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Bio-Efficacy, Dissipation of New Insecticide Molecules on Capsicum (*Capsicum annuum* L. var. grossum Sendt) Pest Complex under Field Conditions

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ABSTRACT

Bioefficacy of seven insecticides viz., spinosad @ 125 ml ha^{-1}, flubendiamide @ 200 ml ha^{-1}, chlorantraniliprole @ 200 ml ha^{-1}, Diafenthiuron 25 WP @ 750 g ha^{-1}, spiromesifen @ 750 ml ha^{-1}, thiamethoxam @150 g ha^{-1} and triazophos @ 1250 ml ha^{-1} along with untreated check were evaluated against thrips, mite and aphids during 2013-14 and 2014-15 under field conditions. Among the seven insecticides, spinosad 45 SC @ 125 ml ha^{-1} was the best and effective treatment in reducing the thrips population and recording highest per cent reduction over control followed by diafenthuiron 25 WP @ 750 g ha^{-1} and thiamethoxam 25 WG 150 g ha^{-1}. Against mite, P. latus, spiromesifen 22.9 SL @ 750 ml ha^{-1} was the most effective one with a maximum reduction of population followed by diafenthuiron 25 WP @ 750 g ha^{-1}, respectively. Initial deposits of 0.60 mg kg^{-1} which dissipated to BDL in 7.0 days in open field when spinosad 45 SC sprayed @ 125 ml ha^{-1} at thrice and the waiting period for safe harvest was worked out to be 7.0. Initial deposits of 1.29 mg kg^{-1} dissipated to BDL in 7.0 days in open field when spiromesifen 22.9 SL @ 750 ml ha^{-1} was sprayed thrice and The waiting period was worked out for safe harvest of capsicum was 7.0days.

Key wards: *Capsicum, Bioefficacy, Insecticides, Dissipation, Waiting periods, Field conditions*

INTRODUCTION

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.

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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[10]. 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.

Butani[7] reported over 20 insect species on chillies (*Capsicum* spp.) from India of which thrips, *Scirtothrips dorsalis* Hood, mite, *Polyphagotarsonemus latus* Banks are among the most damaging pests[2,14,16]. under field conditions. In addition to these pests, aphid, *Myzus persicae* (Sulz.), whitefly, *Bemisia tabaci* (Gennadius), leaf miner, *Liriomyza trifolii* (Burgess), gall midge, *Asphondylia capsici* Barens and nematodes, *Meloidogyne incognita* Chitwood are serious problems on capsicum under protected condition[5,12]. Reddy and Kumar[23] estimated crop loss of 40 to 60 tons per ha of capsicum when the crop was not subjected to insecticidal control. In order to control the thrips, mite, aphids and get higher market price, farmers are indiscriminately using insecticides and acaricides just before marketing. 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. Hence, the present experiments were carried out.

MATERIAL AND METHODS

Bio-efficacy of new insecticide molecules against thrips, mite and aphids in capsicum

Poly house experiments were conducted in 2013-14 and 2014 -15 at Horticultural Garden, College of Agriculture, Professor Jayashankar Telangana State Agricultural University (PJTSAU), Rajendranagar, Hyderabad to evaluate the new insecticides for the management of thrips, mite and aphids with leading popular capsicum variety Royal Wonder of Seminis Pvt. Ltd. The experiments were conducted in Randomized Block Design (RBD) with three replications. Capsicum seedlings raised in the nursery were transplanted at age of 40 days in the main field by adopting a spacing of and 30 X 30 cm and plot size was maintained 6m X 6m. All the recommended agronomical practices were implemented to raise crop except plant protection measures against pod borers.

The selected insecticides belonging to different groups *viz.*, Organophosphates (Triazophas), Neonicotinoids (Thiamethoxam), Microbial insecticide (Spinosad,), Thiourea derivatives (Diafenthiuron), Diamides (Chlorantraniliprole), Pthalic acid diamides (Flubendiamide) and Ketones (Spiromesifen) along with untreated control were evaluated for two years.

Observations on insect populations *viz.*, thrips**,** *Scirtothrips dorsalis* Hood, mites, *Polyphagotarsonemus latus* Banks, Aphids, *Myzus persicae* (Sulzer) were recorded in ten randomly tagged plants, from five terminal leaves (2 from top, 2 from middle and 1 from bottom) per plant. Pre count (1 day before spray) and post count (1,3,5 and 7 days after spray) of the insects was recorded by using destructive sampling procedure. Per cent reduction over control was calculated by using the following formula.

$$\text{Percent population reduction} = 1 - \frac{\text{Post treatment population in treatment}}{\text{Pre treatment population in treatment}} \times \frac{\text{Pre treatment population in untreated control}}{\text{Post treatment population in untreated control}} \times 100$$

Pre count (1 DBS) and post count (mean of 1,3,5 and 7 DAS) population and per cent reduction over control were calculated after each spray. Cumulative mean of three sprays in 2013-14 and 2014-15 under open and poly house conditions and pooled mean of two years are represented in tables and discussed for each recorded pests.

Leaf Curl Index (LCI) was recorded one day before and 10 days after each spray following the methodology of Kumar *et al*.[15].

