

**BIOEFFICACY AND RESIDUE DYNAMICS OF SOME
PESTICIDES USED AGAINST INSECT PESTS
OF BRINJAL AND CHILLI**

Thesis

by

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(H-2018-05-D)**

submitted to



**Dr. YASHWANT SINGH PARMAR UNIVERSITY
OF HORTICULTURE AND FORESTRY
SOLAN (NAUNI) HP - 173 230 INDIA**

in

partial fulfilment of the requirements for the degree

of

**DOCTOR OF PHILOSOPHY
ENTOMOLOGY**

**DEPARTMENT OF ENTOMOLOGY
COLLEGE OF HORTICULTURE**

2023

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This is to certify that the thesis titled, “**Bioefficacy and residue dynamics of some pesticides used against insect pests of brinjal and chilli**” submitted in partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy Entomology** in the discipline of **Plant Protection** to Dr. Yashwant Singh Parmar University of Horticulture & Forestry, (Nauni) Solan (HP) – 173 230 is a bonafide research work carried out by **Ms. Shivani Bhartiya (H-2018-05-D)** daughter of Sh. Surinder Kumar under my supervision and that no part of this thesis has been submitted for any other degree or diploma.

The assistance and help received during course of this investigation have been fully acknowledged.

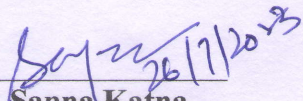
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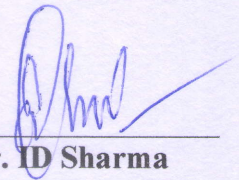
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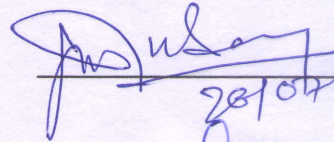
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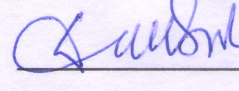

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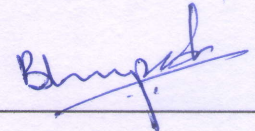

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ACKNOWLEDGEMENTS

*First and foremost, I would like to thank the **Lord Almighty** for blessing me with a joyous life full of wonderful opportunities and prospects to pursue whatever I dream in my life.*

*It is my proud privilege to express my deep sense of gratitude and indebt to my esteemed advisor, **Dr. Sapna Katna** for her incessant guidance, unflinching judgment, keen interest, innovative ideas, affectionate attitude and constant encouragement during the entire course of study.*

*Beside my advisor, I would like to thank the rest of members of my Advisory Committee, **Dr. JK Dubey, Dr. DK Mehta and Dr. Meenu Gupta**, for their insightful comments and encouragement, but also for the hard question which incited me to widen my research from various perspectives.*

*My sincere thanks also goes to **Dr. SC Verma (Prof & Head)** who provided his consistent support and suggestion during this work.*

*Thanks is too small word to express my deep sense of gratitude to **Dr. Ajay Sharma, Dr. Tanuja Banshtu and Dr. Rakesh Kumar**, for their spontaneous help and valuable guidance.*

*There is no substitute for the love and affection bestowed on me by my beloved family, particularly my parents **Sh. Surinder Kumar and Smt. Anjana Kumari** and my in laws **Sh. Kamal Dhiman and Smt. Kunta Dhiman**, thank you for your love, support and unwavering belief in me. Without you, I would not be the person I am today.*

*Above all I would like to thank my beloved husband **Ashish** for his love and constant support and for keeping me sane over the past few months. Thank you for being my muse, editor, proofreader and sounding board. But most of all, thank you for being my best friend. I owe you everything.*

*My keen sense of gratitude to my seniors, **Dr. Arvind Kumar, Dr. Gaganpreet Singh Brar, Dr. Nisha, Shubhra di, Hema di** and my juniors, **Himani, Pankaj, Sakshi, Ankur** for their sincere, selfless and invaluable help, as and when required during my entire degree program.*

*I would like to acknowledge the help and assistance extended by my friends **Sonali and Deepak** during whole course of my research.*

*I would like to show my gratitude to the members of my lab **Hitesh Bhaiya, Kesar bhaiya , Maan Singh Bhaiya, Rajesh bhaiya, Alka Mam and Negi Sir**.*

The warmth showered upon me through every handshake, every smile and many a times through unsaid words is warmly acknowledged.

Needless to say errors and omissions are mine.

Place: Nauni-Solan

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(Shivani Bhartiya)

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LIST OF ABBREVIATION

%	Percentage
/ or ⁻¹	Per or per unit
@	At the rate
μg	Microgram
μm	Micrometer
μL	Micro litre
a	Intercept
ACN	Acetonitrile
a.i.	Active ingredient
ADI	Acceptable daily intake
AOAC	Association of Official Analytical Chemists
b.w.	Body weight
b	Slope of regression equation
CD	Critical difference
BDL	Below determination limit
CIBRC	Central Insecticides Board and Registration Committee
cm	Centimetre
DAD	Diode array detection
DAT	Days after treatment
DAS	Days after spray
df	Degree of freedom
E	East direction
EADI	Estimated average daily intake
EC	Emulsifiable concentrate
EDI	Estimated daily intake
EPA	Environmental Protection Agency
EIL	Economic injury level
ESI	Electrospray Ionisation
EU	European Union
eV	Electron volt
<i>et al.</i>	et alia (Co-workers)
etc	Et cetera
FAO	Food and Agriculture Organization
Fig.	Figure
FYM	Farm yard manure
g	Gram
GAP	Good Agricultural Practices
GC-ECD	Gas Chromatography-electron capture detector

GC-MS MS	Gas chromatography- Tandem Mass Spectrometry
GLC	Gas liquid chromatography
GC-FPD	Gas chromatography-flame photometric detector
ha	Hectare
HP	Himachal Pradesh
HPLC	High-performance liquid chromatography
HQ	Hazard quotient
i.e.	Id EST (that is)
ICH	International Conference on Harmonization
IUPAC	International Union of Pure and Applied Chemistry
ICMR	Indian Council of Medical Research
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
kg	Kilogram
L	Litre
LC	Lethal concentration
LC-MS MS	Liquid Chromatography- Tandem Mass Spectrometry
LD	Lethal dose
LOD	Limit of detection
LOQ	Limit of quantification
LLOQ	Lower limit of quantification
m	Meter
m ²	Square meter
m ³	Cubic meter
mg	Milligram
min	Minute
ml	Millilitre
mm	Millimetre
mol	Mole
m/z	Mass to charge number of ions
MPI	Maximum permissible intake
MRL	Maximum residue level
MS	Mass spectrometry
MRM	Multiple reaction monitoring
MT	Million tonnes
N	North direction
NS	Non significant
nm	Nano meter
NSKE	Neem seed kernel extract
ND	Not detected
NHB	National Horticulture Board

OD	Oil dispersion
NEDI	National estimated daily intake
NSSO	National Sample Survey Organisation
°C	Degree Celsius
PEG	Polyethylene glycol
PHI	Pre harvest interval
ppm	Parts per million
PRL	Pesticide Residue Laboratory
PSA	Primary Secondary Amine
q	Quintal
R ²	Correlation coefficient
RBD	Randomized Block Design
rpm	Rotations per minute
RSD	Relative standard deviation
RT	Retention time
RQ	Respiratory quotient
RyR	Ryanodine receptor
SC	Suspension concentrate
SL	Soluble liquid
SP	Soluble powder
SD	Standard deviation
SPE	Solid phase extraction
S/N	Signal to noise ratio
T _{1/2} or RL ₅₀	Half-life
TMDI	Theoretical maximum daily intake
TMRC	Theoretical maximum residue contribution
UPLC	Ultra-performance liquid chromatography
US FDA	United States Food and Drug Administration
USP	United States Pharmacopeia
x	Times or independent variable
y	Dependent value
v/v	Volume by volume
<i>viz.</i>	Namely
w/v	Weight by volume
WHO	World Health Organisation
WG	Wettable granule
WP	Wettable powder
WS	Water soluble granules
μV	Microvolt

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Chapter 1

INTRODUCTION

Vegetables are an abundant and affordable source of vitamins and minerals, play a significant role in the diet of Indian consumers, the majority of whom are vegetarians by choice or by need. Vegetable consumption is expanding quickly due to this consistent vegetarianism and growing per capita income. For small holder farmers, who predominate in Indian agriculture, the rising demand for vegetables is thought to have a positive economic impact. More than half of the fruits and vegetables are produced on small holdings, which make up 78% of all holdings and 33% of the total area. Due to the labor-intensive nature of vegetable growing and the abundance of labour available to smallholders, they have a unique advantage over larger farms. Also, because most vegetables have short harvest cycles, they offer returns throughout the year (Kundu and Mandal 2020). After China, India is the world's second-largest producer of vegetables. India produced 204.61 million metric tonnes of vegetables between 2021 and 2022. In 2021–2022, there was 11.28 million hectares of land under cultivation for vegetables. Indian vegetables are currently more commonly produced and exported. India exported fresh produce totalling US\$1527.60 million during 2021 and 2022, consisting of US\$ 767.01 million in vegetables (Anonymous, 2022). By 2030, there will likely be an increase in vegetable demand of up to 350 million tonnes.

Solanaceous vegetables are a significant subgroup of vegetables. Both brinjal (*Solanum melongena* L.) and chilli (*Capsicum annum* var. *annum* L.) are the main cash crops grown worldwide and belong to the family Solanaceae. The Asian eggplant (*S. melongena* L.), also known as brinjal in South Asia, aubergine in Europe, and Baigan in Hindi, is the fifth most significant solanaceous crop in terms of economic importance after potatoes, tomatoes, pepper and tobacco. One of the 35 crops included in Annex 1 of the International Convention on Plant Genetic Resources for Food and Agriculture, eggplant is considered to be one of the most vital crops for ensuring food security (Fowler et al. 2003). Brinjal is an important vegetable crop due to its nutritive, therapeutic and commercial value. As a result of its widespread availability at affordable prices, it is referred to as "the poor man's vegetable" (Wankhede and Kale 2010). It functions as an aphrodisiac, cardi tonic, laxative and anti-inflammatory in addition to being a tasty appetiser. Brinjal is widely cultivated all year long in India under diverse agro-climatic conditions on an area of 744 thousand ha with an annual

production of 12768 thousand MT (NHB 2022). It is grown on 1.01 thousand ha in Himachal Pradesh, with an annual production of 20.92 thousand MT (NHB 2022). The brinjal crop is infested by 26 insect pest species and a few non-insect pest species. Among all the pest species, major insect species includes, Jassid (*Amrasca biguttula biguttula* Ishida), aphids (*Aphis gossypii* Glover), whitefly (*Bemisia tabaci* Gennadius), shoot and fruit borer (*Leucinodes orbonalis* Guenee), Epilachna beetle (*Epilachna vigintioctopunctata* Fabricius) and grasshoppers and non-insect pest, red spider mite, *Tetranychus macfurlanei* (Andre) cause severe damage, necessitating initiation of control measures quite frequently (Vevai 1970).

Chilli (*Capsicum annum* var. *annum* L.), also known as hot pepper, chilli pepper, paprika, etc., is grown in India's tropical and subtropical regions (Anonymous 2013). It is cultivated all year long as a commercial crop and used as green. The secondary metabolites in chillies, such as capsaicin, give them their strong flavour (Anonymous 2018). Capsaicin, protein, fixed oil, thiamine and ascorbic acid are the components of chillies that have a medicinal impact (Pawar et al. 2011). Chillies are rich in potassium, magnesium, and iron. The top exporters of chilli are India (25%), China (24%), Spain (17%), Mexico (8%), Pakistan (7.2%), Morocco (7%) and Turkey (4.5%), with a percentage of global exports (Gopal et al. 2018). In India, chilli covers over 400 thousand ha and produces 4221 thousand MT, while in Himachal Pradesh it covers over 1.14 thousand ha with a production of 13.48 thousand MT (NHB 2022). India is the world's greatest producer of chillies, but due to a number of factors the most devastating of which are insect and mite pests its output pattern is extremely irregular (Thamburaj and Singh 2005; Tatagar et al. 2009). On chillies, there are about 35 types of insect pests, including thrips, aphids, whiteflies, fruit borer, cutworm, plant bugs, mites and other minor pests (Sorensen 2005). The most important among these are aphids (*Myzus persicae* Sulzer, *Aphis gossypii* Glover), thrips (*Scirtothrips dorsalis* Hood), yellow mite (*Polyphagotarsonemus latus* Banks) and fruit borer (*Helicoverpa armigera* Hubner) (Puttarudraiah 1959; Solanki and Rai 2006).

For managing the insect pests different methods have been used, however, to keep the pest population below economic injury level (EIL), use of pesticides seems to be the only remedy. The present agricultural scenario in India indicates that it is very difficult to manage insect pests without use of chemical pesticides. Also many farmers rely upon the chemical control to manage various insect pests in the field. Since, Central Insecticides Board (CIB)

approved many pesticides to manage insect pests of both crops like in brinjal, chlorantraniliprole 18.5% SC and chlorpyrifos 20% EC are used against shoot and fruit borer, fenazaquin 10% EC for mites, fenvalerate 20% EC and spiromesifen 22.9% SC for aphids, mites, thrips and likewise in chilli, pesticides like cyantraniliprole 10.26% OD and flubendiamide 20% WG are recommended against fruit borer and thrips, imidacloprid 17.8% SL and spirotetramat 15.31% OD for aphids and thrips (CIBRC 2022) to manage insect pests. However, due to non-judicious and ongoing use of these chemicals resulted in reduced biodiversity of natural enemies, development of pest resistance to pesticides, secondary pest outbreaks, resurgence of pests, residues in soils and risk to human health hazards (Desmarchelier 1985; Devi et al. 1986; Fishwick 1988; Bhaduri et al. 1989). For this reason, many authorized organizations, such as the FAO/WHO (Codex Alimentarius), European Union (EU), FSSAI (Food Safety and Standards Authority of India) have established maximum residue limits (MRLs) to control these residues. Due to variations in climatic conditions, soil types, crop types, spray doses, the pest resistance rates to these pesticides change. As a result researchers had to conduct intensive and continuous studies to monitor the residues of these pesticides.

