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Dissipation studies of chlorantraniliprole on capsicum in field and poly house conditions for food safety

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ABSTRACT : Chlorantraniliprole is a broad spectrum foliar insecticide with contact and systemic action, widely used on vegetables in India for the management of lepidopteran insects both in field and poly houses. Chlorantraniliprole is not registered for use on capsicum in India and hence, maximum residue limits are not available as per Food Safety and Standards Authority of India. However, use of chlorantraniliprole in open field and poly house is very common hence, chlorantraniliprole residues are found in survey samples. A research project was taken to study dissipation pattern of chlorantraniliprole 20 SC in both open fields and poly houses, when applied thrice @ 60 g a.i.ha^{-1}, first spray at fruit initiation followed by second and third spray at 10 days interval as per the farmers practice. Chlorantraniliprole residues were quantified through regular sampling till the residues are below determination level (BDL) of 0.05 mg kg^{-1} following the validated QuEChERS method. The qualitative and quantitative analysis of chlorantraniliprole was performed on LC- MS/MS (PDA). Initial deposits of 0.36 mg kg^{-1} were detected in capsicum samples collected from open filed, which dissipated to BDL in 7.0 days while in poly house, initial deposits of 1.31 mg kg^{-1} were dissipated to BDL in 15.0 days. The waiting period for safe harvest was worked out to be 7.0 and 15.0 days when chlorantraniliprole 20 SC @ 60 ml a.i. ha^{-1} sprayed thrice in open and poly house conditions, respectively. Dissipation is slow in poly house compared to open fields due to various factors. In both situations initial deposits are lower than the MRL (2 mg kg^{-1}) of Codex Alimentarius Commission hence, a pre-harvest interval of 7.0 and 15.0 day is recommended.

KEY WORDS : Chlorantraniliprole, Capsicum, Field, Poly house, Food safety

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Capsicum [*Capsicum annuum* (L.) var. grossum Sendt.] is also called as bell pepper or sweet pepper and is one of the most popular and highly remunerative annual herbaceous vegetable crop. Capsicum is cultivated in most parts of the world, especially in temperate regions of Central and South America and European countries, tropical and subtropical regions of Asian continent mainly in India and China. Various biotic (pest and diseases), abiotic (rainfall, temperature, relative humidity and light intensity) and phenological factors (flower and fruit drop) limits the yield and fruit quality under open field conditions (Hebbar *et al*., 2011). Among the biotic factors, insect pests reduces the quality of produce and even a small blemish on the fruit will drastically reduce its market value.

Fruit borer, *Spodoptera. litura* Fab, is a serious

pest on capsicum under field and protected condition (Kaur *et al*., 2010) Chlorantraniliprolee 20 SC @ 60 g a.i.ha^{-1} emerged as the most effective insecticide for controlling fruit borer. It has broad spectrum of activity against a range of insect pests, pod borer, *Helicoverpa armigera* (Hines and Hutchison,2001 and Gundannavar and Giraddi, 2007), cabbage butter fly, *Pieris rapae* (Linnaeus), diamond back moth (DBM), *Plutella xylostella* (Linnaeus) (Shivalingaswamy *et al*., 2006), cabbage looper, *Trichoplusia ni* (Hubner) (Satpathy*et al.,* 2007) and brinjal shoot and fruit borer (*Leucinodes orbonalis* Guenee) (Aparna and Dethe, 2012). It is the most potential and powerful insecticide for controlling the selective insects in vegetables cultivated in greenhouses (Schoonejans and Staaij, 2001). Chlorantraniliprole may also be used on row crops, vegetables, and ornamentals (Copping and Duke, 2007). Under poly house conditions, cultivation of capsicum gives early and prolonged yield compared to open field cultivation (Singh *et al.*, 2004) but pesticide dissipation takes slow and longer period in poly house conditions than in open field conditions (Sharma *et al.,* 2012). Since capsicum is consumed afresh, they may carry residues which warrant judicious use of pesticides in respect of persistence, dissipation, metabolism, movement and accumulation of residues. The analysis of pesticide residues in capsicum is, therefore, essential to avoid the health hazards to the consumers by prescribing the waiting periods. Therefore, to establish the dissipation pattern of chlorantraniliprole on capsicum both in open field and poly house, the present study was carried out.