2. Dissipation studies of effective insecticides (Spinosad, Spiromesifen):

i. Preparation of working standards

Certified Reference Materials (CRMs) of spinosad**,** spiromesifen 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 spinosad spiromesifen and thiamethoxam were 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. Spinosad 45 SC, Spiromesifen commercial grade **were** procured from local market.

2. Limit of detection and linearity of spinosad, spiromesifen

The working standards of spinosad, spiromesifen were injected in Liquid Chromatograph with Photo Diode Array (PDA). The detector for estimating the lowest quantity of above insecticides which can be detected under standard operating parameters are given in Table 2.

Under LC operational parameters given in Table 2, the retention time of spinosad, spiromesifen are 4.25, 3.84 and 4.12 min, respectively. Working standards of above insecticides (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.

For confirmatory analysis, samples were also injected in LC-MS/MS. The LC operating parameters for spinosad, spiromesifen detection and estimation are presented in Table 2.

Based on the response of the detector (PDA) to different quantities (ng) of CRM standards injected under the LC- MS/MS operational parameters given in table 3.6, it was found that the LOD (limit of detection) for spinosad, spiromesifen was 0.05 ng and the linearity was in the range of 0.05 ng to 0.10 ng, respectively.

iii. 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 spinosad 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 method followed is presented in the flow chart given below in Fig 3.11 and plate 3.7, 3.8, 3.9 and 3.10.

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 analysis on GC, while 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

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

Samples of capsicum were collected from both the poly house and open field from individual treatments in all the replications after three sprays, in labeled polybags. Care was taken to avoid contamination by wearing hand gloves. Pest damage free and crack free capsicum fruits collected in separate polythene bags were brought to the laboratory at regular intervals *i.e*. 0, 1, 3, 5, 7, 10, 15 and 20 days after last spray from both poly house and open field. Collected samples were analysed for residues by the validated methods.

iii. Dissipation pattern of insecticides on capsicum

1 Sample collection

Samples of capsicum were collected from both the poly house and open field from individual treatments in all the replications after three sprays, in labeled polybags. Care was taken to avoid contamination by wearing hand gloves. Pest damage free and crack free capsicum fruits collected in separate polythene bags were brought to the laboratory at regular intervals *i.e*. 0, 1, 3, 5, 7, 10, 15 and 20 days after last spray from both poly house and open field.

2 Sample analysis

Collected samples were analysed for residues following the validated QuEChERS method. The following parameters were calculated to know the dissipation pattern of the insecticides on capsicum.

i. Dissipation per centage:

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

ii. 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 wherever MRLs are available as per the Codex Alimentarius Commission (CAC) / Food Safety and Standards Authority of India (FSSAI) by the following formula.

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

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

iii. Half-life (RL_{50}): The time in days required to reduce the pesticide residues to half of its initial deposits. Mathematically, it is

$$RL_{50} \text{ (or) } t_{1/2} = \frac{Ln(2)}{b} \quad \frac{0.693147}{b}$$

where,

b : Slope of regression line

RESULTS AND DISCUSSION

1. Bio-efficacy of new insecticide molecules against thrips, mite and aphids in capsicum

i. Thrips, (*S. dorsalis*)

Pooled mean of 2013 -14 and 2014-15: The results with regards to overall cumulative mean efficacy of the treatments against thrips, *S. dorsalis* during the two years under open field conditions are presented in Table 4. Mean thrips population in pre count ranged from 2.52 to 7.94 and post count population was lowest in spinosad (0.88 thrips/leaf) followed by diafenthiuron (1.72 thrips/leaf) and were significantly superior over untreated check (11.21 thrips/leaf) and at par with each other. Thiamethoxam (3.27 thrips/leaf), chlorantraniliprole (5.83 thrips/leaf), flubendiamide (5.92 thrips/leaf), spiromesifen (6.02 thrips/leaf) and triazophos (6.55 thrips/leaf) were found to be on par with untreated check (11.21 thrips/leaf) (Table 4.4).

The per cent reduction over untreated check indicated the order of efficacy of insecticides in descending order as spinosad (88.30 %) followed by diafenthiuron (79.47 %) which were at par with each other and significantly superior over the untreated check. The other treatments that followed in the descending order of efficacy were thiamethoxam (64.71 %), chlorantraniliprole (41.94 %), spiromesifen (39.86 %), flubendiamide (39.05 %) and triazophos (33.71 %) which were found to be on par with untreated check except thiamethoxam (Table 4.4).

The mean LCI of two years revealed that, LCI at one DBS (1.54) was significantly reduced to 0.98 in spinosad treated plants followed by diafenthiuron (2.02 to 1.34) and thiamethoxam (2.11 to 1.43). Whereas, LCI was significantly increased from one DBS to 10 DAS in flubendiamide (3.00 to 3.21) chlorantraniliprole (3.05 to 3.27), spiromesifen (3.08 to 3.34) and triazophos (3.18 to 3.39) and untreated check (3.36 to 3.67) (Table 5).