Chemical characteristics of pesticides affect human health all around the world, their residue levels in food products are a significant cause for worry. It is known that exposure to pesticide residues in food and their presence in the environment have an impact on genetic polymorphism and encourage the onset of illnesses (Zhu et al. 2018). Studies have also shown that detrimental effects from repeated exposure to pesticide residues are far more serious than those from a single dose (Moser et al. 2005). Pesticide toxicity can result in a variety of conditions, including dyslipidemia, diabetes, liver, kidney and cardiovascular illnesses (Aramjoo et al. 2021). Government authorities have often campaigned for the development of regulations governing pesticide residues in food products (Xu et al. 2012). MRLs defined by the Codex Alimentarius Commission, the European Union, and other nations throughout the world are largely used to quantify potential dietary exposure to pesticide residues (Zentai et al. 2016). The results of residue analysis from food monitoring programmes can be crucial in ensuring that laws and best agricultural practises are followed (Blankson et al. 2016). According to studies, 30% of all fruits and vegetables consumed are often tainted with pesticides (WHO 2003; Quijano et al. 2016). While research has been done on pesticide residue analyses throughout the globe, to the best of our knowledge, limited research has been done on the health risks associated with these residues in different age

groups in India. The findings of these researches may help to determine the level of possible health risk posed by pesticide residues in the general population. In order to limit the use of pesticides and protect the public health, regulatory agencies can utilise these findings to develop corrective actions that will reduce the percolation of pesticide residues among ingested fruits and vegetables.

So, keeping these points in view, the present investigation was carried out to evaluate the bioefficacy of pesticides recommended by CIBRC (Central Insecticide Board and Registration Committee) on brinjal and chilli crops, their persistence on crops under the mid-hill conditions of Himachal Pradesh. Therefore, the present studies were undertaken to generate bioefficacy, validation, persistence and dietary risk assessment data for some pesticides on brinjal and chilli with following objectives:

OBJECTIVES:

- i) To study the bioefficacy of some pesticides against major insect pests of brinjal and chilli.
- ii) To validate the analytical method (QuEChERS) for estimation of pesticide residues on brinjal and chilli.
- iii) To study the persistence and dietary risk assessment of validated pesticides in/on brinjal and chilli.

Chapter-2

REVIEW OF LITERATURE

The following sections summarise the literature on many aspects and parameters of the current study, "Bioefficacy and residue dynamics of some pesticides used against insect pests of brinjal and chilli," both in India and abroad:

- 1) General information of pesticides
- 2) Bioefficacy study of pesticides in brinjal
- 3) Bioefficacy study of pesticides in chilli
- 4) Validation of an analytical method
- 5) Persistence studies on crop and soil
- 6) Risk assessment

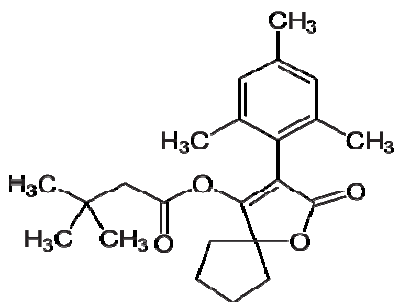
1 General information of pesticide

1.1 Spiromesifen

1.1.1 General information of pesticide

The novel non-systemic insecticide spiromesifen was developed by Bayer Crop Science in the 1990s and is a member of the new chemical class of tetronic acid derivatives. It was approved in 2006 for use on crops like okra, tomato and chilli against whiteflies (*Bemisia* spp., *Trialeurodes* spp.), as well as mites (Bedford et al. 1994). Due to its distinctive structure, it is an effective tool for managing resistance in various cropping systems, including cotton, tea, vegetables, fruits and ornamentals (Nauen et al. 2002). It is a lipid biosynthesis inhibitor (Dekeyser 2005).

1.1.2 Chemical designation



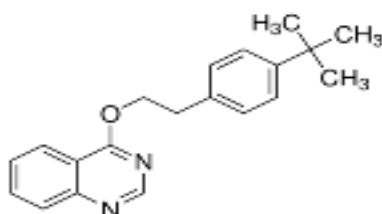
IUPAC name	[2-oxo-3-(2,4,6-trimethylphenyl)-1-oxaspiro[4,4]non-3-en-4-yl]3,3 dimethylbutanoate
Trade name	Oberon, Forbid
Molecular formula	C ₂₃ H ₃₀ O ₄
Molecular weight	370.489 g/mol
Formulation	Suspension concentrate
Application type	Foliar spray

1.2 Fenazaquin

1.2.1 General information of pesticide

Fenazaquin is a non-systemic acaricidal chemical which belongs to the quinazoline class of substances and is highly effective at preventing phytophagous mite infestations in a variety of crops, including fruits and vegetables (Solomon et al. 1993). The fenazaquin works by disrupting the biochemistry of insect mitochondria by ingestion and cutaneous contact (EPA 2007). In laboratory and field studies, fenazaquin exhibits high contact action against tetranychid and eriophid mites (Dreikorn et al. 1991; Shanker et al. 2001). It is intended for managing mites that infest a number of crops, including citrus fruits, pears and apples. It possesses significant ovicidal activity in addition to having good knockdown effect on motile forms (Anonymous 2017).

1.2.2 Chemical designation



Common name	Fenazaquin
IUPAC name	4-[2-(4-tert-butylphenyl)ethoxy]quinazoline
Trade name	Magister, Pride
Molecular formula	C ₂₀ H ₂₂ N ₂ O
Molecular weight	306.4 g/mol
Formulation	Emulsifiable concentrate, suspension concentrate

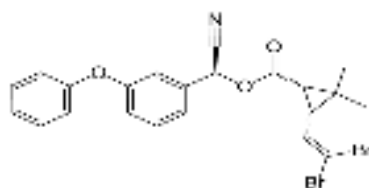
1.3 Chlorantraniliprole

1.3.1 General information of pesticide

Chlorantraniliprole, a plant systemic insecticide belongs to group anthranilic diamide with a unique mode of action called ryanodine receptor activators that disrupt normal muscle

function (Lahm et al. 2007). Primary activity of chlorantraniliprole is through ingestion with some contact toxicity against Lepidopteran pests but also against Orthoptera, Coleoptera, Diptera and Hemiptera pests (Hannig et al. 2009). With exceptional insecticide efficacy, high intrinsic activity on different life stages of insects, no cross-resistance to any current insecticide, low mammalian toxicity, good larvicidal properties and excellent protection profile for honeybees and other beneficial pollinators, arthropods, soil microorganisms and earthworms (Dinter et al. 2018).

1.3.2 Chemical designation



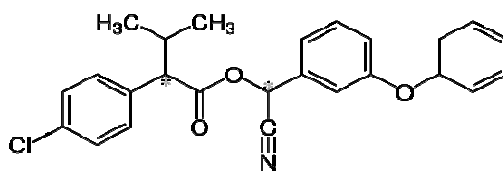
Common name	Chlorantraniliprole
IUPAC name	5-bromo- <i>N</i> -[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-2-(3-chloropyridin-2-yl) pyrazole-3-carboxamide
Trade name	Acelepryn, Coragen, DuPont E2Y45 SC, Altacot, Ferterra, Prevathon
Molecular formula	C ₁₈ H ₁₄ BrCl ₂ N ₅ O ₂
Molecular weight	483.1 g/mol
Formulation	Flowable concentrate for seed treatment, granule, suspension concentrate, water dispersible granule.

1.4 Fenvalerate

1.4.1 General information of pesticide

Fenvalerate belongs to a pyrethroid class of insecticides and used to combat a variety of insect pest species, such as caterpillars, sucking insects, flies, leaf-eating insects, fleas, bollworms and scale insects in different agricultural crops (FAO 1996) including strains resistant to organochlorine, organophosphorus and carbamate insecticides (Worthing and Walker 1987). Almost 90% of the chemical is used in cotton and also applied to a variety of other crops, including vines, tomatoes, potatoes, pome fruit and a wide range of other crops (WHO 1990). It is also employed in the fields of public health and animal husbandry, such as for management of flies in cow barns (Worthing and Walker 1987). It works by interfering with sodium ion (Na⁺) permeability in activated nerve membranes, which affects both the peripheral and central nervous systems. Fenvalerate can enter the body through the skin, lungs, or digestive system (FAO 1996).

1.4.2 Chemical designation



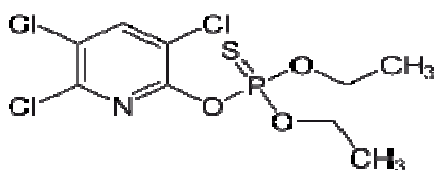
Common Name	: Fenvalerate
IUPAC name	: cyano (3-phenoxyphenyl) methyl 4-chloro-(1-methylethyl) benzene acetate
Molecular formula	: C ₂₅ H ₂₂ ClNO ₃
Trade name	: Sumicidin, Pydrin
Molecular weight	: 419.9 g/mol

1.5 Chlorpyrifos

1.5.1 General information of pesticide

Chlorpyrifos, an organophosphorothionate, is utilised as an effective insecticide all over the world because of its affordable price and broad-spectrum activity compared to other products (Testai et al. 2010). The Dow Chemical Co. released it in 1965 under the trade names "Dursban" and "Lorsban," as well as the code number "DOWCO 179". It is effective by contact, ingestion and vapours action and has a wide range of insecticidal activity and is used to control cockroaches, fleas, ticks on cattle and pests in animal homes, it has been widely employed in agriculture and forestry on a variety of crops and in residential and non-residential applications (Testai et al. 2010).

1.5.2 Chemical designation



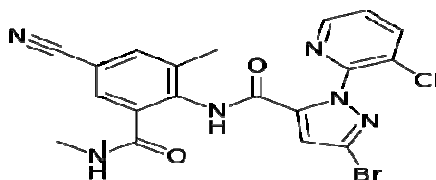
IUPAC name	diethoxy-sulfanylidene-(3,5,6-trichloropyridin-2-yl) oxy-λ ⁵ -phosphane
Trade name	Oberon , Forbid
Molecular formula	C ₉ H ₁₁ Cl ₃ NO ₃ PS
Molecular weight	350.6 g/mol
Formulation	Suspension concentrate
Application type	Foliar spray

1.6 Cyantraniliprole

1.6.1 General information of pesticide

The class of insecticides known as bisamide includes cyantraniliprole which is a systemic insecticide that is active through contact and ingestion, with ingestion having greater potency. As part of a "Global Joint Review" project, the regulatory authorities of France, the UK, Canada and Australia worked together to evaluate cyantraniliprole. A ryanodine receptor (RyR) modulator, it kills insects by causing uncontrolled RyR activation. Exposure to it causes drowsiness, paralysis and eventually death in insects. It is a broad-spectrum insecticide approved by the EPA for use against insects with mandibulate and piercing-sucking mouthparts. The use of cyantraniliprole on turf, oilseed crops, bush berries and vegetables is authorised (Anonymous 2014).

1.6.2 Chemical designation



IUPAC name	5-bromo-2-(3-chloropyridin-2-yl)-N-[4-cyano-2-methyl-6-(methylcarbamoyl)phenyl]pyrazole-3-carboxamide
Trade name	Benevia, Cyazypyr, Exirel, Verimark, Spinner
Molecular formula	C ₁₉ H ₁₄ BrClN ₆ O ₂
Molecular weight	473.7 g/mol
Formulation	Liquid, granular, granular bait
Application type	Foliar spray

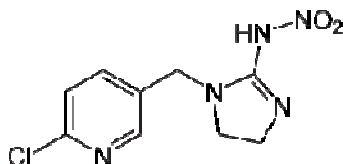
1.7 Imidacloprid

1.7.1 General information of pesticide

In 1984, Nihon Bayer Agrochem chemists made the discovery of imidacloprid while introducing a 3-pyridimethyl group to the nitromethylene heterocycle (Shiokawa et al. 1986). In France, sugar beet received imidacloprid initial registration in 1991 (Sur and Stork 2003; Nauen et al. 1998). The first synthetic neonicotinoid insecticide used to combat sucking pests like aphids, thrips, whiteflies and leaf hoppers (Leicht 1993). Imidacloprid affects various

types of post-synaptic nicotinic acetylcholine receptors in the neurological system (Buckingham et al. 1997). Similar effects are produced by imidacloprid on both target and non-target beneficial insects (Fossen 2006). Imidacloprid has the ability to allow residues to enter treated plants, travel through the plant via xylem transport and then migrate translaminarily (between leaf surfaces) (Buchholz and Nauen 2002).

1.7.2 Chemical designation



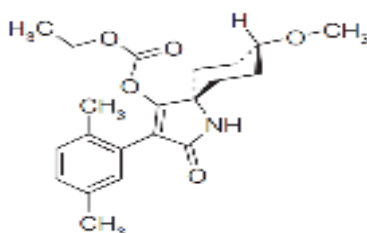
IUPAC name	1-(6-chloro-3-pyridylmethyl)-Nnitroimidazolidin-2-ylideneamine
Trade name	Admire, Advantage, Gaucho, Merit, Confidor, Premise, Provado
Molecular formula	C ₉ H ₁₀ ClN ₅ O ₂
Molecular weight	255.7 g/mol
Formulation	Granules, wettable powder

1.8 Spirotetramat

1.8.1 General information of pesticide

Spirotetramat is a broad-spectrum systemic insecticide that is used on a variety of agricultural crops to suppress sucking pests. It is a member of the chemical family of keto enols, subclass tetramic acid derivatives. When acetyl CoA carboxylase is inhibited, its pesticidal method of action disrupts lipogenesis. It is a good trans laminar insecticide that is ambi-mobile (Bruck et al. 2009).