RESEARCH METHODS

Chemicals and reagents :

Certified reference materials (CRMs) of chlorantraniliprole was obtained from Dr. Erhenstorfer, Germany were used to prepare primary standards. Intermediary and working standards were prepared using acetone and hexane as solvents (1:9 ratio). Working standards of chlorantraniliprole was prepared in the range of 0.01 ppm to 0.5 ppm in 10 ml calibrated graduated volumetric flask using distilled n-hexane as solvent. All the standards were stored in deep freezer maintained at -40^{0}C. For sample preparation primary secondary amine (Agilent), magnesium sulfate anhydrous (Emsure grade of Merck), sodium sulfate anhydrous (Emparta ACS grade of Merck), acetonitrile (LC MS gradient grade of Merck), acetic acid glacial (LC MS grade of Merck), acetone (Emplure grade of Merck), n-hexane (LC MS grade of Merck) were used during the study. Chlorantraniliprole 45 SC commercial grade was procured from local market.

Analytical instruments and limits of detection :

The working standards of chlorantraniliprole was injected in gas chromatograph with electron capture detector (ECD) for estimating the lowest quantity of the insecticide which can be detected with injector split ratio of 1:10 under standard operating parameters as given in Table A.

To confirm the analysis of chlorantraniliprole analysed on ECD as it is detected on both detectors simultaneously using "Universal Y splitter" at the detector end and injecting one micro litre of each working standard. The GC operating parameters for above mentioned pesticides detection and estimation are presented in Table A.

Under the GC operational parameters given in Table A, the retention time of chlorantraniliprole was 4.18 min, respectively. The working standards of above mentioned

Table A : Details of GC parameters for the analysis of chlorantraniliprole

Gas chromatograph	Gas chromatography- AGILENT- 7890B
Column	VF-5ms capillary column 30 m length, 0.25 mm Internal diameter, 0.25 mm film thickness; 1% methyl siloxane
Column oven (^{0}C)	Initial 220^o C for 5 min- increase @ 10^o C/min upto 280^{o}C hold for 4 min
Detectors	Electron capture detector (ECD)
Detector temperature (^{0}C)	300^{0}C
Injector temperature (^{0}C)	260^{0}C
Injector status	Split ratio 1 : 10
Carrier gas	Nitrogen, Iolar II, Purity 99.999%
Carrier gas flow (ml min^{-1})	1 ml min^{-1}
Make-up flow (ml min^{-1})	25 ml min^{-1}
Retention time (min)	4.18 min.
Total run time (min)	15 min

pesticide (0.01 ppm, 0.025 ppm, 0.05 ppm, 0.075 ppm, 0.10 ppm, 0.25 ppm and 0.50 ppm) were injected six times and the linearity lines were drawn.

Based on the response of the detector (ECD) to different quantities of chlorantraniliprole (ng) of CRM standards were injected. It is found that the LOD (limit of detection) is 0.01 ng, and the linearity is in the range of 0.01 ng to 0.10 ng as given in Fig A.

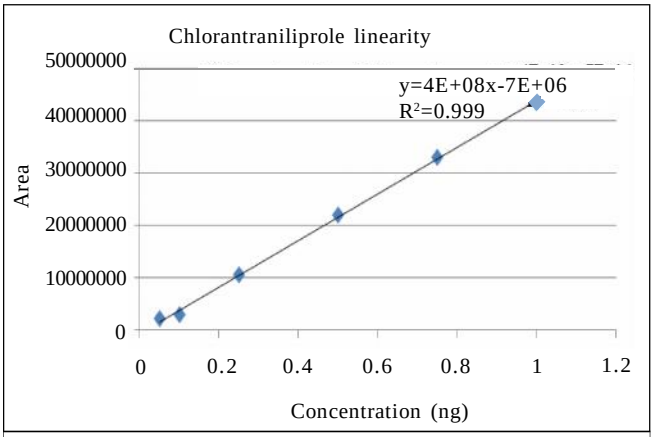

Fig. A : Calibration curve for chlorantraniliprole (Concentration vs area)