The results obtained from both years of open field experiment clearly showed that, spinosad was significantly superior over most of the treatments and showed lower mean no. of thrips per leaf (0.88) and mean reduction of thrips population (88.3 %). Spinosad, a naturally occurring mixture of spinosyn A and spinosyn D, is a secondary metabolite from the aerobic fermentation of *Saccharopolyspora spinosa* on nutrient media. The superior efficacy is due to the excitation of insect nervous system leading to involuntary muscle contraction, prostration with tremors and paralysis. These effects are consistent with the activation of nicotinic acetylcholine receptors by a mechanism that is clearly novel and unique. Spinosad also effects GABA receptor function that may contribute further to its insect activity.

The present results are in concurrence with Prasad and Ahmed[19]. who reported that spinosad was superior in reducing thrips, *S. dorsalis* population and increased fruit yield of chilli in Andhra Pradesh. Similar reports by Hossaini *et al*.[11], using spinosad @ 0.4 ml l^{-1} + White sticky trap @ 40 traps ha^{-1} resulted in the lowest thrips *(T. tabaci)* population with highest marginal benefit cost ratio (1 : 1.99) in garlic insect pest management. The efficacy of spinosad @ 75 g a.i.ha^{-1} against *S. dorsalis* in cotton was also reported by Bheemanna *et al*.[6]. Srinivas *et al*., reported that spinosad @ 45 g a.i.ha^{-1} was effective against chilli thrips, *S.dorsalis*. The present findings on efficacy of spinosad is in conformity with the findings of Vanisree *et al.*, who also reported that spinosad 0.015 % was most effective in reduction of thrips, *S. dorsalis* population in chilli in Andhra Pradesh.

In the present study, the next best treatment was diafenthiuron in reducing mean thrips population (1.72) and increased mean per cent reduction of population (79.47). It is a proinsecticide, activated by oxidative desulfurization of the insecticidal carbodiamide and belongs to thiourea group and inhibits the mitochondrial ATP synthesis. Mandal found the lowest thrips population (1.87/leaf) and highest per cent reduction (67.9 %) in diafenthiuron on chilli. Present findings are also in conformity with the findings of Patel *et al*., who reported that diafenthiuron @ 50 and 60 g a.i.ha^{-1} was effective against chilli thrips. The findings of Tatagar are also in close agreement with the present observation. They reported that spraying with diafenthiuron resulted in less incidence of thrips on chillies.

Next in priority was thiamethoxam 25 WG 150 g ml ha^{-1}, which showed significant superiority in reducing mean thrips population and moderate mean per cent reduction of thrips population. It is a highly active neonicotinoid insecticide used as foliar application and has systemic properties with relatively low application rate resulting in reduction of thrips population after application in capsicum. The present results are in line with Ghosh *et al.*, who reported that after 3rd day and 10th day after application of insecticides, 92.80 and 87.50 per cent reduction and lowest no. of thrips population was recorded in thiamethoxam @ 40 g a.i.ha^{-1} compared to acetamiprid @ 30 g a.i ha^{-1} and fipronil @ 70 g a.i.ha^{-1} in chilli. Similar finding were reported by Nandini *et al*.[17], Raj *et al*.[20], Rajaram and Ramamurthy[21] on efficacy of thiamethoxam against thrips. Highest efficacy against thrips was observed with thiamethoxam 25 WG @ 0.1 g l^{-1} followed by indoxacarb 14.5 % SL @ 0.5 ml l^{-1}. Sarangi and Panda also reported that the chemical management of chilli thrips, *S. dorsalis* by thiamethoxam @ 200 g a.i. ha^{-1} was as effective as seedling root dip (SRD).

It is interesting to note that spinosad, diafenthiuron and thiamethoxam reduced the incidence of the thrips population after the three sprays while the rest of the insecticides increased the incidence compared to before spraying. This observation indicated that these three insecticides effectively controlled thrips up to a week after spraying.

The literature pertaining to leaf curl index (LCI) caused by thrips, *S.dorsalis* (up ward curling) is scanty. But Reddy and Kumar[23]. reported that the rating for thrips damage (RFTD) on capsicum was 1.52 to 1.92 under open field condition at IIHR, Bengaluru. In the present study during both the years under open field conditions, LCI was found to depend on population levels of thrips during the crop season. Higher population per leaf resulted in high LCI even after spray. However, LCI was reduced after spray in the insecticides viz., spinosad 45 SC @ 125 ml ha^{-1}, diafenthiuron 25 WP @ 750 g ha^{-1} and thiamethoxam 25 WG @ 150 g ha^{-1} which were found to be effective in reducing population

ii. mite (*Polyphagotarsonemus latus* Banks) Pooled mean of 2013-14 and 2014 -15:

The results with regards to overall cumulative mean efficacy of the treatments against mite, *P. latus* during the two years under open field conditions are presented in Table 6. Mean mite population in pre count ranged from 5.46 to 15.88 and post count population was lower with spiromesifen (0.62 mites/ leaf) followed by diafenthuiron (4.08 mites/ leaf), triazophos (5.73 mites/ leaf) and thiamethoxam (9.43 mites/ leaf) which were significantly superior over rest of the treatments and untreated check (17.60 mites/ leaf). The descending order of efficacy of the other treatments were chlorantraniliprole (12.84 mites/leaf), flubendiamide (14.69 mites/leaf) and spinosad (15.21 mites/leaf) which were found to be at par with over untreated check (17.60 mites/leaf).