1.8.2 Chemical designation



IUPAC name	Cis-3-(2,5-Xylyl)-4-(ethoxycarbonyloxy)-8-methoxy-1- azaspiro [4.5] dec-3-en-2-one
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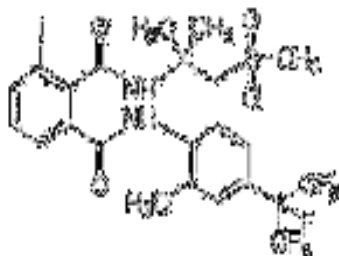
Trade name	Movento, Ultor, Kontos
Molecular formula	C ₂₁ H ₂₇ NO ₅
Molecular weight	373.45 g/mol
Formulation	OD, SC
Application type	Foliar spray

1.9 Flubendiamide

1.9.1 General information of pesticide

The first benzene dicarboxamide or phthalic acid diamide insecticide, flubendiamide, was developed in collaboration with Bayer Crop Science after being discovered by Nihon Nohyaku (Mate et al. 2014). The substance has a novel method of action and is a new pesticide with great activity against a variety of lepidopteran insects (Ebbinghaus et al. 2007). It mostly affects insects by ingestion, where it opens ryanodine-sensitive intracellular calcium release channels (ryanodine receptors) (Ebbinghaus et al. 2007; Masaki et al. 2006). Flubendiamide has no ovicidal activity, although it is most effective on larvae than adults. Lepidopteran pests, including resistant strains, are mostly controlled by flubendiamide in rice, cotton, corn, grapes and other fruits and vegetables (Tohnishi et al. 2005; Masaki et al. 2006).

1.9.2 Chemical designation



IUPAC name 1-N-[4-(1,1,2,3,3,3-heptafluoropropan-2-yl)-2-methylphenyl]-3-iodo-2-N-(2-methyl-1-methylsulfonylpropan-2-yl)benzene-1,2-dicarboxamide

Trade name	Belt, Fame
Molecular formula	C ₂₃ H ₂₂ F ₇ IN ₂ O ₄ S
Molecular weight	682.4 g/mol
Formulation	SC, WG
Application type	Foliar spray

2. Bioefficacy study of pesticides in brinjal

2.1 Efficacy of selective insecticides against shoot and fruit borer

Brinjal (*Solanum melongena* L.) is attacked by more than 25 insect pests (Patil and Mehta 2008) of which brinjal shoot and fruit borer, *L. orbonalis* is the most destructive one. The shoot and fruit borer inflicting yield losses as high as 85-90 per cent (Jagginavar et al. 2009) has now been considered as the key pest of brinjal (Latif et al. 2010). Many traditional pesticides are used against this pest with new emerging pesticides like chlorantraniliprole with higher efficiency. Many workers have studied the efficacy of these pesticides against shoot and fruit borer and are mentioned below:

According to Bhandarkar and Borle (1980), the brinjal fruit borer can be controlled with the help of fenvalerate (0.04%), phenthoate, quinalphos and monocrotophos (all at 0.05%). When compared to other pesticides, fenvalerate (0.01, 0.02 and 0.15%) and carbaryl (0.15%) were effective at controlling shoot and fruit borer. In order to inhibit *L. orbonalis* larvae, Tiwari et al. (1984) tested the effectiveness of fenvalerate (@ 30, 50 and 70 g a.i/ha) and cypermethrin (@15, 22.5 and 30 g a.i/ha) at intervals of 15, 20 and 25 days. They came to the conclusion that both insecticides were quite successful at controlling pests, especially when used sparingly and continuously. In another study conducted by Mehta et al. (1998) on effectiveness of the insecticides such as malathion (0.05%), endosulfan (0.07%), deltamethrin (0.08%), fenvalerate (0.01%), monocrotophos (0.036%) and fenitrothion (0.05%) against *L. orbonalis*, resulted in least amount of fruit damage by fenvalerate (6.09 % on a weight basis and 6.38 % on a number basis).

Reddy and Srinivasa (2005) conducted a field trial to assess various insecticides, including a brand-new chemical for the management of the *L. orbonalis*. The results showed that endosulfan (0.07%), was equally as efficient against both shoot and fruit borer on brinjal as quinalphos and carbofuran at 0.07% and 0.05%, respectively further followed by chlorpyrifos.

The insecticides flubendiamide 480 SC and chlorantraniliprole 20% SC were evaluated by Misra (2008) against brinjal shoot and fruit borer. The results showed that after the fourth spray, chlorantraniliprole 20% SC at 40 and 50 g a.i./ha reduced shoot damage and fruit damage by 95–97 and 87–90 per cent, respectively. On plots treated with chlorantraniliprole 20 SC @ 40 and 50 g a.i./ha, the healthy fruit yield was noticeably

highest. Varma et al. (2009) evaluated efficacy of different pesticides against brinjal shoot and fruit borer and observed that fruit infestation and weight loss in brinjal fruit vary from 3.76 to 45.45 per cent and 3.00 to 67.71 per cent in 1st year and 5.71 to 44.26 per cent and 3.00 to 51.33 per cent in 2nd year, respectively. Among all the treatments used chlorpyrifos showed the minimum infestation followed by NSKE (5%) and Nerium (10%). Sharma and Kaushik (2010) evaluated efficacy of spinosad 45 SC, emamectin benzoate 5 WSG, cypermethrin 10 EC, quinalphos 25 EC, endosulfan 35 EC, lambda cyhalothrin 5 EC, chlorpyrifos 20 EC against shoot and fruit borer and also against natural enemies (ladybird beetles) on eggplant. In contrast to chemical insecticides, which proved toxic to natural enemies, spinosad @ 162.5 ml/ha was found to be the most effective treatment for shoot and fruit borer, resulting in the least amount of damage to shoots, flower buds and fruit as well as the highest fruit yield and cost-benefit ratio.

At Kovilpatti, Tamil Nadu, Rajavel et al. (2011) evaluated the bio efficacy of chlorantraniliprole at various dosages, including 20 g a.i./ha, 30 g a.i./ha, 40 g a.i./ha, 50 g a.i./ha and 60 g a.i./ha. They came to the conclusion that chlorantraniliprole 20 SC @ 60 g a.i./ha resulted in 21.32 and 4.99 per cent reduction in brinjal shoot and fruit infestation followed by application of 50 g a.i./ha with 22.18 (shoot infestation) and 5.43 per cent (fruit infestation) with yield of 13.22 t/ha and 12.73 t/ha, respectively. In another field experiment against the brinjal fruit and shoot borer, Dattatray et al. (2012) studied the effectiveness of newer insecticides, including chlorantraniliprole 18.5% SC, flubendiamide 39.35% SC, indoxacarb 14.5% SC, chlorfenapyr 10% SC and spinosad 45% SC. They found that chlorantraniliprole 18.5% SC was superior to other treatments, recording the lowest shoot (8.20%) and fruit (8.24 % and 8.41 % both on number and weight basis) infestation with the highest marketable fruit yield of 492.87 q/ha. Similar studies were conducted by Shirale et al. (2012) to evaluate the efficacy of chlorantraniliprole 18.50% SC (Coragen), flubendiamide 39.35% SC (Fame), indoxacarb 14.50% SC (Avaunt), chlorfenapyr 10% SC (Intrepid) and spinosad 45% SC (Spintor) against brinjal fruit and shoot borer, *Leucinodes orbonalis* (Guenee) and concluded that chlorantraniliprole 18.5% SC showed minimum shoot infestation of 8.20 per cent followed by flubendiamide 39.35% SC (9.44%). Chlorantraniliprole 18.50% SC treatment caused the least amount of fruit damage of 8.84 (number basis) and 8.41 per cent (weight basis), which was much less than the next-best treatment, flubendiamide 39.35% SC, which caused 10.92 and 10.40 per cent (number and weight basis) of fruit damage. In comparison to the plots treated with other pesticides, the

chlorantraniliprole 18.50% SC sprayed plots produced noticeably greater yields of 528.52 q/ha. In comparison to the output of 231.41 q/ha in the plots sprayed with traditional insecticide (Endosulfan 35% EC) and 141.88 q/ha in untreated plots, the marketable yield ranged from 355.04 to 492.87 q/ha in the plots sprayed with next generation insecticides. Similarly, Kameshwaran and Kumar (2015) also observed that chlorantraniliprole @ 40 g a.i./ha showed lowest shoot infestation of 2.02, 1.69, 3.52 and 3.40 per cent after 1st, 2nd, 3rd and 4th spray at 14 days after treatment, respectively followed by emamectin benzoate. The treatment with chlorantraniliprole 20 SC @ 40 g a.i./ha resulted in a low per cent of fruit infestation (number basis), ranging from 6.29 to 10.46 per cent in all five pickings, followed by emamectin benzoate 25 WG @ 11 g a.i./ha (10.71 to 16.66%) and outperforming the untreated control (31.63 to 38.25%). In comparison to the untreated control, which ranged from 31.56 to 39.25 per cent, the fruit infestation was low in the treatment with chlorantraniliprole 20 SC @ 40 g a.i./ha, with a range of 7.29 to 11.46 per cent, followed by emamectin benzoate 25 WG @ 11.71 g a.i./ha (11.71 to 15.66 per cent). The highest yield was observed in the treatment with chlorantraniliprole 20 SC @ 40 g a.i./ha (27.08 t/ha) with maximum benefit cost ratio (1:21.58) followed by emamectin benzoate 25 WG @ 11 g a.i./ha (23.61 t/ha) (1:18.52).

Another study on efficacy of different insecticide was conducted by Devi et al. (2014) at Raipur, India with seven insecticides i.e. spinosad @ 160 ml/ha, profenophos @ 1000 ml/ha, chlorantraniliprole @ 400 ml/ha, deltamethrin 1 % + triazophos @ 2000 ml/ha, emamectin benzoate @ 125 g/ha, acephate @ 666.66 g/ha and carbosulfan @ 875 ml/ha. A result showed that chlorantraniliprole 20 % EC @ 400 ml/ha was most effective in reducing shoot and fruit infestation with 8.58 and 8.88 per cent, respectively. The effectiveness of chlorantraniliprole along with other insecticides viz., abamectin @ 1.5 ml/l, emamectin benzoate @ 0.3 g/l, spinosad @ 0.25 ml/lit, karanjin @ 2 ml/l, Borer gourd (*Bacillus thuringiensis* var. *Kurstaki* 108 CFU/ml + *Beauveria bassiana* 108 CFU/ml + *Verticillium lecanii* 108 CFU/ml + *Metarhizium anisopliae* 108CFU/ml) @ 2 ml/l and tobramycin (tozen) @ 0.33 ml/lit was evaluated by Mainali et al. (2015) at Khumaltar, Nepal. The study revealed that chlorantraniliprole with shoot infestation of 6.57 per cent and fruit infestation of 6.31 per cent along with spinosad with 12.08 and 11.15 per cent infestation proved to be most effective among all the treatments, respectively. Maximum brinjal fruit yield was recorded in plots treated with chlorantraniliprole (32.03 Mt/ha) followed by spinosad (30.93 Mt/ha) with 34.39 per cent and 29.77 per cent increase in marketable fruit yield over untreated check,

respectively. Bioefficacy of spinosad, emamectin benzoate, chlorpyrifos, profenofos, fenvalerate and cypermethrin were evaluated in the field in comparison to a control. Emamectin benzoate (40.1%), followed by cypermethrin (40.43%) was most effective against the brinjal fruit borer and caused a reduced infestation, while fenvalerate provided intermediate control (41.31%) of borer (Anwar et al. 2015).

Raina et al. (2016) evaluated bioefficacy studies on five foliar sprays of insecticides viz., cypermethrin 25EC @ 43.75 g a.i/ ha, fenvalerate 20EC @ 40 g a.i/ ha, deltamethrin 2.8EC @ 14 g a.i/ ha, chlorpyrifos 20EC @ 200 g a.i/ ha, fenprothrin 15 EC+ pyriproxyfen 5 EC @ 150 g a.i/ ha, malathion 50EC @ 250 g a.i/ ha and nimbecidine 0.03% @ 3 ml/l against shoot and fruit borer of brinjal. Results revealed that deltamethrin proved most effective in reducing shoot damage (60.40%) over control followed by fenvalerate (50.90%), cypermethrin (50.30%), chlorpyrifos (49.85%), fenprothrin 15 EC+ pyriproxyfen 5 EC (49.47%), malathion (43.96%) and nimbecidine (28.88%). Highest per cent reduction over control in fruit infestation on number and weight basis was found in case of deltamethrin (88.87% and 88.89%) followed by fenvalerate (82.82% and 83.32%) and other treatments. Among all the treatments deltamethrin proved to be the best in producing highest marketable yield (132.37 q/ ha) with highest cost benefit ratio of (1:8.7) followed by fenvalerate (110.60 q/ha) (1:8.5).

Niranjana et al. (2017) evaluated efficacy of chlorantraniliprole with other insecticides against shoot and fruit borer of brinjal at Coimbatore, Tamil Nadu and revealed that chlorantraniliprole 18.5 % SC was superior over all other treatments with 15.40 and 9.90 per cent of shoot and fruit infestation with highest marketable yield (1890 kg/ha) in brinjal. On the other side, Kushwaha and Painkra (2016) performed a field trial at Allahabad, to check the efficacy of chlorantraniliprole 20 % SC (0.006 %) alongside with other treatments and found that chlorantraniliprole was the most effective treatment in reducing the attack caused by the borer in brinjal with 2.98 per cent of shoot and 3.26 per cent of fruit infestation and cost benefit ratio of 1:5.48, respectively. The bioefficacy study of chlorantraniliprole 18.5 % SC (0.4 ml/l) with other insecticides viz., chlorfenapyr 10 % SC (2 ml/l), indoxacarb 14.5 SC % (1 ml/l), spinosad 45 % SC (0.5 ml/l), chlorpyrifos 20 % EC (2.5 ml/l), *Bacillus thuringiensis* (Bt) (2 g/l), *Metarhizium anisoplae* (2.5 g/l), azadirachtin 0.03 % EC (5 ml/l) and *Beauveria bassiana* (2.5 g/l) at Umiam, Meghalaya, were carried out by Tripura et al. (2017) to check the effectiveness of the insecticides against

shoot and fruit borer of brinjal and documented that chlorantraniliprole showed minimum shoot infestation of 6.32 per cent and fruit infestation of 8.52 per cent with a highest yield of 250.30 q/ha.