Method validation :

Prior to pesticide application and field sample analysis, the residue analysis method was validated following the SANCO document (12495/2011). The capsicum fruits (5 kg) collected from untreated control plots were brought to the laboratory and the stalks were removed prior to samples preparation. The sample was homogenized using Robot Coupe Blixer (High volume homogenizer) and homogenized sample of each 15 g was taken into 50 ml centrifuge tubes. The required quantity of chlorantraniliprole intermediate standards prepared from CRM were added to each 15 g sample to get fortification levels of 0.05 ppm, 0.25 ppm and 0.5 ppm in three replications each. These foritifcation levels were selected to know the suitability of the method to detect and quantify pesticides in capsicum below maximum residue limits (MRLs) of Codex Alimentarius Commission (CAC).

The AOAC official method 2007.01 (Pesticide Residues of Foods by Acetonitrile Extraction and Partitioning with Magnesium Sulphate) was slightly modified to suit to the facilties available at the laboratory and the same was validated for estimation of LOQ (Limit of Quantitation) in capsicum matrix. The final extract of the sample was evaporated using turbovap and made up to 1 ml (equal to 1 g sample) using suitable solvent (n-Hexane: Acetone (9:1) for LC analysis, filtered 1 ml final extract (equal to 0.5 g sample) was directly injected in LC and the residues of pesticides recovered from fortified samples were calculated using the following formula.

$$\text{Residues (mg kg}^{-1}) = \frac{a \times b \times c \times d}{e \times f \times g} \times R$$

where,

a : Sample peak area
b : Concentration of standard (ppm)
c : µl standard injected
d : Final volume of the sample
e : Standard peak area
f : Weight of sample analysed
g : µl of sample injected
R : Recovery factor
Sample weight (15 g) x aliquot taken.

$$\text{Weight of the sample analysed} = \frac{\text{Sample weight (15g)}}{\text{Volume of a cetonitrile (30ml)}} \times \text{aliquot taken}$$

Capsicum samples fortified with chlorantraniliprole at 0.05 mg kg^{-1}, 0.25 mg kg^{-1} and 0.5 mg kg^{-1}, respectively were analyzed and the mean recovery of the residues

Table B : Recovery of chlorantraniliprole residues in capsicum samples

Details	Fortified level					
	0.05 mg kg^{-1}		0.25 mg kg^{-1}		0.50 mg kg^{-1}	
	Residues recovered (mg kg^{-1})	Recovery %	Residues recovered (mg kg^{-1})	Recovery %	Residues recovered (mg kg^{-1})	Recovery %
R^1	0.050	100.80	0.244	97.71	0.446	89.15
R^2	0.053	105.20	0.232	92.78	0.433	86.68
R^3	0.046	91.70	0.234	93.55	0.445	89.00
Mean		99.23		94.68		88.27
SD		6.907		2.652		1.379
RSD		6.961		2.801		1.563

R^1, R^2 and R^3 : Replications Standard deviation (SD) Replicated standard deviation (RSD)

using the method was 99.23 per cent, 93.55 per cent and 89.00 per cent, respectively (Table B). The results show that the method is suitable for the analysis of chlorantraniliprole residues upto 0.05 mg kg^{-1} and the limit of quantitation (LOQ) is 0.05 mg kg.

Field experiments :