The highest per cent reduction of mite population was recorded in spinosad (97.29 %) followed by diafenthiuron (71.32 %), triazophos (61.31 %) and thiamethoxam (43.45 %) which were at par with each other and significantly superior over rest of the treatments and untreated check. The other treatments that followed in the ascending order of efficacy were chlorantraniliprole (20.60 %), flubendiamide (13.42 %) and spinosad (11.21%) which were found to be significantly superior over untreated check.

The mean LCI of two years revealed that, LCI at one DBS (1.53) was significantly reduced to 0.69 at 10 DAS in spiromesifen treated plants followed by diafenthiuron (1.78 to 1.09) and triazophos (2.03 to 1.72). Where as LCI was significantly increased from one DBS to 10 DAS in flubendiamide (2.48 to 2.71), chlorantraniliprole (2.49 to 2.70), thiamethoxam (2.50 to 2.67), spinosad (2.52 to 2.73) and untreated control (2.72 to 3.00) (Table 7).

The results obtained from both years of open field experiment showed that, spiromesifen was significantly superior over rest of the treatments by recording lower mean no.of mites per leaf (0.62) and mean reduction of mite population (97.29 %). Spiromesifen is a tetraonic acid derivative insecticide and acaricide effective against *P. latus*[9].

The present results are in concurrence with Varghese and Mathew who tested certain insecticides and acaricides against chilli mite, *P. latus*. Spiromesifen 45 SC @ 100 g a.i.ha^{-1} and propargite 57 EC @ 570 g a.i. ha^{-1} were found to be effective in reducing chilli mite population.

Similarly the efficacy of spiromesifen 45 SC at 100 g a.i.ha^{-1} in reducing chilli mite in comparison to other insecticides was reported by Nagaraju *et al*.[18]. The efficacy of spiromesifen 45 SC at 120 g a.i.ha^{-1} in reducing chilli mite in comparison to dicofol 18.5 EC @ 185 g a.i.ha^{-1} was reported by Kavitha *et al*.[13]. Spiromesifen 45 SC @ 120 g a.i.ha^{-1} showed long lasting efficacy by reducing the leaf curl damage from 41.8 per cent to 12.5 per cent without producing any phytotoxicity. These reports are in line with the present findings.

The present findings are also in conformity with the findings of Seal and Klassen who reported the effectiveness of spiromesifen @ 300 - 400 ml ha^{-1} in reducing the incidence of chilli thrips in Scotch Bonnet variety of chilli.

In the present study, the next best treatment was diafenthiuron in reducing the mean mite population (4.08 mites/ leaf) with increased mean per cent reduction of population (71.32 %). The present results are in concurrence with Srinivas *et al*.[27], Dhandapani *et al*.[8], who reported that the diafenthiuron 600 g a.i ha^{-1} brought down the eggs and active stages of *P. latus* by 90 - 95 per cent followed by fenzaquin 125 g a.i ha^{-1}. Bifenthrin and fenpropathrin were found to be less effective against *P. latus.*

Next in priority was thiamethoxam which showed significant superiority in reducing the mean mite population (5.73 mites/ leaf) with increased mean per cent reduction of population (61.31%). Triazophos is an organophosphate and belongs to acetylcholinesterase (AChE) inhibitor group. Triazophos is a broad-spectrum insecticide and acaricide with contact and stomach action. It is non-systemic, but penetrates deeply into plant tissues. The present findings are in line with Mahalingappa *et al*., who evaluated the bio-efficacy of certain insecticides against mite, *(P. latus*) infesting chilli and concluded that triazophos 0.08 % was most effective against mites. Nagaraju *et al*.[18], reported that the triazophos 40 EC (0.15 %), dicofol 18.5 % (0.25%) and triazophos 40 EC (0.15%)

alternated with Neemark (0.50%) at an interval of 15 days was found to be effective in reducing leaf curl disease by recording highest yield (19.97 q/ha). Kandasamy *et al*., found the triazophos 0.04 % to be effective insecticide against chilli mite and in reducing the population by 89.00 - 93.70 per cent.

Triazophos @ 750 g a.i.$ha^{-1}$was found highly effective in reducing the mite incidence for 7-14 days after spray and recorded the highest yield compared to thiodicarb @ 750g a.i.ha^{-1} and fenezaquin @ 200 g a.i.ha^{-1} in chilli ecosyste[1]. Treatments with triazophos gave the highest yields (> 3.25 t/ha), followed by phosalone and amitraz in chilli[22]. These findings confirm the present results that triazophos 40 EC @ 1250 ml ha^{-1} was effective insecticide against mites on capsicum under open field conditions.

The insecticides spiromesifen, diafenthiuron, thiamethoxam and triazophos reduced the incidence of mite population up to seven days after spraying, while in others an increase the mite population after spray.

II. Dissipation studies of effective insecticides (Spinosad, Spiromesifen)

Spinosad : Spinosad @ 125 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 Tables 8.