Khanzada et al. (2018) conducted study on the effectiveness of chlorantraniliprole 18.5 SC (0.002 %) along with other insecticides, viz., indoxacarb 14.5 SC (0.002 %), emamectin benzoate 5 SG (0.002 %), cartap hydrochloride 50 SP (0.05 %), spinosad 45 SC (0.01 %), acephate 75 SP (0.05%) and malathion 50 EC (0.05 %). The results revealed that chlorantraniliprole (0.002 %) was most superior in reducing shoot infestation (8.25 %) and fruit infestation on number basis (5.95 %) and on weight basis (5.5 %) respectively. Vinayaka et al. (2019) when chlorantraniliprole alongside with other insecticides viz., emamectin benzoate 5 % SG, azadirachtin 5 % EC, pyriproxyfen 5 % EC + fenpropathrin 15 % EC, lambda cyhalothrin 5% EC, *Bacillus thuringiensis* 5 % WP and spinosad 45% SC were evaluated against brinjal shoot and fruit borer, the results showed that chlorantraniliprole 18.5% SC was most effective in reducing the infestation caused by borer by 13.63, 23.21 and 22.83 per cent after 1st, 2nd and 3rd spray with a yield of 20.69 t/ha, respectively.

Dey et al. (2019) check the effectiveness of chlorpyrifos at different concentration @ 750, 1000 and 2000 ml/ha against brinjal shoot and fruit borer and revealed that chlorpyrifos @ 2000 ml/ha showed highest mean shoot reduction over control by 65.95, 69.15 and 68.90 per cent with lowest fruit infestation (weight basis) of 8.65, 8.4 and 8.75 per cent after 1st, 2nd and 3rd spray, respectively. The highest yield of 17.46 t/ha was also obtained from the treatment chlorpyrifos @ 2000 ml/ha.

Narayan et al. (2019b) conducted a field trial on bioefficacy of cyantraniliprole 10.26% OD (0.0143%), fenpropathrin 30% EC (0.0204%), flubendiamide 39.36 SC (0.0098%), cartaphydrochloride 75% SG (0.075%), emamectin benzoate 5% SG (0.002%), lambda cyhalothrin 5% EC (0.003%) and chlorantraniliprole 18.5% SC (0.0074%) against shoot and fruit borer of brinjal and revealed that among all the pesticides used in the trial chlorantraniliprole 18.5% SC (0.0074%) showed lowest shoot infestation of 6.21, 5.27 and 5.50 per cent followed by cyantraniliprole 10.26% OD, emamectin benzoate 5% SG and flubendiamide 39.36% SC after first, second and third spray at 14 DAT (days after treatment), respectively. In case of fruit damage (number basis), chlorantraniliprole 18.5% SC showed significantly minimum per cent fruit damage ranged from 10.58 to 14.64 per cent in three pickings followed by cyantraniliprole 10.26% OD, emamectin benzoate 5% SG and

remaining all insecticidal treatments as compared to untreated control. On weight basis, the minimum per cent fruit infestation was observed in the treatment chlorantraniliprole 18.5% SC ranged from 8.65 to 10.22 per cent followed by cyantraniliprole 10.26% OD and emamectin benzoate 5% SG. The highest marketable yield was also recorded from the plots treated with chlorantraniliprole 18.5% SC (68.38 q/ha) followed by cyantraniliprole 10.26% OD (63.04 q/ha) and emamectin benzoate 5% SG (60.49 q/ha) treated plot which found superior over untreated control (30.17 qt/ha).

2.2 Efficacy of selective insecticides against jassids

In a field study conducted by Shaikh and Patel (2012) bioefficacy of nine different insecticides (imidacloprid 0.002%, diafenthiuron 0.05%, profenophos 0.05%, triazophos 0.08%, cartap hydrochloride 0.05%, thiacloprid 0.012%, clothianidin 0.025%, thiamethoxam 0.025% and spiromesifen 0.024%) against jassid in brinjal was evaluated. The data on pooled over sprays revealed that thiamethoxam (2.78 jassid per leaf) recorded significantly lower jassid population than rest of the treatments, except diafenthiuron (3.00 jassid per leaf) and thiacloprid (3.42 jassid per leaf), with which it was at par. Diafenthiuron also found significantly effective in reducing the jassid population than rest of the insecticides except thiacloprid (3.42 jassid per leaf) and profenophos (3.95 jassid per leaf), with which it was at par. Imidacloprid (4.74 jassid per leaf) was at par with clothianidin (4.47 jassid per leaf) and profenophos (3.95 jassid per leaf) on one hand and with cartap hydrochloride (5.40 jassid per leaf) on another hand of chronological order of effectiveness. Triazophos (7.28 jassid per leaf) and spiromesifen (7.23 jassid per leaf) recorded significantly higher jassid population among the insecticides tested and both were at par with each other. The bioefficacy of deltamethrin, imidacloprid and chlorantraniliprole against jassids, *A. biguttula biguttula* on brinjal at various intervals was investigated by Dahatonde et al. (2014). According to the results, imidacloprid 17.8 SL and chlorantraniliprole 18.5 both recorded the lowest jassid population (2.11 and 3.77 jassids/three leaves, respectively). As compared to imidacloprid and chlorantraniliprole, deltamethrin 2.8 EC at this specific concentration was shown to be less efficient against sucking pest of brinjal.

Kharade et al. (2018) conducted study on bioefficacy of imidacloprid (0.0044%), dimethoate (0.04%), quinalphos (0.05%), emamectin benzoate (0.002%), chlorantraniliprole (0.0074%) and indoxacarb (0.019%) against brinjal jassids and whitefly which revealed that imidacloprid was found most effective treatment in reducing the population of jassid (1.03

jassids/3 leaves) and whitefly (1.32 whiteflies/3 leaves) respectively. Followed by dimethoate 0.04 per cent (2.07 jassids/3 leaves) (2.57 whiteflies/3 leaves) which was found to be statistically at par with chlorantraniliprole 0.0074 per cent (2.35 jassids/3 leaves) (2.68 whiteflies/3 leaves).

Kharel et al. (2016) study bioefficacy of spiromesifen 240 SC @ 90, 120 and 150 g a.i./ha, diafenthiuron 50 WP @ 250 and 312 g a.i./ha and seed treatment with thiamethoxam 35 FS+ thiamethoxam 25 WG @ 3 g/kg seed + 25g a.i./ha with standard check of thiamethoxam 25 WG and triazophos 40 EC @ 25 and 40 g a.i./ha, respectively against sucking insect pests of green gram. The results of experiment revealed that diafenthiuron 50 WP @ 312 g a.i./ha was most promising treatment in reducing population of jassid (*Empoasca kerri*) (1.61 and 0.8 jassid/cage) after both sprays followed by spiromesifen 240 SC @ 150g a.i./ha (jassids- 2.12 and 1.30/cage) as compared to standard checks.

Singh et al. (2019a) investigated the relative effectiveness of several pesticides against the jassids (*Empoasca kerri*) and whiteflies (*Bemisia tabaci*) of green gram. Eight pesticides were evaluated for their efficiency against the insect pest of green gram and the results showed that acetamiprid (0.004%; 75.46%), imidacloprid (0.005%; 74.30%) and fipronil (0.01%; 73.24%) were the most successful. The treatments of thiamethoxam (0.005%) (64.37%) and dimethoate (0.03%) (62.18%) stood in the middle order of efficacy and spiromesifen (0.001%) (58.28%) and fenpropathrin (0.05%) (60.48%) found to be least effective against insect pest of green gram. The use of acetamiprid resulted in a total avoidable loss and per cent avoidable loss of zero (0.04%), whereas the use of spiromesifen after a second spray resulted in a maximum avoidable loss of 0.001%.

Vikas (2020) also conducted a study on bioefficacy of different pesticides against jassids in brinjal and revealed that the plots treated with chlorpyrifos @ 200 g a.i./ha recorded 62.63, 69.84 and 76.30 per cent reduction in the population of jassids after 1st, 2nd and 3rd spray, respectively. The bioefficacy study against soybean jassids was explored by Bhamare et al. (2021) with different insecticides viz., ethion (0.100%), chlorantraniliprole (0.004%), emamectin benzoate (0.001%), indoxacarb (0.010%), triazophos (0.050%), quinalphos (0.050%) and profenophos (0.100%). Profenophos (0.100%) was the most successful treatment for reducing the number of jassids (3.83 and 2.60 jassids per three leaves), followed by quinalphos (0.050%) (4.03 and 2.90 jassids per three leaves), triazophos (0.050%) (4.47 and 3.50 jassids per three leaves), chlorantraniliprole (0.004%) (5.03 and 3.60

jassids per three leaves), indoxacarb (0.010%) (7.20 and 5.00 jassids per three leaves), emamectin benzoate (0.001%) (7.40 and 5.40 jassids per three leaves) and ethion 0.100 per cent (7.67 and 5.50 jassids per three leaves) after first and second sprays, respectively. Chlorantraniliprole at 0.004 % (34.87 q/ha) had the best grain yield and quinalphos at 0.050 % (1:19.72) had the highest incremental cost-benefit ratio.

Choudhary et al. (2022b) studied relative efficacy of twelve insecticides, viz., pyriproxyfen 10.8 EC (0.005%), buprofezin 25 SC (0.04%), vertimec 1.9 EC (9.5 mg/l), diafenthiuron 50 WP (0.05%), chlorfenapyr 10 SC (0.01%), emamectin benzoate 5 SG (0.005%), chlorantraniliprole 18.5 SC (0.005%), pymetrozine 50 WG (0.025%), flubendiamide 39.35 EC (0.01%), pyridalyl 10 EC (0.015%), bifenthrin 10 EC (0.016%) and dimethoate 30 EC (0.03%) against leafhopper, *Empoasca fabae* (Harris), aphid, *Aphis craccivora* Koch and whitefly, *Bemisia tabaci* (Genn.) in Indian bean. The decrease in population showed that the most efficient leafhopper treatments were diafenthiuron 50 WP (92.90% reduction), dimethoate 30 EC (91.77% reduction) and chlorantraniliprole 18.5 SC (90.58% reduction). After three days following the first spray, the same pesticides showed a reduction in aphid population of 95.17, 94.60 and 94.04%, respectively. The most successful treatments for whiteflies were pyriproxyfen 10.8 EC (90.10% decrease), dimethoate 30 EC (92.04% reduction) and diafenthiuron 50 WP (93.60% reduction). The least effective treatments included pyridalyl 10 EC, vertimec 1.9 EC and pymetrozine 50 WG. The bioefficacy of 10 insecticides evaluated by Hithesh et al. (2022) against whiteflies, thrips and jassids in green gram showed that thiomethoxam + -cyhalothrin, imidacloprid and triazophos were the most successful in reducing the population of jassids, whiteflies and thrips. Whitefly and thrips populations subjected to imidacloprid killed off at rates of 14.3 and 13.5% till 18 DAS, respectively. The exposed pesticides' relative sustained toxicity was in the range of imidacloprid > thiomethoxam + λ -cyhalothrin > triazophos > flonicamid > λ -cyhalothrin > profenophos + cypermethrin > chlorantraniliprole > spinosad > profenophos.

2.3 Phytotoxicity and effect on non-target organisms

2.3.1 Phytotoxicity

In a study conducted by Fanigliulo et al. (2010) no phytotoxicity symptoms on leaves, flowers and fruits were recorded when two different doses of spiromesifen @ 45 and 60 g a.i./ha was applied on chilli for the management of mites and whitefly. Sangeetha and Ramaraju (2013) recorded that the treatment of fenazaquin @ 75, 100, 125 and 150 g a.i./ha did not show any phytotoxic symptom on okra when it was used for the management of two

spotted spider mite. Dey et al. (2019) who evaluated phytotoxic effect of chlorpyrifos 20EC on brinjal crop and observed that on interval of 1, 3, 7 10 and 15 days (after each spray) no phytotoxicity symptoms i.e. leaf injury, wilting, epinasty and hyponasty, necrosis, etc. were observed in all the treatments including higher dosages of chlorpyrifos 20% EC. Chlorantraniliprole (Coragen 18.5 SC) when applied at @ 100, 125 and 150 ml/ha against fruit borer in the chilli showed no phytotoxic symptoms to the crop (Randhawa et al. 2020). Halder et al. (2022) also supported these results when they reported no visible signs of phytotoxicity on brinjal when chlorantraniliprole @ 20, 40 and 80 g a.i./ha was applied for the management of brinjal shoot and fruit borer.

2.3.2 Effect on non-target organism

Natkar et al. (2016) found that comparatively lower beetle population was observed in plots treated with chlorpyrifos 20 EC @ 2.00 ml/l (0.19 coccinellids/ plant) in soyabean. According to Niranjana et al. (2017), chlorantraniliprole 18.5% SC was much more efficient than other insecticides at reducing the shoot and fruit borer infestation in brinjal farms while having the least negative effects on the natural enemies that were already present.

Dhamala et al. (2018) concluded from their study that populations of spiders and coccinellids in the brinjal and cabbage ecosystems were negatively impacted by chlorfenapyr and chlorpyrifos. In brinjal, chlorpyrifos at higher doses (400 g a.i./ha) was found to have the lowest mean spider population with 2.51 spiders per 5 plants, followed by the same insecticide at the recommended dose (200 g a.i./ha) with 2.74 spiders per 5 plants, whereas chlorfenapyr @ 200 and 100 g a.i./ha recorded 2.49 and 5.02 spiders per 5 plants. This concluded that greater doses of chlorpyrifos (78.65%) followed by recommended dose (75.44%) and higher doses of chlorfenapyr (32.74%) in brinjal were shown to have the highest per cent reduction of coccinellids. Khinchi and Kumawat (2021) who noticed that after spray of chlorantraniliprole 18.5% SC @ 100 ml/ha in field of soyabean the population of coccinellids increased by 4.73 to 6.93 coccinellids/plant at 7th and 14th day of 2nd spray after control.