Capsicum crop (Royal Wonder of Seminis Pvt. Ltd) was grown in field and laid out in Randomized Block Design at spacing of 60×45 cm with each plot size of 20 m^2 and critical good agricultural practices (GAPs) recommended by University were followed such as field preparation, seed rates (150-200 g ha^{-1}), fertilizer applications (nitrogen @ 40 kg ha^{-1}, phosphorus @ 60 kg ha^{-1} and potassium @ 47.5 kg ha^{-1} were applied in the form of urea, single super phosphate (SSP) and muriate of potash (MOP), respectively nitrogen was given in the form of urea as pocket application in three equal splits at different growth stages of crop *i.e* at 30, 60, 90 days after trans planting. Phosphorus was applied at the time of transplanting which potash @ 30 kg ha^{-1} was applied as basal dose and 17.5 kg ha^{-1} at 30, 60 and 90 days after transplanting (DAT) and irrigations at regular weekly intervals. In poly house conditions as per the recommended package of practices by IIHR, Bengaluru, crop was raised. Drip irrigation was given to provide 2-4 lit of water per square meter per day. Water soluble fertilizers were given through fertigation during entire crop growth period, starting from third week after transplanting. Fertigation was given twice a week with 19:19:19 @ 10 kg, potassium nitrate @ 4.5 kg and calcium nitrate @ 4.5 kg ha^{-1}, respectively. chlorantraniliprole 45 SC in both open fields and poly houses, applied thrice @ 75 ml a.i. ha^{-1}, first spray at fruit initiation followed by second and third spray at 10 days interval by using high volume knapsack sprayer with a spray solution of 500 L ha.

Calculation methods :

Capsicum fruit samples were collected at regular intervals *i.e.* 0, 1, 3, 5, 7, 10, 15 and 20 days after last spray for dissipation studies. Qualitative and quantitative analysis of residues of chlorantraniliprole were done following validated methods explained in 'C' using the analytical instruments given in 'B'. Half-life and TBDL (Time required for residues to reach below determination level) were calculated as per (Hoskins, 1961). from first order dissipation kinetics. OECD (Organization for Economic Co-operation and Development) MRL calculator is used for calculation of MRL and chronic hazard risk analysis was performed using TMDI (Theoretical Maximum Daily Intake) for arriving at MRL for recommendation.

RESEARCH FINDINGS AND DISCUSSION

The findings of the present study as well as relevant discussion have been presented under following heads :

Dissipation and risk analysis of chlorantraniliprole:

Chlorantraniliprole @ 200 ml ha^{-1} was sprayed thrice and the dissipation dynamics was studied in open field and poly house situations by collecting samples at 0, 1, 3, 5, 7, 10, 15 and 20 days after third spray and results are presented in Table 1 and and Fig. 1.

Table 1 : Dissipation of chlorantraniliprole in capsicum in open field conditions

Days after last spray	Residues of chlorantraniliprole (mg kg^{-1})				Dissipation %
	R^1	R^2	R^3	Average	
0	0.40	0.31	0.39	0.36	0.00
1	0.23	0.24	0.23	0.23	36.11
3	0.13	0.14	0.13	0.13	63.88
5	0.06	0.08	0.06	0.07	80.55
7	BDL	BDL	BDL	BDL	100.00
10	BDL	BDL	BDL	BDL	-
15	BDL	BDL	BDL	BDL	-
20	BDL	BDL	BDL	BDL	-
Regression equation	Y = 2.531 + (-0.138) X				
R^2	0.994				
Half-life	2.00 days				
Safe waiting period	7.00 days				

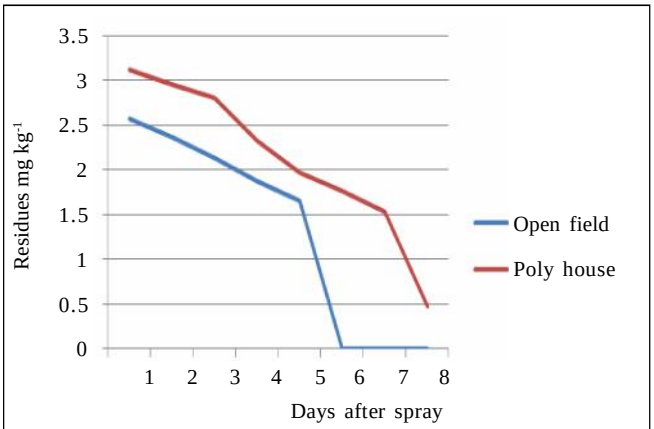

Fig. 1 : Dissipation of chlorantraniliprole in capsicum in open field and poly house conditions

Initial deposits of 0.36 mg kg^{-1} of chlorantraniliprole were detected at 2 hours (0 days) after last spray, dissipated to 0.23, 0.13 and 0.07 mg kg^{-1} by 1, 3 and 5 days, respectively after last spray, in open field conditions. The residues reached BDL at 7th day after spray. The dissipation pattern showed decrease of residues from first day to 7th day and residues dissipated by 36.11, 63.88, 80.55 and 100.00 per cent at 1, 3, 5 and 7 days, respectively. The regression equation was Y = 2.531 + (-0.138) x with R^2 of 0.994. The half- life and safe waiting period for capsicum when chlorantraniliprole @ 125 ml ha^{-1} sprayed thrice were 2.00 and 7.00 days.

