	0.0457	91.42	0.0904	90.45
R2	0.0096	96.62	0.0462	92.58	0.0914	91.49
R3	0.0102	102.80	0.0460	92.11	0.0926	92.61
Mean		99.18		92.04		91.52
SD		3.22		0.59		1.08
RSD		3.25		0.64		1.18

Hence, the method described above is suitable for the analysis of samples collected from the field amples sprayed with fipronil to study the dissipation pattern in green chilli. Residues (mg kg^{-1}) were calculated using the formula given below.

$$\text{Residues (mg kg}^{-1}) = \frac{\text{Sample peak area X conc of std (ppm) X µl std. injected X Final volume of the sample (2 ml)}}{\text{Standard Peak area X weight of sample analysed (2 g) X µl of sample injected}} \text{ X recovery factor}$$

The following parameters were calculated to know the dissipation pattern of the insecticides on chilli.
Dissipation per centage:

$$\text{Per cent dissipation} = \frac{\text{Initial deposit - Residues at given time}}{\text{Initial deposit}} \text{ X } 100$$

Waiting period: Waiting period (T_{tol}) is defined as the minimum number of days to lapse before the insecticide reaches the tolerance limit. The waiting periods were calculated by the following formula.

$$T\text{tol} = \frac{[a - \text{Log tol}]}{b}$$

Where
T_{tol} = Minimum time (in days) required for the pesticide residue to reach below the Tolerance limit.
a = Log of apparent initial deposits obtained in the regression equation (Y = a+bX)
tol = Tolerance limit of the insecticide (MRL)
b = Slope of the regression line

3. Results and Discussion

Fipronil @ 500 g a.i. ha^{-1} was sprayed thrice *viz.*, first spray was given at 50 per cent flowering while second and third spray at 10 days after each spray and chilli samples were collected at regular intervals of 0, 1, 3, 5, 7, 10, and 15 days after third spray. The samples were processed and estimated for residues of fipronil on gas chromatograph (GC - ECD). The dissipation pattern of fipronil was presented in table 2 and depicted in figure 1. The results indicated that the initial deposits of 1.47 mg kg^{-1} were dissipated to below detectable levels by 15th day after third spray on chilli. The residues of 0.97, 0.52, 0.41, 0.36, and 0.16 mg kg^{-1} were recorded at 1, 3, 5, 7 and 10 days after last spray, respectively.

Based on the first order kinetics, waiting periods have been worked out using linear semi-logarithmic regression analysis (Hoskins, 1961) [2]. The dissipation pattern showed a continuous decrease of residues from 1st to 15th day. The residues dissipated to 34.01, 64.62, 72.11, 75.51, 89.11 and 100 per cent on 1, 3, 5, 7, 10, and 15 days after last spray, respectively. The time required to reach below tolerance limit (T_{tol}) of 0.001 mg kg^{-1} (as per FSSAI) was 36.34 days. The regression equation was Y= 1.1483 + (-0.114) X with R^2 = 0.7948.

The results were in agreement with the findings of Urvashi Bhardwaj *et al.* (2012) [7] reported that average initial deposits of fipronil on cabbage heads were 1.226 and 2.704 mg kg^{-1}, respectively, following three sprays of fipronil at 75 g a.i.ha^{-1} and 150 g a.i.ha^{-1} dosages, while Sunayana Saini *et al.* (2014) [5] established that the initial deposits of fipronil in chilli were 0.409 and 0.808mg kg^{-1}, respectively at 50 and 100 g a.i.ha^{-1}. The variation of initial deposits in the present investigation may be due to variation in climatic conditions, matrix and variation in the dosage of the insecticide applied, (Khay *et al*., 2008) [4].

The present findings differ from the results of Yap Chin Ann and Zehnder Jarropp (2016) [9] reported the initial deposits of 0.23 mg kg^{-1} when fipronil 80WG applied at 90.0 g a.i ha^{-1} on black pepper. The pre-harvest interval value was 12 days with proposed maximum residue limit was 0.20 mg kg^{-1}. The variation may be due to change in the matrix of black pepper and chilli.