3. Bioefficacy study of pesticides in chilli

3.1 Efficacy of selective insecticides against thrips

Seed treatment and root dip with imidacloprid 70 WS @ 10, 20 and 30 g/kg and foliar spray @ 250, 375 and 500 ml/ha was carried out to study the bioefficacy against thrips in chilli. It was noted that seeds treated with different dose of imidacloprid protected seedlings

from thrips attack upto 45 days also foliar spray of same chemical recorded higher reduction in thrips population with higher yield (Santharam et al. 2003). Another study at Agricultural Research Station, Hanumanamatti, was carried out by Prabhu et al. (2014) who evaluated efficacy of imidacloprid 17.8% SL against chilli thrips during rabi and summers during 2011 and 2012. Results revealed that imidacloprid @ 50 g a.i./ha resulted in a 25.07 per cent increase in green chilli yield and a reduction of 70.47 per cent thrips damage.

Kumawat et al. (2015) studied the bioefficacy of different insecticides viz., tolfenpyrad 15 EC @ 125 g a.i./ha, fipronil 5 SC @ 40 g a.i./ha, imidacloprid 17.8 SL @ 22.25 g a.i./ha, flubendiamide 480 SC @ 72 g a.i./ha, acephate 75 SP @ 585 g a.i./ha, novaluron 10 SC @ 75 g a.i./ha and buprofezin 25 SC @ 250 g a.i./ha against insect pests of chilli during 2012. The results showed that two sprays of imidacloprid 17.8 SL at 22.5 g a.i./ha at seven days interval were the most effective and significantly better than all other treatments, causing 91.05, 88.64 and 90.02 per cent mean reductions in aphid, whitefly and jassid population, respectively; however, two sprays of fipronil 5 SC at 40 g a.i./ha at seven days interval was most effective against thrips with 90.99 per cent reduction. The maximum marketable yield of chilli was substantially recorded with imidacloprid 17.8 SL at 22.5 g a.i./ha sprayed twice (117.08 q/ha). In another study conducted by Rana et al. (2016) on effectiveness of imidacloprid 350 SC (@100, 125 and 150 ml/ha) against sucking pests of chilli it was revealed that plots treated with imidacloprid 350 SC at 150 ml/ha was significantly superior over all treatments with per cent reduction of 68.81, 65.76 and 60.03 per cent and 80.82, 76.83 and 71.27 per cent at 3, 5 and 7 days after 1st and 2nd spray in 2013 and 69.84, 64.91 and 60.46 per cent and 81.76, 77.73 and 72.31 per cent reduction of thrips during 2014, respectively which was at par with imidacloprid 350 SC at 125 ml/ha whereas, least effectiveness was recorded in the plots treated with imidacloprid 200 SL at 250 ml/ha, imidacloprid 350 SC at 100 ml/ha and fipronil 5% SC at 800 ml/ha and were at par to each other.

Hosamani et al. (2016) also performed an efficacy trial against sucking pest of chilli. Treatments include imidacloprid at three doses i.e., @ 15 g a.i./ha, 50 g a.i./ha, 75 g a.i./ha, fipronil 5% SC @ 50 g a.i./ha, dimethoate 30% EC @ 600 g a.i./ha and untreated control. The results revealed that the highest per cent reduction of thrips (73.02%) and aphids (79.69%) over untreated control was found in the plots treated with imidacloprid @ 75 g a.i./ha whereas, imidacloprid @ 50 g a.i./ha recorded a reduction in thrips and aphid population with 70.63 and 77.40 per cent, respectively which was at par with imidacloprid @

50 g a.i./ha. The lowest per cent reduction of thrips (22.22%) and aphids (54.39%) was recorded in dimethoate 30% EC @ 600 g a.i./ha. In another study by Sathua et al. (2017) on efficacy of four different insecticides (acephate, imidacloprid, cypermethrin, dimethoate) and three botanicals (*Allium sativum* extract, *Allium cepa* extract and NSKE) against chilli thrips, it was revealed that plots treated with imidacloprid 17.8 SL and acephate 75 SP both significantly reduced the maximum thrips population by 82.46 and 80.86 per cent, respectively. Of all treatments, plots treated with imidacloprid 17.8 SL (45.42%) and cypermethrin 12.5 EC (38.15%) had the largest per cent increase in yield over control. Analyzing the C: B ratio for each treatment, it was discovered that imidacloprid 17.8 SL (1:16.66) had the highest ratio and dimethoate 0.03 EC had the lowest (1:7.39).

Sangle et al. (2017) evaluated bioefficacy study of seven insecticides against thrips and whitefly in chilli (variety GVC-111). Field results showed that among the different insecticides, imidacloprid 17.8 SL @ 0.005% (5.12 thrips/3 leaves and 0.96 whiteflies/leaf), acetamiprid 20 SP 0.004% (0.58 whiteflies/leaf) and triazophos 40 EC @ 0.04% (1.09 whiteflies/leaf) found most effective with a maximum yield in plots treated with imidacloprid (110.25 q/ha) followed by thiamethoxam (106.55 q/ha), triazophos (103.79 q/ha) and acetamiprid (102.91 q/ha) also highest cost benefit ratio was recorded in imidacloprid (1:23.17) followed by thiamethoxam (1:20.45), acetamiprid (1:19.60) and triazophos (1:17.69). Another study was performed by Mukade et al. (2018) in which efficacy of nine pesticides fipronil 5% SC @ 1000 ml/ha, spiromesifen 22.9% SC @ 400 ml/ha, buprofezin 25% SC @ 300 ml/ha, imidacloprid 17.8% SL @ 250 ml/ha, thiacloprid 21.7% SC @ 300 ml/ha, cyantraniliprole 10.26% OD @ 600 ml/ha, spinosad 45% SC @ 160 ml/ha, flonicamid 50% WG @ 200 g/ha and quinalphos 25% EC 1000 ml/ha was evaluated against thrips, whitefly and aphid on chilli. The results showed that plots treated with cyantraniliprole 10.26% OD @ 600 ml/ha was significantly superior over other treatments with higher yield of 5.45 t/ha. The highest ICBR (1:8.04) was obtained from the plots treated with imidacloprid 17.8% SL followed by thiacloprid 21.7% SC (1:7.54). Another study by Patil et al. (2018) on bioefficacy of different insecticides against the combined statistics make it clear that all insecticidal treatments had a big impact in reducing the thrips population. After two sprays, fipronil at 0.005% (3.30 thrips/leaf) and fenpropathrin at 0.03 % (3.78 thrips/leaf) treatments proved to be the most effective at controlling thrips. Whereas, ethion + cypermethrin 0.1% (6.42 thrips/leaf) and lambda-cyhalothrin 0.005% (6.50 thrips/leaf) were the next most effective treatments. Even after two sprays, the treatment with fenazaquin (0.005%) was

found to be the least successful since it recorded the highest population of thrips (8.58 thrips/leaf).

Priyadarshini et al. (2019) conducted bioefficacy study of different pesticides viz., imidacloprid 17.8% SL (@ 25, 37.5 and 50 g a.i./ha), chlorpyrifos 20% EC (@ 200 g a.i./ha), profenofos 50% EC (@ 750 g a.i./ha) and fipronil 5% SC (@ 50 g a.i./ha) against chilli thrips during 2016 at Kalyani, Nadia, West Bengal. Highest reduction of thrips was noticed from the treatments imidacloprid 17.8% SL @ 50 a.i. g/ha and the lowest per cent reduction was observed in the plots treated with chlorpyrifos 20% EC @ 200 a.i. g/ha followed by fipronil 5% SC @ 50 a.i. g/ha. Evaluation of bioefficacy of thiamethoxam 25 WG, tolfenpyrad 15 EC, chlorfenapyr 10 SC, cyantraniliprole 10.26 OD, diafenthiuron 50 WP, lambda cyhalothrin 5 EC and a standard check of imidacloprid 17.8 SL @ 0.20 g/l, 2.00, 0.25, 1.50, 1.00, 0.50 and 0.25 ml/l against onion thrips was carried out by Shweta et al. (2019). Based on field tests, it was determined that imidacloprid 17.8 SL @ 22.25 g a.i./ha and thiamethoxam 25 WG @ 25 g a.i./ha both had a significant advantage over onion thrips, with 5.19 thrips per plant and 4.90 thrips per plant, after the first, second and third sprays during the experimental period, respectively. The treatments with 6.89, 7.29 and 7.56 thrips per plant, respectively, were cyantraniliprole 10.26 OD @ 76.95 g a.i./ha, diafenthiuron 50 WP @ 250 g a.i./ha and tolfenpyrad 15 EC @ 150 g a.i./ha. However, with 8.67 and 8.46 thrips per plant, lambda cyhalothrin 5 EC @ 12.5 g a.i./ha and chlorfenapyr 10 SC @ 12.5 g a.i./ha were shown to be the least effective. The data on bulb yield showed that the plots treated with imidacloprid 17.8 SL @ 22.25 g a.i./ha and thiamethoxam 25 WG @ 25 g a.i./ha had the highest bulb yield, with 25.39 and 24.67 t/ha, respectively. However, lambda cyhalothrin 5 EC @ 12.50 g a.i./ha treated plots (17.94 t/ha) had the lowest bulb yield.

In a field trial on efficacy of chlorfenapyr 240 SC (@ 144, 192, 240 and 288 g a.i./ha), imidacloprid @ 50 g a.i./ha and fipronil @ 10 g a.i./ha against thrips of chilli by Thakur et al. (2021) it was concluded that the highest reduction in thrips population was in the plots treated with chlorfenapyr @ 288 g a.i./ha (90.69%) followed by chlorfenapyr @ 240 g a.i./ha (89.80%), fipronil 5% SC (89.51%), imidacloprid (74.18%), chlorfenapyr @ 240 g a.i./ha (69.74%) and chlorfenapyr @ 144 g a.i./ha (68.44 %). The highest cost benefit ratio was calculated in the plots treated with fipronil 5% SC (3.20) followed by imidacloprid 17.8 SL (2.99).

Choudhary et al. (2022a) also evaluated bioefficacy of different insecticides against chilli thrips. The results revealed that spinosad @70 g a.i./ha (3.33 thrips/plant), emamectin benzoate @11 g a.i./ha (3.78 thrips/plant), imidacloprid 200 SL @40 g a.i./ha (3.11 thrips/plant), fipronil 5 SC @30 g a.i./ha (3.56 thrips/plant) and spiromesifen @ 100 g a.i./ha (4.56 thrips/plant) were found to be effective against *S. dorsalis* in chilli. Thuppukonda and Kumar (2022) also conducted a field trial to check efficacy of seven insecticides (azadirachtin 1% EC, imidacloprid 70% WG, thiamethoxam 25%, indoxacarb 14.5 SC, acetamiprid 20% SP, fipronil 5% SC, diafenthiuron 50% WP and neem oil 1500 ppm) against *S. dorsalis* during kharif season in 2021. It was found that highest per cent reduction of thrips was recorded in imidacloprid 70% WG (94.52%) followed by acetamiprid 20% SP (92.313%) and indoxacarb 14.5 SC (90.98%). Next best treatment was fipronil 5% SC (88.57%) and diafenthiuron 50% WP (85.92%) whereas least effectiveness was found in thiamethoxam 25% WG (84.40%) and neem oil 1500 ppm (81.78%) among all treatments. Highest market value was recorded from plots treated with imidacloprid 70% WG (130.4 q/ha) with highest benefit ratio of 1:10.64 which was followed by acetamiprid 20% SP (1:10.08), indoxacarb 14.5 SC (1:9.16), fipronil 5% SC (1:8.45), diafenthiuron 50% WP (1:7.32), thiamethoxam 25% WG (1:6.97), neem oil 1500ppm (1:5.64) when compared to control (1:3.41).

3.2 Phytotoxicity and effect on non-target organisms

3.2.1 Phytotoxicity

Karthik et al. (2015) found that no phytotoxic symptoms appeared on okra leaves, flowers or fruits following the foliar application of imidacloprid 70 WG at 49 g a.i./ha at 1, 3, 7 and 10 days after spray. Balikai and Mallapur (2017) reported that gherkin plants sprayed with flubendiamide @ 60, 120 and 180 g a.i./ha did not show any phytotoxic symptoms at 1, 3, 7, 10 and 15 days.

All the doses of cyantraniliprole 10 OD (75, 150 and 300 g a.i./ha) as foliar application in different seasons did not cause any noticeable phytotoxic symptoms at 1, 3, 5, 7, 10 and 15 days after application in potato (Vinothkumar 2020).

3.2.2 Effect on non-target organism

Maximum reduction of coccinellid population was recorded when imidacloprid 17.8% SL was applied @ 175ml/ha (0 and 0.33 beetles/plant) followed by 150 ml/ha (0.11 and 0.50

beetles/plant) at 3 and 7 days after spray, respectively in tomato field (Kar 2017). At application rate of 90 g a.i./ha for flubendiamide and 84 and 180 g a.i./ha for thiacloprid the mean population of spiders was recorded as 5.27, 6.23 and 5.28 spiders per five plants, respectively. The mean population of coccinellids were 5.33, 6.40 and 5.40 per five plants at standard checks, flubendiamide @ 90 g a.i./ha and thiacloprid @ 84 and 180 g a.i./ha, respectively in brinjal (Sangamithra et al. 2018). A maximum beetle population of 6.7, 8.15, 8.67 and 10.30 beetles/5 shoots and 5.67, 5.00, 5.67, 6.00 and 6.33 beetles/5 shoots was observed on the first, third, seventh and fourteenth days after first and second spray in mustard field, respectively (Ahlawat et al. 2018). Another study conducted by Narayan et al. (2019a) also revealed that control plot recorded higher population of ladybird beetles with 2.65 beetles per plant followed by cyantraniliprole 10% OD (0.0143%) (1.34 beetles/plant) and flubendiamide 39.36% SC (0.0098%) with 1.08 beetles per plant in brinjal crop.