Initial deposits of 0.60 mg kg^{-1} of spinosad were detected at 2 hours (0 days) after last spray, dissipated to 0.34, 0.14 and 0.07 mg kg^{-1} at 1, 3 and 5 days after last spray, respectively 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 44.26, 77.04, 88.52 and 100.00 per cent at 1, 3, 5 and 7 days, respectively. The regression equation was Y = 2.767 + (- 0.210) X with R^2 of 0.994. The half - life and safe waiting period for capsicum when spinosad @ 125 ml ha^{-1} sprayed thrice were 1.43 and 7.00 days.

Dissipation of spinosad @ 17.5 g a.i ha^{-1} in cabbage and cauliflower. It persisted up to 10 days in cabbage and cauliflower. The half - life of spinosad residues were 2.8 days, respectively. The variation in intial deposits and half - life (1.43 and 3.37 days, open and poly house conditions respectively) in capsicum to cabbage and cauliflower may be due to variation in dosages of application and change in matrix[3].

Dissipation behaviour of spinosad on chilli at two application rates (73.0 g a.i ha^{-1} and 146 g a.i ha^{-1}), half - life and waiting periods were 1.48 days and 0.70 days respectively, for 73.0 g a.i.ha^{-1} [4]. whereas 6.72 days and 5.55 days, respectively for 146 g a.i.ha^{-1} application rate.

Dissipation kinetics of spinosad in cabbage when applied in two doses @ 15 and 30 g a.i.ha^{-1} of spinosad the initial deposits were observed as 0.33 and 0.56 μg kg^{-1} at single and double dosages, respectively, and dissipated below its limit of quantification of 0.01 μg kg^{-1} after 5 and 7 days at single and double doses, respectively. Spinosad dissipation kinetics in cowpea pods found that initial deposits of 0.94 and 1.9 μ g kg^{-1} reached below detectable level on the 7th day and 15th day at single and double doses. The variation in the initial deposits (0.61 and 1.60 mg kg^{-1} in open and poly house conditions, respectively) half - life (1.43 and 3.37 days), waiting periods (7.00 and 20.00 days) and dissipated to BDL (7.00 and 20.00 days) of capsicum to chilli, cow pea may be due to variation in dosages of application, change in matrix and climatic conditions .

ii. spiromesifen Initial deposits of 1.29 mg kg^{-1} of spiromesifen was detected at 2 hours after last spray, dissipated to 0.62, 0.16 and 0.05 mg kg^{-1} by 1, 3 and 5 days after last spray, respectively under 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 51.93, 87.59, 96.12 and 100.00 per cent at 1, 3, 5 and 7 days, respectively. The regression equation is Y = 3.086 + (-0.282) X with R^2 of 0.997. The half - life value was worked out by using linear semi-logarithmic regression analysis and found to be 1.06 days. The safe harvest period was 7.00 days after third spray of spiromesifen when sprayed @ 125 ml ha^{-1} in open field conditions (Table-9).

Sharma *et al.*[24], reported the persistence of spiromesifen in apple in four locations and the initial deposits of spiromesifen were 0.91, 0.99, 0.99 and 0.88 $\mu g.kg^{-1}$ at recommended dose, respectively. Raj *et al.*[20], reported the dissipation of spiromesifen on okra and the initial deposits 0.96 and 1.81µ g g^{-1} at standard (48 g.a.i.ha^{-1}) and double (96 g.a.i.ha^{-1}) dose, gradually declined and persisted up to 3rd and 5th day at lower and higher dose. The residues fell below quantification limit of 0.01 µ. g^{-1} on the 5th and 7th day at standard and double the dose. The variation in the initial deposits (1.29 and 1.61 mg kg^{-1} in open and poly house conditions, respectively) half - life (1.06 and 2.09 days), waiting periods (7.00 and 10.00 days) and dissipated to BDL (7.00 and 10.00 days) of capsicum to other crops reported by earlier workers may be due to variation in dosages of application, change in matrix and climatic conditions.

Table 1. Scoring procedure for sucking pests damage

S.No	Score	Symptom
1	**0**	No symptoms
2	**1**	1-25% leaves/plant showing curling
3	**2**	25-50% leaves/plant showing curling, moderately damaged
4	**3**	51-75% leaves/plant showing curling, heavely damaged, malformation of growing points and reduction in plant height
5	**4**	>76% leaves/plant showing curling,severe and complete destruction of growing points,drastic reduction in plant height , defoliation and severe malformation

Table 2. Details of LC-MS/MS operating parameters for the analysis of spinosad, spiromesifen