In poly house, initial deposits of 1.31 mg kg^{-1} of chlorantraniliprole were detected at 2 hours after last spray, dissipated to 0.91, 0.63, 0.21, 0.09 and 0.05 mg kg^{-1} by 1, 3, 5, 7 and 10 days after last spray, respectively. The dissipation pattern showed decrease of residues from first day to 15th day and the residues dissipated by 30.53, 51.90, 83.96, 93.12 96.18 and 100.00 per cent at 1, 3, 5, 7, 10 and 15 days, respectively. The regression equation was Y = 3.126 + (-0.150) X with R^2 of 0.976. The half - life value was 2.17 while safe harvest period for capsicum when chlorantraniliprole @ 125 ml ha^{-1} was sprayed thrice in poly house condition was 15.00 days after last spray.

Chlorantraniliprole on cauliflower at recommended dose (9.25 g a.i.ha^{-1}) and double the recommended dose (18.50 g a.i.ha^{-1}) was estimated (Hoskins,1961) and observed that, initial deposits of chlorantraniliprole as 0.18 and 0.29 mg kg^{-1}, respectively. The variation in initial deposits of 0.36 and 1.31 mg kg^{-1}, under open and poly house conditions, respectively, in capsicum to cauliflower (initial deposits 0.18 and 0.29 mg kg^{-1} and half- life 1.36 days) may be is due to variation in dosages of application and change in matrix.

Comparison of dissipation pattern of chlorantraniliprole in capsicum in open field and poly house conditions indicated that, initial deposits, half - life and waiting periods were less in open field conditions than poly house conditions (Fig. 1). This

Table 2 : Dissipation of chlorantraniliprole in capsicum in poly house conditions

Days after last spray	Residues of chlorantraniliprole (mg kg^{-1})				Dissipation %
	R^1	R^2	R^3	Average	
0	1.23	1.36	1.33	1.31	0.00
1	0.84	0.89	0.98	0.91	30.53
3	0.61	0.64	0.63	0.63	51.90
5	0.20	0.21	0.22	0.21	83.96
7	0.09	0.08	0.09	0.09	93.12
10	0.05	0.05	0.05	0.05	96.18
15	BDL	BDL	BDL	BDL	100.00
20	BDL	BDL	BDL	BDL	--
Regression equation	Y = 3.126 + (-0.150) X				
R^2	0.976				
Half-life	2.17 days				
Safe waiting period	15.0 days				

data infers that the dissipation is slow in poly houses compared to open fields due to varying factors such as cool climatic conditions and less sun light penetration in poly house.

Conclusion :

As per the Insecticide Act, chlorantraniliprole is not registered for use on capsicum under open field and poly house conditions and also MRLs are not fixed as per FSSAI. The present study conducted based on the results of survey in the Telangana and Andhra Pradesh states and also farmers practice, chlorantraniliprole 20 SC @ 60 ml a.i.ha^{-1} used to manage the fruit borers on capsicum. Initial deposits of 0.36 mg kg^{-1} were detected in capsicum samples collected from open filed, which dissipated to BDL in 7.0 days while in poly house, initial deposits of 1.31 mg kg^{-1} were dissipated to BDL in 15.0 days. The waiting period for safe harvest was worked out to be 7.0 and 15.0 days when chlorantraniliprole 20 SC @ 60 ml a.i.ha^{-1} sprayed thrice in open and poly house conditions, respectively. Dissipation is slow in poly house compared to open fields due to various factors. In both situations initial deposits are lower than the MRL (2 mg kg^{-1}) of Codex Alimentarius Commission hence a pre-harvest interval of 7.0 and 15.0 day is recommended.

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