4 Validation of method

4.1 Method validation

Method validation is a process of proving that analytical techniques are appropriate for their intended purpose. In more detail, analytical technique validation involves generating substantiated proof that the recommended approach will reliably produce correct test results that assess a product in comparison to its set specifications and quality characteristics. The approach should be suitable for routine tasks in the Quality Control environment and be validatable, transferrable, durable, dependable, accurate and exact. If the method has not been fully created, it should not move on to the validation phase. Validation tests must be carried out using accredited and calibrated instruments and equipment and they must be adequately recorded (Chowdary et al. 2020).

The scope of validation criteria guidelines supplied by various organisations varies greatly; however obtaining reliable analytical test findings is always the goal of validation. The quality and safety of items that are measured using the analytical method depend on this. As a result, technique validation is a crucial prerequisite for ISO/IEC 17025 certification of food testing laboratories. The following are fundamental criteria for method validation, however they are not exhaustive:

4.1.1 Specificity/Selectivity

The ability of the analytical technique to distinguish and quantify the analyte in complicated mixtures is referred to as specificity. When identifying contaminants and

validating identification tests, a specificity study must be done (Chowdary et al. 2020). Selectivity and specificity are two words that can be used interchangeably. If the reaction of an analyte can be discriminated from all other responses, the technique is said to be selective (Kalra 2011). A placebo formulation, synthesis intermediates, excipients, degradation products, process contaminants, etc. may be included in the sample components or matrix (Chandran and Singh 2007). The response of the analyte in test mixtures containing the analyte and all potential sample matrixes is compared with the response of a solution containing only the analyte. Such approaches are referred to be non-specific since any contribution from the matrix to the response results in a constant or proportionate systematic inaccuracy. A statistical method has been published that uses a one-sided t-test to compare the intercept to zero (Shah et al. 1991; Bolton 1997). The slopes of matrix and non-matrix standards are compared, or the matrix effect is assessed using a conventional addition technique, in the absence of primary standards (Shah et al. 1991). Methods of establishing specificity and its expression by different International agencies are depicted in Table 2.1

Table 2.1 Comparison of different guidelines for “specificity” parameter of analytical method validation

Guidelines	ICH	US FDA	AOAC	USP	IUPAC	EU
Reference document	ICH guideline Q2(R2) on validation of analytical procedures (ICH 2022)	Guidance for Industry- Bio analytical method validation (US FDA 2018)	AOAC Peer Verified Methods Program, Manual on policies and procedures (AOAC 1993)	General Chapter h1225i, Validation of compendial methods, United States Pharmacopei a XXV, Rockville, MD, The United States Pharmacopei al Convention Inc. p. 2149-2152 (USP 2003)	Harmonized guidelines for single laboratory validation of methods of analysis (IUPAC 2002)	Analytical quality control and method validation procedures for pesticide residues analysis in food and feed, SANTE/1131 2/2021, Directorate General for Health and Food Safety, European Commission (SANTE 2021)
Specificity Definition	Specificity and selectivity are both terms to describe the extent to which other substances interfere with	Ability of the method to assess, unequivocally, the analyte in the presence of other	Ability of a method to measure only what it is intended to measure.	Ability to assess unequivocally the analyte in the presence of components, which may be	The degree to which a method can quantify the analyte accurately in the presence of	The ability of the detector to provide signals that effectively identify the analyte.

	the determination of a substance according to a given analytical procedure.	components that are expected to be present (e.g., impurities, degradation products, matrix components, etc.)		expected to be present	interferants.	
Method	<p>When the impurities are available:</p> <ul style="list-style-type: none"> • spiking drug substance or drug product with appropriate levels of impurities and/or excipients and demonstrating that the assay result is unaffected by the presence of these materials • When the impurities are not available: comparing the test results of samples containing typical impurities, related substances or degradation products with a second well-characterized procedure 	<ul style="list-style-type: none"> • Analysis of blank samples of appropriate biological matrix obtained from at least six sources and test for interference. 	<ul style="list-style-type: none"> • Reagent blanks and field blanks should be run to ensure no interfering compounds are present. • To verify the specificity of the method for the analyte(s) of interest, results should be tested under different experimental conditions, e.g., two different analytical principles or two different detection techniques. • The method should be able to distinguish the analyte from known interfering materials and the behavior of the analyte during analysis should be indistinguishable from the corresponding standard material in the appropriate matrix. 	<ul style="list-style-type: none"> • When the impurities are available: Spiking of pure substance (drug or drug product) in appropriate level of impurities/excipients and demonstrate the result is unaffected. • When the impurities are not available: Comparing the test results of sample containing impurities or degradation product to second well-characterized procedure. These comparisons should include sample under relevant stress condition. • In chromatographic method: Peak purity 	<p>Selectivity index should be calculated.</p> <p>Selectivity index = b_{an}/b_{int}</p> <p>b_{an} = Slope of calibration curve</p> <p>b_{int} = Slope of response independently produced by a potential interferant.</p>	<p>Linearity check from five concentration levels</p>

				test to be done by diode array and mass spectrophotometry.		
Expression/calculation	Not specified	Not specified		<ul style="list-style-type: none"> • Proof of discrimination of analyte in the presence of impurities, e.g., for chromatography chromatogram should be submitted. • Peak purity test to demonstrate that the peak is not attributable to more than one component. • For assay two results should be compared and for impurity tests two profiles should be compared. 	Selectivity Index	Calculated concentration from true concentration
Acceptance criteria	Not specified	<ul style="list-style-type: none"> • Blank and zero calibrators should be free of interference at the retention times of the analyte(s) and. • Spiked samples should be $\pm 20\%$ LLOQ. 	Not specified	Not specified	Not specified	$\leq 20\%$

ICH: International Conference on Harmonization, **AOAC:** Association of Official Analytical Chemists, **EU:** European Union Commission, **IUPAC:** International Union of Pure and Applied Chemistry, **US FDA:** United States Food and Drug Administration, **USP:** United States Pharmacopeia

4.1.2 Linearity and range:

The capacity of an analytical process to produce test findings that are directly proportional to the concentration (quantity) of analyte in the sample is known as linearity whereas, when an analytical technique has an appropriate level of precision, accuracy and linearity, the range is the interval between the upper and lower concentrations of the analyte (Chowdary et al. 2020). The correlation coefficient and y-intercept of the linear regression line for the response versus concentration plot are frequently used to assess the acceptability of linearity data. A correlation coefficient greater than 0.99 is typically viewed as evidence of adequate fit of the data to the regression line. The response achieved for the analyte at the target level should not exceed a few per cent of the y-intercept (Chandran and Singh 2007). To avoid the possibility of misinterpretation, two approaches have been suggested. In the first approach, deviation from the regression line is plotted against concentration or log concentration. Positive and negative values should differ from the mean equally. Plotting the ratio of reaction to concentration vs concentration or log concentration is another strategy that is suggested. Across the whole range, the resultant line should be linear. Nonlinear calibration may be necessary for some analytical techniques, although a linear model with univariant regression is recommended (Miller 1991; Shah et al. 1991). The range is often given in the same units as the test findings, such as parts per million, percentages, or amounts per unit volume, depending on the analytical method used to get the data. Table 2.2 compares several recommendations for the linearity and range parameter of analytical method validation.

Table 2.2 Comparison of different guidelines for ‘linearity and range’ parameter of analytical method validation

Guidelines	ICH	US FDA	AOAC	USP	IUPAC	EU
Linearity and range: Definition	Range: The range of an analytical procedure is the interval between the lowest and the highest reportable results in which the analytical procedure has a suitable level of precision, accuracy and response.	Calibration/ Standard Curve: is the relationship between the instrument response and the calibration standards within the intended quantitation range.	Linearity: Defines the ability of the method to obtain test results proportional to the concentration .	Linearity: Ability (within range) to obtain test results, which are directly proportional to the concentration (amount) of analyte in the sample. Range: Interval between the upper and lower	Not explicitly defined	Linearity: Defines the ability of the method to obtain test results proportional to the concentration.

				concentration (amounts) of analyte in the sample including the concentrations for which suitable level of accuracy, precision and linearity has been demonstrated		
Method	Linearity: Experimental demonstration of the linear relationship between analyte concentrations and peak responses (or the ratio of peak response if an internal standard was used) with reference materials at 5 or more concentration levels	<ul style="list-style-type: none"> • Not specified 	Not specified	Drug (different dilution) and/or separately weighed synthetic mixture. Measurement of response and plot response vs. concentration of analyte and demonstration of linearity by: <ul style="list-style-type: none"> • Visual inspection of plot. • Appropriate statistical methods 	<ul style="list-style-type: none"> • Visual examination of residual plot. • Application of statistical testing (significance testing) • Test for lack of fit can be weighted/simple regression 	Calculated concentration from true concentration
Recommendation	<ul style="list-style-type: none"> • Minimum of 5 concentrations are recommended for linearity For Range: Assay of drug/finished product: 80-120% of test concentration For content uniformity: 70-130% of test concentration • For impurity: From reporting level to 120% of specification. For purity 	<ul style="list-style-type: none"> • One blank sample (matrix sample without internal standard (IS)) • One zero sample (matrix sample p IS) • 6-8 non-zero samples covering expected range including LLOQ. 	4 conc. levels are to be selected.	<ul style="list-style-type: none"> • Minimum of 5 concentrations are recommended for linearity For Range: Assay of drug/finished product: 80-120% of test concentration. • For content uniformity: 70-130% of test concentration • For dissolution 	<ul style="list-style-type: none"> • Six or more calibration standards are evenly spaced over the range of interest. • Range: 0–150% or 50–150% of target concentration depending on which of this is more suitable. • Calibration standard should be 	Minimum of 5 concentrations are recommended

	testing: 80-100% of specification limit.			testing: $\pm 20\%$ over specified range • For impurity: from reporting level to 120% of specification.	run at least in duplicate. Preferably in triplicate or more	
Acceptance criteria	Not specified	Non-zero calibrators should be $\pm 15\%$ of nominal (theoretical) concentrations, except at LLOQ where the calibrator should be $\pm 20\%$ of the nominal concentrations in each validation run. • 75% and a minimum of six non-zero calibrator levels should meet the above criteria in each validation run.	Not specified	Not specified	Not specified	$\leq 20\%$

ICH: International Conference on Harmonization, US FDA: United States Food and Drug Administration, AOAC: Association of Official Analytical Chemists, USP: United States Pharmacopeia, IUPAC: International Union of Pure and Applied Chemistry

4.1.3 Accuracy:

It is the degree to which the measured value and the actual value agree (Chowdary et al. 2020). Thompson et al. (2002) defined accuracy or trueness as the closeness between the concentration obtained by the analytical assay and the true value. The assessment of accuracy can be obtained in several ways and the method should be appropriate to the matrix: one way to determine accuracy is to compare the results of the method with those from a recognised reference method. Another method is to analyse a sample with known concentrations and compare the measured value with the true value provided with the material (Kalra 2011).

Anonymous (2004) indicated that accuracy should be completed at a least of five concentration levels for LOQ. The accuracy of a technique must be assessed at multiple levels of fortification, which may vary depending on the range of potential results. A value of zero per cent results in the greatest accuracy (Peris-Vicente et al. 2014). Table 2.3 lists the recommendations made by an international body about accuracy.

Table 2.3 Comparison of different guidelines for ‘accuracy’ parameter of analytical method validation:

Guidelines	ICH	US FDA	AOAC	USP	IUPAC	EU
Accuracy: Definition	The accuracy of an analytical procedure expresses the closeness of agreement between the value which is accepted either as a conventional true value or as an accepted reference value and the value measured	Accuracy is the degree of closeness of the determined value to the nominal or known true value under prescribed conditions. Accuracy is also sometimes termed trueness.	Closeness of the determined value to the true value.	Closeness of test results obtained by that method to true value.	Trueness is the closeness of agreement between a test result and accepted reference value of the property being measured. Smaller bias means greater trueness	The closeness of agreement between an analytical result and the true or accepted reference value.
Method	<ul style="list-style-type: none"> • Spiking Study Acceptable recovery of spiked impurity standards in sample matrix at multiple spiking levels Or: Comparison with well-defined secondary procedure: Comparison of the measurement results to the ‘true’ values obtained from alternative validated procedures 	Replicate analysis of samples containing known amounts of analyte.	<ul style="list-style-type: none"> • Use of certified reference materials. • Use of reference method of known uncertainty. • Use of recovery from spiked samples 	<ul style="list-style-type: none"> • Application of procedure to analyze synthetic mixture of known purity. • Comparison of result with already established procedure. • Accuracy may be inferred once precision, linearity and specificity have been established. 	<ul style="list-style-type: none"> • Bias is determined by comparing response of method to a reference like: • Use of certified reference material. • Use of reference material. • Use of reference methods • Use of spiking/recovery Significance testing is recommended 	Average recovery for each spike level tested
Recommendation	• Accuracy should be	• Accuracy should be	Three concentration	Minimum of nine	Not specified	A minimum of 5

	assessed using an appropriate number of determinations and concentration levels covering the reportable range (e.g., 3 concentrations /3 replicates each of the full analytical procedure).	established with at least three independent runs, four QC (quality control) levels per run and \geq five replicates per QC level.	levels throughout the range <ul style="list-style-type: none"> • Low concentration of range • Medium concentration of range • High concentration of range • Amount added for fortification should be a substantial fraction or more than the amount present in the sample. 	determination s: <ul style="list-style-type: none"> • Low concentration of range \times 3 replicate • Medium concentration of range \times 3 replicate • High concentration of range \times 3 replicates 		replicates is required) at the targeted LOQ or RL of the method and at least one other higher level, for example, 2-10x the targeted LOQ or the MRL.
Acceptance criteria	Not specified	<ul style="list-style-type: none"> • Accuracy: Within-run and between runs: • \pm 15% of nominal concentrations; except \pm 20% at LLOQ. 	Not specified	Not specified	Not specified	70-120 %

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4.1.4 Limit of detection (LOD) and Limit of quantification (LOQ):

The lowest concentration of analyte that can be consistently identified using the approach but not necessarily quantified is referred to as the limit of detection (LOD) by Chandran and Singh (2007). Several methods have been suggested to calculate the detection limit depending on the nature of method. It may be calculated using the signal-to-noise ratio for chromatographic techniques that have a constant background noise level. Under these circumstances, the LOD will be the concentration at which the response signal-to-noise ratio is 3 (Shrivastava and Gupta 2011). The LOQ is the lowest concentration of an analyte in a sample that can be accurately and precisely quantified. The determination of LOQ can be done in a variety of ways. The LOQ parameter is utilised specifically for contaminants, degradation products and/or residual solvents when quantifying samples at low levels in compounds. LOQ based on signal to noise ratio (S/N): This technique can only be used if

there is little baseline noise. LOQ can be computed via computer-aided software or calculated in accordance with US Pharmacopoeia. If there are no impurities in the test solution or a synthetic mixture of product components in the placebo preparation, the associated substance and leftover solvents can be spiked with the lowest concentration of contaminants. The signal-to-noise ratio of the low concentration solution is approximately 10, which might be the LOQ (Geetha et al. 2012). Table 2.4 and Table 2.5 enlist the recommendations made by an international body about limit of detection and limit of quantification.