<table>
<tr><td>LC-MS/MS</td><td colspan="4">SHIMADZU LC-MS/MS 8040</td></tr>
<tr><td>Detector</td><td colspan="4">Mass Spectrophotometer</td></tr>
<tr><td>Column</td><td colspan="4">KINETEX, 100 X 3, 2 um</td></tr>
<tr><td>Column Oven Temperature</td><td colspan="4">40°C</td></tr>
<tr><td>Retention Time (RT)</td><td colspan="4">5.1</td></tr>
<tr><td>Nebulizing gas</td><td colspan="4">Nitrogen</td></tr>
<tr><td>Nebulizing flow gas</td><td colspan="4">2.0 lit.min⁻¹</td></tr>
<tr><td>Pump Mode/ flow</td><td colspan="4">Gradient/ 0.4 ml. min⁻¹</td></tr>
<tr><td>Retention time,</td><td colspan="4">Spinosad- 4.25 min.</td></tr>
<tr><td></td><td colspan="4">Spiromesifen – 3.84</td></tr>
<tr><td rowspan="5">LC Program</td><td colspan="4">A : Ammonium formate in water</td></tr>
<tr><td colspan="4">B : Ammonium formate in methanol</td></tr>
<tr><td>Insecticide</td><td>Time</td><td>methanol</td><td>Water</td></tr>
<tr><td>Spinosad</td><td>4.25</td><td>55</td><td>45</td></tr>
<tr><td>Spiromesifen</td><td>10.00</td><td>95</td><td>5</td></tr>
<tr><td rowspan="3">Precursor ion and Quantifier ion</td><td>Insecticide</td><td>Precursor ion</td><td colspan="2">Quantifier ion</td></tr>
<tr><td>Spinosad</td><td>433.40</td><td colspan="2">223.40</td></tr>
<tr><td>Spiromesifen</td><td>371.00</td><td colspan="2">273.10</td></tr>
</table>

Table 3. Cumulative efficacy of certain insecticide molecules against thrips, *S. dorsalis* on capsicum under open field conditions during 2013-14 and 2014-15

Tr.No	Treatments	Dose (g or ml ha⁻¹)	2013-14 Mean of three sprays#			2014-15 Mean of three sprays#			Mean of 2013-14 and 2014-15		
			Pre count (Mean no. of thrips/ leaf) (1 DBS)*	Post count (Mean of 1,3,5,7 DAS)*	Per cent Reduction$	Pre count (Mean no. of thrips/ leaf) (1 DBS)*	Post count (Mean of 1,3,5,7 DAS)*	Per cent Reduction $	Pre count (Mean no. of thrips/ leaf) (1 DBS)*	Post count (Mean of 1,3,5,7 DAS)*	Per cent Reduction $
T_1	Spinosad 45 SC	125	2.52 (1.87)a	1.09 (1.44)c	84.08 (66.45)a	2.51 (1.87)b	0.67 (1.29)a	92.52 (74.09)a	2.52 (1.87)d	0.88 (1.37)c	88.3 (69.97)a
T_2	Flubendiamide 480 SC	200	4.99 (2.44)b	5.49 (2.54)ab	33.88 (35.58)cd	5.93 (2.63)ab	6.35 (2.71)b	44.23 (41.67)b	5.46 (2.54)abc	5.92 (2.63)ab	39.05 (38.66)cd
T_3	Chlorantraniliprole 20 SC	200	4.64 (2.37)b	4.90 (2.42)abc	41.23 (39.93)bc	6.02 (2.65)ab	6.75 (2.78)b	42.65 (40.75)b	5.33 (2.51)abc	5.83 (2.61)ab	41.94 (40.34)cd
T_4	Diafenthiuron 25 WP	750	2.77 (1.94)a	2.03 (1.74)bc	73.43 (58.94)a	3.26 (2.06)c	1.41 (1.55)a	85.51 (67.59)a	3.02 (2.00)cd	1.72 (1.64)bc	79.47 (63.03)ab
T_5	Spiromesifen 22.9 SL	750	4.92 (2.43)b	5.20 (2.49)ab	37.98 (38.03)bcd	6.11 (2.66)ab	6.83 (2.79)b	41.74 (40.22)b	5.52 (2.55)abc	6.02 (2.65)ab	39.86 (39.13)cd
T_6	Thiamethoxam 25 WG	150	4.12 (2.26)b	4.00 (2.24)abc	52.22 (46.25)b	4.29 (2.30)bc	2.54 (1.88)a	77.20 (61.45)a	4.21 (2.28)bcd	3.27 (2.06)abc	64.71 (53.53)bc
T_7	Triazophos 40 EC	1250	5.58 (2.56)c	6.40 (2.72)ab	24.93 (28.27)d	6.03 (2.65)ab	6.69 (2.77)b	42.49 (39.89)b	5.81 (2.61)ab	6.55 (2.74)ab	33.71 (33.17)d
T_8	Untreated check	--	6.68 (2.70)d	9.00 (3.05)a	0.00e	9.2 (3.08)a	13.42 (3.61)c	0.00c	7.94 (2.90)a	11.21 (3.23)a	0.00d
		SEm±	0.15	0.20	3.00	0.20	0.29	3.84	3.00	3.84	4.28
		CD (P= 0.05)	0.47	0.62	9.18	0.62	0.89	11.77	9.18	11.77	13.13
		CV (%)	11.43	15.21	13.25	14.07	10.82	14.57	13.25	14.57	17.59

mean of five leaves per plant, ten plants per replication, three replications per treatment., * Figure in the parenthesis are square root transformed values.