Table 2: Dissipation pattern of fipronil 5% SC (500 g a.i ha^{-1}) in chilli after three sprays

Days after last spray	Residues of fipronil (mg kg^{-1})				Dissipation %
	R1	R2	R3	Average	
0	1.47	1.45	1.48	1.47	--
1	0.96	0.98	0.97	0.97	34.01
3	0.52	0.53	0.51	0.52	64.62
5	0.41	0.41	0.40	0.41	72.11
7	0.36	0.37	0.35	0.36	75.51
10	0.15	0.19	0.14	0.16	89.11
15	BDL	BDL	BDL	BDL	100.00

Regression equation	Y = 1.143 + (-0.114) X
R^2	0.794
MRL (As per FSSAI) mg kg^{-1}	0.001
Waiting period (days)	36.34

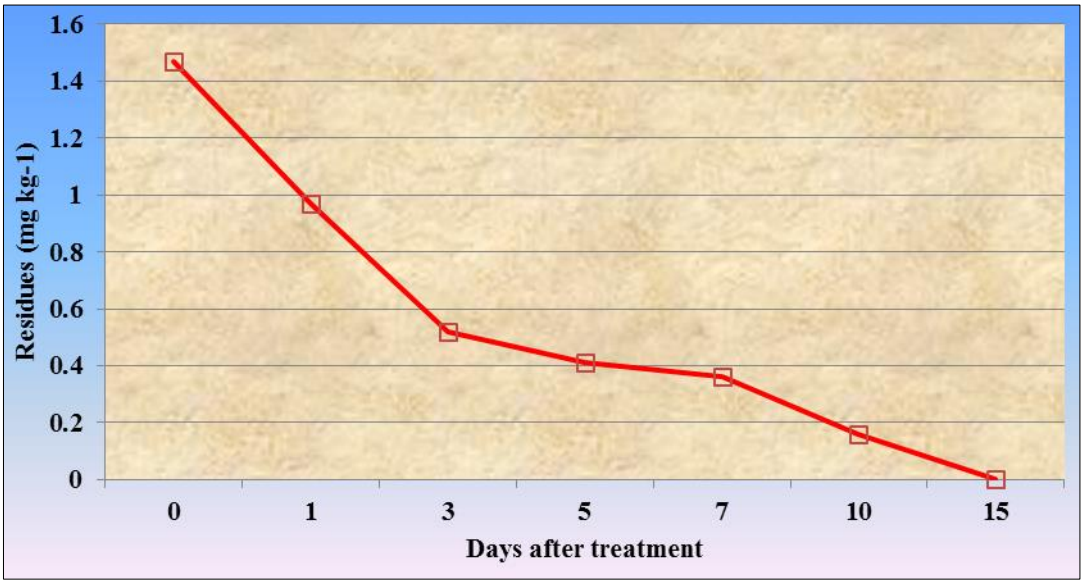

Fig 1: Dissipation kinetics of fipronil residues in chill after three sprays

4. Conclusion

From this experiment, it can be concluded that initial deposits of fipronil at 500 g a.i. ha^{-1}after three sprays were 1.47 mg kg^{-1} after third spray in chilli which dissipated to below detectable level at 15 days. The waiting period determined for fipronil at 500 g a.i. ha^{-1} after third spray in chilli was 36.34 days.

5. References

1. Butani DK. Pests and diseases of chilli and their control. Pesticides 1976;10:38-41.
2. Hoskins WM. Mathematical treatments of loss of pesticide residues. Plant Protection Bulletin, FAO 1961;9:163-168.
3. Horticultural Statistics, India 2015.
4. Khay S, Choi JH, Abd El-Aty MA. Dissipation behavior of lufenuron, benzoyl phenyl urea insecticides, in/on Chinese cabbage applied by foliar sprayingunder greenhouse conditions. Bulletin of Environmental Contamination and Toxicology 2008;81:369-372.
5. Sunayana Saini, Reena Chauhan, Mamta Rani, Beena Kumari. Persistence of fipronil and its metabolites in soil under cover of chilli crop. Pesticide Research Journal 2014;26(1):1-5.
6. Thania SV, Thomas BM, Thomas G, Naseema Beevi S, George X. Dissipation study of dimethoate, ethion and oxydemeton methyl in chilli. Pesticide Research Journal 2011;23(1):68-73.
7. Urvashi Bhardwaj, Rajinder Kumar, Sarabjit Kaur, Sanjay Kumar Sahoo, Kousik Mandal, Battu RS *et al*. Persistence of fipronil and its risk assessment on cabbage, *Brassica oleracea var. capitata* L. Ecotoxicology and Environmental Safety 2012;79:301-308.
8. www. Indiastat.com
9. Yap Chin Ann, Zehnder Jarropp. Residue and dissipation of fiproniland Its metabolites in black pepper (*Piper nigrum* L.) IOSR Journal of Environmental Science, Toxicology and Food Technology 2016;10(6):28-37.