Table 2.4 Comparison of different guidelines for ‘limit of detection’ parameter of analytical method validation

Guidelines	ICH	US FDA	AOAC	USP	IUPAC	EU
Detection limit: Definition	The detection limit is the lowest amount of an analyte in a sample which can be detected but not necessarily quantitated as an exact value	Explicitly not described	Lowest content that can be measured with reasonable statistical certainty	Lowest amount of analyte in the sample, which can be detected but not necessarily quantitated under stated experimental conditions.	Smallest amount of conc. of analyte in the sample that can be reliably distinguished from zero.	Explicitly not described
Method	<ul style="list-style-type: none"> • By visual evaluation • Based on S/N ratio -Applicable to procedure, which exhibit baseline noise. -Actual lowest concentration of analyte detected in compared with blank response -Based on S.D. of response and slope $LOD = 3\sigma/s$ s = Slope of calibration curve σ = S.D. of response; can be obtained by: <ul style="list-style-type: none"> - Standard deviation of blank response. -Residual standard deviation of the regression line. 	Not described.	Based on more than 20 blank readings	<ul style="list-style-type: none"> • For non-instrumental: Analysis of sample with known concentration of analyte and by establishing minimum concentration at which analyte can be reliably detected. • For instrumental: Process for non-instrumental can be adopted. Detection limit should be sufficiently low for analysis of samples with 	Not specified	Not described

	-Standard deviation of the y-intercept of the regression line -Sy/x i.e. standard error of estimate			known concentration of analyte above and below the required detection limit.		
Expression/ Calculation	Not described	Not described	The mean value of the matrix blank readings (n ≥ 20) plus three standard deviations of the mean, expressed in analyte concentration	Not specified	Not specified	Not described
Acceptance criteria	Not specified	Not described	Not specified	Not specified	Not specified	Not described

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Table 2.5 Comparison of different guidelines for ‘limit of quantification’ parameter of analytical method validation

Guidelines	ICH	US FDA	AOAC	USP	IUPAC	EU
Quantitation limit: Definition	The quantitation limit is the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy.	The lowest amount of an analyte that can be quantitatively determined with acceptable precision and accuracy (Lower limit of quantification).	The limit of quantitation is the lowest amount of analyte in a sample, which can be quantitatively determined with precision and accuracy appropriate to analyte and matrix considered.	Lowest amount of analyte in a sample, which can be quantitatively determined with suitable precision and accuracy.	Not defined	Lowest amount of analyte in a sample, which can be quantitatively determined with lowest amount of suitable precision and accuracy.
Method	By visual evaluation Based on S/N ratio -Applicable to procedure, which exhibits base line noise. -Low conc. of analyte is compared with	Not specified	Not specified	<ul style="list-style-type: none"> By visual evaluation Based on S/N ratio -Applicable to procedure, which exhibits base line noise. -Low conc. of analyte is compared with	Not recommended; only recommends expressing uncertainty of measurement as function of concentration	Lowest spike level meeting the method performance criteria for recovery and precision

	<p>blank.</p> <p>Based on S.D. of response and slope $LOQ = 10 \frac{\sigma}{s}$ $s = \text{Slope of calibration curve}$</p> <p>$\sigma = \text{S.D. of response}$; can be obtained by:</p> <ul style="list-style-type: none"> -Standard deviation of blank response -Residual standard deviation of the regression line -Standard deviation of the y-intercept of the regression line -$S_{y/x}$ i.e. standard error of estimate 			<p>blank</p> <p>Based on S.D. of response and slope $LOQ = 10 \frac{\sigma}{s}$ $s = \text{Slope of calibration curve}$</p> <p>$\sigma = \text{S.D. of response}$; can be obtained by:</p> <ul style="list-style-type: none"> -Standard deviation of blank response -Residual standard deviation of the regression line -Standard deviation of the y-intercept of the regression line -$S_{y/x}$ i.e. standard error of estimate 		
Recommendation	<p>If the QL was estimated, the limit should be subsequently validated by the analysis of a suitable number of samples known to be near or at the QL. In cases where the QL is well below (e.g. approximately 10 times lower than) the reporting limit, this confirmatory validation can be omitted with justification.</p> <p>For impurity tests, the quantitation limit for the analytical procedure should be equal to or below the reporting threshold.</p>	Not specified	Not specified	Not specified	Not specified	Not specified

Expression/ Calculation	Not specified	Not specified	Mean value of the matrix blank reading plus 10 standard deviations of the mean, expressed in analyte concentration	Expressed as analyte concentration (% or ppb)	Not specified	Expressed as analyte concentration
Acceptance criteria	Not specified	Not specified	Not specified	Not specified	Not specified	≤ MRL

ICH: International Conference on Harmonization, **AOAC:** Association of Official Analytical Chemists, **EU:** European Union Commission, **IUPAC:** International Union of Pure and Applied Chemistry, **US FDA:** United States Food and Drug Administration, **USP:** United States Pharmacopeia

4.1.5 Precision:

Precision measures how closely two measurements that were taken from the same sample under the same conditions at the same time were in agreement with one another (Lindner and Wainer 2006). For an analytical procedure, there are four different forms of accuracy that may be assessed: instrument precision (also known as injection repeatability), repeatability (also known as intra-assay precision), intermediate precision and reproducibility. Although only the first three levels of accuracy are covered by official rules, all four degrees of precision are covered in certain studies (Green 1996). In order to evaluate the effectiveness of the instrument employed in the analytical process, instrument precision is assessed by repeatedly measuring the same sample solution. Table 2.6 provides a comparison of several precision determination guidelines.

Table 2.6 Comparison of different guidelines for ‘precision’ parameter of analytical method validation:

Guidelines	ICH	US FDA	AOAC	USP	IUPAC	EU
Precision: Definition	The precision of an analytical procedure expresses the closeness of agreement (degree of scatter) between a series of measurements obtained from multiple samplings of the same homogeneous sample under the	Precision is the closeness of agreement (i.e., degree of scatter) among a series of measurements obtained from multiple samplings of the same homogenous sample under the prescribed	Degree of agreement of measurements under specific conditions.	Degree of agreement among individual test results when the method is applied repeatedly to multiple samplings of a homogenous sample.	Closeness of agreement between test results obtained under stipulated conditions.	The closeness of agreement between independent analytical results obtained by applying the experimental procedure under stipulated conditions.

	prescribed conditions. Precision can be considered at three levels: repeatability, intermediate precision and reproducibility.	conditions.				
Method	Not specified	Analytical procedure is applied repeatedly to multiple aliquots of single homogenous volume of biological matrix.	Determination of % relative standard deviation (RSD) of multiple aliquots	Determination of % relative standard deviation (RSD) of response of multiple aliquots	Determination of % relative standard deviation (RSD) or % coefficient of variation (CV) and F-test for normally distributed error is applied.	Determination of % relative standard deviation (RSD) of response of multiple aliquots
Recommendation	<p>Repeatability should be assessed using: a minimum of 9 determinations covering the reportable range for the procedure (e.g. 3 concentrations/ 3 replicates each); b) a minimum of 6 determinations at 100% of the test concentration.</p> <p>Intermediate precision should be established depends on the circumstances under which the procedure is intended to be used. The applicant should establish the effects of random events</p>	Precision should be established with at least three independent precision runs, four QC (quality control) levels per run and \geq five replicates per QC level	<p>4 conc. levels are to be selected. $1/2 \times$ $1 \times$ $3/2 \times$ $2 \times$</p> <p>Repeatability: to be established within laboratory</p> <p>Different days</p> <p>Different analysts</p> <p>Different calibration curves</p> <p>Different batches of reagents</p> <p>Different matrices.</p> <p>Reproducibility: Between labs.</p>	<p>Repeatability (Same operating condition over short interval of time): Minimum of nine determinations over the entire range</p> <ul style="list-style-type: none"> • Low concentration of range $\times 3$ replicates • Medium concentration of range $\times 3$ replicates • High concentration of range $\times 3$ replicates (or) • At target concentration $\times 6$ determinations <p>Intermediate precision (within laboratory variation):</p> <ul style="list-style-type: none"> • Different Days • Different Analysts • Different Equipment etc. 	<p>Minimum of two concentration:</p> <ul style="list-style-type: none"> • At or near highest concentration in range • At or near lowest concentration in range 	A minimum of 5 replicates is required) at the targeted LOQ or RL of the method and at least one other higher level, for example, $2-10 \times$ the targeted LOQ or the MRL.

	on the precision of the analytical procedure. • Reproducibility is assessed by means of an inter-laboratory trial.					
Expression/ Calculation	Standard deviation, RSD and confidence interval	Coefficient of variation	RSD	Standard deviation, RSD and confidence interval	SD $\{(\sigma_{tot} = \sigma_r^2/n + \sigma_{run}^2)^{1/2}$ where n = no. of repeat results} or RSD	Standard deviation, RSD
Acceptance criteria	Not specified	At LLOQ: CV $\pm 20\%$ • Other than LLOQ: $\pm 15\%$	Not specified	Not specified	Not specified	$\leq 20\%$

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4.1.6 Repeatability

Repeatability describes the accuracy over a brief period of time while using the same operating conditions (Geetha et al. 2012). According to Bland and Altman (1986), repeatability is the estimate of precision obtained when measurement results are produced in one facility and tests are carried out on identical test items over a brief period of time by one operator using the same equipment under circumstances that are as consistent as possible (e.g. incubation time and temperature). A homogeneous sample or the same sample generated in a minimum of six replicates using the test concentration of 100% (Geetha et al. 2012).

4.1.7 Reproducibility

Reproducibility describes method accuracy in the presence of laboratory variance, such as various days, analysts and equipment, etc. According to the analytical procedure, a total of six sample preparations may be made at each testing location. To guarantee statistical parity across diverse testing sites, results are analysed. Reproducibility is acceptable under the same conditions as intermediate accuracy (Geetha et al. 2012). It can be stated as the standard deviation (s), variance, probability distribution factor, etc. of an appropriate number of measurements on the same samples examined over a period of many days with at least two distinct calibration standards. The accuracy linked to reproducibility circumstances limited to

a single facility is referred to as "intermediate precision" or "intra-laboratory reproducibility," among other titles. This entails taking duplicate measurements on several days while trying to reproduce the conditions that the method is used under on a regular basis (e.g. measurements made by different analysts using different sets of equipment) (Brar 2018).

4.1.8 Ruggedness

Robustness/ ruggedness of an analytical technique is the measure of its capability to stay unaffected by small but purposeful modification in method parameters and offers an indication of its dependability during typical usage (Geetha et al. 2012). According to Ravisankar et al. (2015), robustness is the capacity of an analytical technique to remain intact in the presence of tiny, intentional changes to the method parameters. IUPAC takes into account the impact of changing the instrument, operator, reagent brand, concentration, pH of the solution and time allotted (run time) for the process to be completed (AOAC 1993 and Thompson et al. 2002).

4.1.9 Measurement of Uncertainty

The measurement of uncertainty is a single parameter that represents the range of values that might be based on the measurement result (often a standard deviation with a coverage factor or confidence interval) (Kalra 2011). Every testing facility should have and use methods for calculating measurement uncertainty. Testing laboratories must use methodologies for assessing measurement uncertainty in addition to common performance parameters (accuracy, robustness, sensitivity, linearity, limit of detection, etc). The definition of uncertainty is “a parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand” (Stepan et al. 2004).

Regardless of whether they are based on random or systematic effects, all uncertainties are stated as standard deviations, according to GUM (Guide to the Expression of Uncertainty in Measurement) (Anonymous 2011). In essence, there are two distinct methods for calculating this standard deviation. The traditional method (type A assessment) is predicated on the idea that measurement findings would vary randomly according to a probability distribution. Replicated measurements and statistical analysis of the measured values are used to estimate the standard deviation of this distribution (measurements series). For estimating uncertainties that are brought on by systematic effects, the alternative

approach (type B assessment) is typically utilised. It makes use of logically assuming probability distributions that take into consideration the information that is currently known regarding the numbers in question as well as the standard deviation of these distributions (Anonymous 2006).

The two classes of uncertainty evaluation are defined in GUM as follows.

Type A: Evaluation using statistical analysis of measurement series

Type B: Evaluation using means other than statistical analysis of measurement series.

In practice the uncertainty on the result may arise from many possible sources, including examples such as incomplete definition of the measurand, sampling, matrix effects and interferences, environmental conditions, uncertainties of masses and volumetric equipment, reference values, approximations and assumptions incorporated in the measurement method and procedure and random variation (Anonymous 2011).