$ Figure in the parenthesis are Arc-sin transformed values

DOS : Ist Spray : 15-11-2013., IInd spray: 22-11-2013., IIIrd spray : 29-11-2013., DBS : Days Before Spray., DAS : Days After Spray., NS : Non significant

DMRT : Means followed by a common letter are not significantly different (P= 0.0

Table 4. Leaf curl index (LCI) Score caused by thrips, *S. dorsalis* on capsicum under open field conditions during 2013-14 and 2014-15

Tr.No.	Treatments	Dose (g or ml ha⁻¹)	Mean of three sprays 2013-14		Mean of three sprays 2014-15		Mean 2013-14 and 2014-15	
			1 DBS	10 DAS	1 DBS	10 DAS	1 DBS	10 DAS
T_1	Spinosad 45 SC	125	1.55(1.59)*	1.01(1.41)b	1.54(1.59)	0.94(1.39)b	1.55(1.59)	0.98(1.40)c
T_2	Flubendiamide 480 SC	200	2.97(1.99)	3.17(2.04)a	3.02(2.00)	3.25(2.06)a	3.00(2.00)	3.21(2.05)ab
T_3	Chlorantraniliprole 20 SC	200	3.04(2.01)	3.20(2.04)a	3.04(2.01)	3.33(2.08)a	3.04(2.01)	3.27(2.06)ab
T_4	Diafenthiuron 25 WP	750	2.05(1.74)	1.46(1.56)ab	1.99(1.72)	1.21(1.48)b	2.02(1.78)	1.34(1.53)bc
T_5	Spiromesifen 22.9 SL	750	3.15(2.03)	3.29(2.07)a	3.01(2.00)	3.39(2.09)a	3.08(2.02)	3.34(2.08)ab
T_6	Thiamethoxam 25 WG	150	2.16(1.77)	1.51(1.58)ab	2.05(1.74)	1.34(1.53)b	2.11(1.76)	1.43(1.55)abc
T_7	Triazophos 40 EC	1250	3.25(2.06)	3.38(2.09)a	3.10(2.02)	3.40(2.09)a	3.18(2.04)	3.39(2.09)a
T_8	Untreated check	--	3.44(2.01)	3.55 (2.04)a	3.27(1.96)	3.78(2.10)a	3.36(1.98)	3.67(2.07)ab
		SEm±	0.40	0.29	0.36	0.40	0.33	0.48
		CD (P = 0.05)	NS	0.90	1.11	1.25	1.23	1.25
		CV (%)	9.7	10.12	13.66	17.40	16.50	14.21

* Figure in the parenthesis are square root transformed values.

DMRT : Means followed by a common letter are not significantly different (P= 0.05)

DBS : Day Before Spray, DAS : Days After Spray, NS : Non significant

Table 6. Cumulative efficacy of certain insecticide molecules against mite, *P. latus* on capsicum under open field conditions during 2013-14 and 2014-15

T.No	Treatments	Dose (g or ml ha^{-1})	2013-14 Mean of three sprays#			2014-15 Mean of three sprays#			Mean of 2013-14 and 2014-15		
			Pre count (Mean no. of mites/ leaf) (1 DBS)*	Post count (Mean of 1,3,5,7 DAS)*	Per cent Reduction$	Pre count (Mean no. of mites/ leaf) (1 DBS)*	Post count (Mean of 1,3,5,7 DAS)*	Per cent Reduction$	Pre count (Mean no. of mites/ leaf) (1 DBS)*	Post count (Mean of 1,3,5,7 DAS)*	Per cent Reduction$
T_1	Spinosad 45 SC	125	22.08 (4.80)a	22.89 $(4.88)^{a}$	13.58 $(21.61)^{f}$	7.42 $(2.90)^{a}$	7.53 $(2.92)^{a}$	8.83 $(17.28)^{c}$	14.75 (3.96)	15.21 $(4.02)^{ab}$	11.21 $(19.55)^{d}$
T_2	Flubendiamide 480 SC	200	19.51 $(4.52)^{ab}$	21.85 $(4.78)^{a}$	18.01 $(25.10)^{f}$	7.41 $(2.90)^{a}$	7.53 $(2.92)^{a}$	8.83 $(17.28)^{c}$	13.46 (3.80)	14.69 $(3.96)^{ab}$	13.42 $(21.48)^{d}$
T_3	Chlorantraniliprole 20 SC	200	16.77 $(4.21)^{ab}$	18.12 $(4.37)^{ab}$	32.71 $(34.87)^{e}$	7.41 $(2.90)^{a}$	7.56 $(2.92)^{a}$	8.49 $(16.93)^{c}$	12.09 (3.61)	12.84 $(3.72)^{ab}$	20.60 $(26.48)^{d}$
T_4	Diafenthiuron 25 WP	750	11.42 $(3.52)^{ab}$	5.23 $(2.49)^{cd}$	79.47 $(63.03)^{b}$	4.94 $(2.43)^{ab}$	2.94 $(1.98)^{b}$	63.17 $(52.61)^{b}$	8.18 (3.03)	4.08 $(2.25)^{d}$	71.32 $(57.59)^{b}$
T_5	Spiromesifen 22.9 SL	750	8.42 $(3.01)^{b}$	1.23 $(1.69)^{d}$	94.84 $(80.33)^{a}$	2.49 $(1.86)^{b}$	0.02 $(1.01)^{c}$	99.74 $(87.04)^{a}$	5.46 (2.54)	0.62 $(1.27)^{e}$	97.29 $(80.49)^{a}$
T_6	Thiamethoxam 25 WG	150	17.82 $(4.33)^{ab}$	14.29 $(3.91)^{abc}$	43.70 $(41.13)^{d}$	6.07 $(2.65)^{a}$	4.58 $(2.36)^{ab}$	43.19 $(41.06)^{b}$	11.95 (3.39)	9.43 $(3.23)^{bc}$	43.45 $(41.22)^{c}$
T_7	Triazophos 40 EC	1250	13.26 $(3.77)^{ab}$	7.76 $(2.96)^{bcd}$	68.82 $(56.03)^{c}$	5.53 $(2.55)^{a}$	3.71 $(2.17)^{ab}$	53.80 $(48.17)^{b}$	9.40 (3.22)	5.73 $(2.59)^{cd}$	61.31 $(52.78)^{c}$
T_8	Untreated check	--	23.97 $(4.92)^{)a}$	26.91 $(5.22)^{a}$	0.00^{g}	7.78 $(2.87)^{a}$	8.29 $(2.92)^{d}$	0.00^{c}	15.88 (3.97)	17.6 $(4.19)^{a}$	0.00e
		SEm±	1.30	1.34	2.43	0.29	0.24	3.84	0.23	0.48	3.38
		CD (P= 0.05)	4.28	4.90	7.44	0.89	0.73	11.77	0.73	1.42	11.73
		CV (%)	10.20	10.79	10.75	15.26	13.52	16.56	11.04	14.51	16.80

#No.of mites/leaf, mean of five leaves per plant, ten plants per replication, three replications per treatment.

* Figure in the parenthesis are square root transformed values. $ Figure in the parenthesis are Arc-sin transformed values.

DBS : Days Before Spray., DAS : Days After Spray., NS : Non significant

DOS :I[st]Spray :6-12-2013; II[nd]Spray 13-12-2013 and III[rd] Spray :21-12-2013

DMRT : Means followed by a common letter are not significantly different (P= 0.05)

Table 7. Leaf curl index (LCI) Score caused by mite, *P. latus* on capsicum under open field conditions during 2013-14 and 2014-15

T.No	Treatments	Mean of three sprays 2013-14		Mean of three sprays 2014-15		Mean 2013-14 and 2014-15	
		1 DBS	10 DAS	1 DBS	10 DAS	1 DBS	10 DAS
T_1	Spinosad 45 SC	2.69(1.92)*	2.75(1.93)a	2.35(1.83)	2.70(1.92)a	2.52(1.87)	2.73(1.93)a
T_2	Flubendiamide 480 SC	2.61(1.90)	2.80(1.94)a	2.35(1.83)	2.61(1.90)a	2.48(1.86)	2.71(1.92)a
T_3	Chlorantraniliprole 20 SC	2.66(1.91)	2.81(1.95)a	2.32(1.82)	2.58(1.89)a	2.49(1.86)	2.70(1.92)a
T_4	Diafenthiuron 25 WP	1.90(1.70)	0.97(1.40)ab	1.65(1.62)	1.20(1.48)bc	1.78(1.66)	1.09(1.44)b
T_5	Spiromesifen 22.9 SL	1.51(1.58)	0.50(1.22)b	1.55(1.59)	0.87(1.36)c	1.53(1.59)	0.69(1.30)b
T_6	Thiamethoxam 25 WG	2.65(1.91)	2.80(1.94)a	2.35(1.83)	2.54(1.88)ab	2.50(1.87)	2.67(1.91)a
T_7	Triazophos 40 EC	1.76(1.66)	0.97(1.40)ab	2.30(1.81)	2.47(1.86)ab	2.03(1.74)	1.72(1.64)ab
T_8	Untreated check	2.90(1.92)	3.12(1.91)a	2.54(1.82)	2.87(1.91)a	2.72(1.87)	3.00(1.88)a
	SEm+	0.40	0.16	0.41	0.11	0.20	0.41
	CD	NS	0.50	NS	0.33	0.44	1.25
	CV %	13.83	14.33	10.88	10.66	15.67	12.68

* Figure in the parenthesis are square root transformed values.

DMRT : Means followed by a common letter are not significantly different (P= 0.05)

DBS : Day Before Spray., DAS : Days After Spray., NS : Non significant

Table 8. Dissipation of spinosad in capsicum in open field conditions

Days after last spray	Residues of spinosad (mg kg^{-1})				Dissipation %
	R1	R2	R3	Average	
0	0.61	0.59	0.63	0.60	0.00
1	0.39	0.34	0.29	0.34	44.26
3	0.13	0.16	0.13	0.14	77.04
5	0.06	0.06	0.07	0.07	88.52
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 = 2.767 + (- 0.210) X				
R^2	0.994				
Half-life	1.43 days				
Safe waiting period : 7.00 days					

Table 9. Dissipation of spiromesifen in capsicum in open field conditions

Days after spray	Residues of spiromesifen (mg kg^{-1})				Dissipation %
	R1	R2	R3	Average	
0	1.32	1.26	1.28	1.29	0.00
1	0.58	0.66	0.62	0.62	51.93
3	0.15	0.18	0.16	0.16	87.59
5	0.05	0.06	0.04	0.05	96.12
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 = 3.086 + (-0.282)X				
R^2	0.997				
Half life	1.06 days				
Safe waiting period	7 days				

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