4.2 Method validation by different authors

Method validation of different pesticides has been studied by different authors and are given in Table 2.7

5. Persistence studies of different pesticides

5.1 Spiromesifen

5.1.1 Residue estimation

The residues were extracted by following the modified QuEChERS method and quantified analysis was done with the help of LC-MS/MS. The separation was achieved on C₁₈ column (150 × 4.6 mm, 5µm particle size) with a flow rate of 0.3 mL/min at 30°C. An elution gradient was used with solvent A: Water + 5 mM ammonium formate + 0.1% (v/v) formic acid and solvent B: Methanol + 5mM ammonium formate + 0.1% formic acid. The MS parameters of spiromesifen were optimized in positive ionization mode. The masses were monitored and optimized using standard parameters: Precursor ion 393.0 m/z and Product ions 294.9 m/z (Collision energy: 14eV) and 312.9 m/z (Collision energy: 5eV). The retention time (RT) of 19.23 min was obtained (Singh et al. 2021).

Table 2.7 Method validation by different authors on different crops

Crop	Insecticide	Selectivity	Linearity	LOQ/LOD	Precision	Accuracy/Recovery	Reference
Vegetables	Chlorantraniliprole	Retention time- 9.82 min. Instrument used: HPLC	$R^2 = 0.996$	LOD- 0.03 mg/kg LOQ- 0.10 mg/kg	Repeatability: ranged from 1.6-4.4% (RSD_r) Reproducibility: Ranged from 5.5- 9.1% (RSD_R)	Spiked level: 0.10-1 mg/kg Recovery above 85%	Singh et al. 2012
Vegetables, fruits, grains		Retention time- 8 min. Instrument used: LC with UV-vis	$R^2 =$ >0.990	LOD- 200 pg LOQ- 0.01 mg/kg	-	Spiked level: 0.01, 0.05 and 0.1 mg/kg Recoveries in range 94.60-101.10%	Xu et al. 2010
Cabbage, Tomato	Spiromesifen	Retention time- 39 min. Instrument used: GC-ECD and GC-MS	Conc. level- 0.003-1 μ g/ml $R^2 > 0.99$	LOD- 0.003 μ g/ml LOQ- 0.01 mg/kg	Precision and Accuracy Spiked at- 0.01-0.5 mg/kg Recoveries in range of 91.13-100.21% (cabbage) 72.56-92.78% (tomato)	Lekha et al. 2016	
Tomato		Retention time- 5.5 min. Instrument used: HPLC- PDA	Conc. level- 0.05-10 μ g/ml $R^2 = 1.00$	LOQ- 0.05 μ g/g	Precision and Accuracy Spiked at- 0.05 and 0.5 μ g/g Recovery= 83.83 and 94.33 %	Rao et al. 2015	
Okra	Chlorpyrifos, Imidacloprid	Retention time- 17.2 min. (Chlorpyrifos)	Conc. level- 1.0- 5.0 μ g/g	LOD- 0.01 μ g/g LOQ- 0.05	Precision and Accuracy Spiked at- 0.05, 0.1 and 1.0 μ g/g Recovery= 80.00 \pm 2.0, 87.7 \pm 1.5 and 91.5 \pm 4.8	Shrivastava et al. 2021	

		Instrument used: GC-ECD 12.3 min. (Imidacloprid) Instrument used: HPLC-UV	$R^2 = 0.999$ (for both)	$\mu\text{g/g}$	% (Chlorpyriphos) Recovery= 86.00 ± 3.5 , 86.00 ± 3.6 and $91.8 \pm 3.7\%$ (Imidacloprid)		
Brinjal	Chlorpyriphos	Retention time- 9.61 min. Instrument used: GC-FPD	Conc. level- 0.05-1.00 mg/kg $R^2 > 0.990$	LOD- 0.01 mg/kg LOQ- 0.05 mg/kg	Precision Spiked at 0.05, 0.25 and 0.5 mg/kg Repeatability- recoveries were in range of 97.00-98.80% RSD- 4.85-7.25% Reproducibility- 95.40-96.80% with RSD- 6.23-8.34%	Accuracy Spiked at 0.05, 0.25 and 0.5 mg/kg Recoveries in range of 96.80-98.00% with RSD- 6.65-8.21%	Brar 2018
Capsicum, Tomato	Fenazaquin	Retention time- 25.46 min. Instrument used: GC-MS	Conc. level- 0.01-1.00 $\mu\text{g/ml}$ $R^2 > 0.99$	LOD- 0.01 mg/kg LOQ- 0.05 mg/kg	Precision Spiked at 0.05, 0.25 and 0.5 mg/kg 1. Tomato Repeatability- recoveries were in range of 99.52-109.00% RSD- 4.81-9.86% Reproducibility- 98.71-102.20% with RSD- 4.06-6.54% 2. Capsicum	Accuracy Spiked at 0.05, 0.25 and 0.5 mg/kg 1. Tomato Recoveries in range of 89.95-98.11% RSD- 4.91-9.38% 2. Capsicum Recoveries in range of 87.74-96.36% RSD- 7.02-9.26%	Singh 2021

					Repeatability- recoveries were in range of 96.50-101.96 % RSD- 4.65-6.91% Reproducibility- 89.72-97.61% with RSD- 4.80-9.33%		
Pepper, Tomato and Cucumber	Imidacloprid	Retention time- 3.49 min. Instrument used: HPLC	Conc. level- 0.01-0.60 mg/kg $R^2 > 0.991$	LOQ- 0.01 mg/kg	Reproducibility- 0.2% (RSD)	Spiked at 0.05 and 0.25 mg/kg Recoveries in range of 88-94% (at 0.25 mg/kg) 96-99% (at 0.05 mg/kg)	Amadeo et al. 2000
Tomato		Retention time- 6.20 min. Instrument used: HPLC- PDA	Conc. level- 0.01-1.00 $\mu\text{g/ml}$ $R^2 > 0.99$	LOD- 0.01 mg/kg LOQ- 0.05 mg/kg	Precision Spiked at 0.05, 0.25 and 0.5 mg/kg Repeatability- recoveries were in range of 97.60-107.50 % RSD- 5.10-8.54% Reproducibility- 90.60-101.80% with RSD- 6.69-9.56%	Accuracy Spiked at 0.05, 0.25 and 0.5 mg/kg Recoveries in range of 89.75-100.71% RSD- 4.12-8.49%	Singh 2021
Vegetables	Spirotetramat	Retention time- 8.52 min. Instrument used: HPLC- PDA	$R^2 = 0.991$	LOD- 0.01 mg/kg LOQ- 0.03 mg/kg	Precision Spiked level- 0.03-1.0 mg/kg Repeatability- % RSD in range of 0.55 to 5.56%	Accuracy Spiked level- 0.03-1.0 mg/kg Recoveries were above 80%	Singh et al. 2013

					Reproducibility- %RSD in range of 2.83 to 6.62%%	
Cowpea		Retention time- 2.98 min. Instrument used: LC- MS/MS	Conc. level- 0.0005– 0.5 mg/L $R^2 > 0.99$	LOD- 0.0005 mg/kg LOQ- 0.005 mg/kg	Precision and Accuracy Spiked level-0.005, 0.05 and 0.5 mg/kg Recoveries were in range of 82.4–94.4%, %RSD- 2.3–9.5%	Li et al. 2022
Potato	Cyantraniliprole	Instrument used: UHPLC- PDA	Conc. level- 0.01 to 0. 8 μ g/ml $R^2 = 0.999$	LOD- 0.003 μ g/g LOQ- 0.011 μ g/g	Precision and Accuracy Spiked level-0.05, 0.25 and 0.5 mg/kg Recoveries were in range of 95.34, 95.77 and 98.01%, %RSD- 2.66, 2.41 and 2.47%	Monica et al. 2021
Cabbage		Retention time- 2.3 min. Instrument used: HPLC- PDA	Conc. level- 0.001–10 mg/L $R^2 = 0.991$	LOD- 0.001 mg/kg LOQ- 0.005 mg/kg	Precision and Accuracy Spiked level-0.001–0.5 mg/kg Recoveries were in range of 89.80–97.52%, %RSD- 0.67–5.33%	Kumar et al. 2021
Pakchoi		Retention time- 1.82 min. Instrument used: UPLC- MS-MS	Conc. level- 0.005 to 1 mg/kg $R^2 = 0.992$	LOD- 0.1ng LOQ- 0.01 mg/kg	Precision and Accuracy Spiked level- 0.01, 0.05 and 0.1 mg/kg Recoveries were in range of 83.3 %–102.4 %, %RSD- 83.3 %–102.4 %	Sun et al. 2012

Dubey et al. (2021) used QuEChERS method for extraction and cleanup for estimation of spiromesifen residues and chromatographic separation of spiromesifen in okra, chilli, capsicum and brinjal samples was achieved by using GC-MS equipped with DB-5 capillary column coupled with a mass selective detector (GCMS-QP 2010 plus). The flow rate of helium as a carrier gas was kept at 1.02 ml/min. Residues were estimated using selected ion monitoring mode. The selected ions for spiromesifen were 57, 272 and 99 m/z. The retention time of spiromesifen was 24.78 min.

5.1.2 Persistence studies on crop

Initial deposits of 0.51-0.56 mg/kg and 0.78-0.84 mg/kg were found when spiromesifen was applied to chilli at application rate of 96 and 192 g a.i./ha, respectively. The values of the half-life ranged from 2.0 to 2.5 days (Sharma et al. 2007). A similar study was conducted by Varghese et al. (2011) on persistence of spiromesifen at the application rate of 96 g a.i./ha on chilli which revealed that spiromesifen residues persisted up to 5 days with a half life value of 2.62 days. Raj et al. (2012) investigated a study on dissipation of spiromesifen on okra fruits at application rates of 120 and 240 g a.i./ha and found that the initial deposits of 0.964 and 1.819 mg/kg with half-lives of 1.68 and 1.65 days were recorded at respective doses.

Thomas et al. (2014) conducted an experiment on persistence of spiromesifen @ 150 and 300 g a.i./ha on tomato fruits which resulted in initial deposits of 0.488 and 0.730 mg/kg and dissipated with half life of 2.05 and 2.29 days, respectively. Another study on tomato was conducted by Sharma et al. (2014b) who found that initial residues in a range of 0.17 to 0.50 mg/kg and 0.33 to 1.38 mg/kg of spiromesifen were recorded when tomato crop was sprayed at the application rate of 150 and 300 g a.i./ha. At 10th day after spray residues were found below LOQ of 0.05 mg/kg at both the doses. At X and 2X dose spiromesifen had a half life of 0.93-1.38 days and 1.04-1.34 days, respectively. Initial spiromesifen residue levels on cabbage were 0.640 and 1.549 mg/kg in 2013 and 0.723 and 1.438 mg/kg in 2014 following treatments @125 and 250 g a.i./ha with half lives of 2.9 and 3.9 days in 2013 and 3.2 and 4.5 days in 2014, respectively. At 15–17 days at regular dose and 24-27 days at double dose, the residue level were below the maximum residue limit of 0.02 mg/kg (Siddamallaiiah and Mohapatra 2016). Xavier and Chandran (2016) studied the persistence of spiromesifen in chilli fruits which revealed that at the application rate of 96 and 192 g a.i./ha initial deposits of 0.62 and 1.20 µg/g were found which persisted upto 21 and 27 days, respectively which further dissipated with a half life of 3.65 and 3.19 days and a safe waiting period of 0.74 and 4.49 days at respective doses.

When spiromesifen was sprayed on capsicum at a rate of 125 ml a.i./ha, Pathipati et al. (2017a) detected initial deposits of 1.61 mg/kg that reduced to BDL at the 10th day after spray. The safe waiting period before harvest and the half-life were 2.09 and 10.00 days, respectively. Sushil et al. (2018) investigated the persistence and dissipation behaviour of four pesticides in hot pepper i.e. quinalphos (25% EC), chlorpyrifos (20% EC) @ 300 g a.i./ha, ethion (50% EC) @ 500 g a.i./ha and spiromesifen (22.9% SC) @ 96 g a.i./ha. According to the study, the deposits of chlorpyrifos, ethion, quinalphos and spiromesifen were all greater than 1.189 mg/kg and dissipated with a half lives of 4.93, 8.85, 4.42 and 3.20 days, respectively.

On cucumbers, Chauhan et al. (2018) conducted a field trial for spiromesifen to check the dissipation pattern of the insecticide. The initial deposits in/on cucumber fruits were 0.47 and 0.79 mg/kg, after two applications @ 96 and 192 g a.i. /ha, respectively. However, on the 10th day residues were found below the determination level at both the doses with a half life of 5.6 and 4.8 days, respectively. According to Vinothkumar et al. (2018), the mean initial deposit following two sprays of spiromesifen in/on brinjal fruit at 96 g a.i./ha and 192 g a.i./ha was 0.715 µg/g and 1.123 µg/g, respectively. For a single dose and a double dose, respectively, the computed half life and safe waiting period were 1.32 and 2.18 days, 1.40 and 2.18 days.

Singh et al. (2021) studied the persistence and dissipation pattern of spiromesifen in brinjal under sub-tropical agro-climatic conditions. Results showed that in treated samples on 0 day (2hr) initial residues of spiromesifen was 0.091 and 0.192 mg/kg at 96 g a.i./ha and 192 g a.i./ha with a dissipation of 73.62 and 87.50 per cent on 3rd and 5th day, respectively. The half life of spiromesifen at X and 2X dose was 3.64 and 4.10 days with a safe waiting period of 1 day on both doses, respectively.

Persistence of spiromesifen on okra, chilli, capsicum and brinjal was conducted by Dubey et al. (2021) who revealed that at application rate of 144 g a.i./ha, average residues of spiromesifen were 1.327 mg/kg, 0.727 mg/kg, 0.800 mg/kg and 0.738 mg/kg with a per cent dissipation of 96.00, 93.81, 91.75 and 94.44 per cent in 7 days, respectively. The half-life of spiromesifen as 1.6, 1.8, 1.9 and 1.7 days with a safe harvesting interval of 8.9, 5.2, 6.0 and 6.9 days, respectively for okra, chilli, capsicum and brinjal was recorded.

5.1.3 Persistence studies in soil

In chilli and cotton, the dissipation of spiromesifen was investigated at 96 and 192 g a.i./ha and 120 and 240 g a.i./ha, respectively. After 15 days of treatment, no residues were

found in either of the two cropped soils (Sharma et al. 2007). Similar studies were carried out by Raj et al. (2012) who investigated the spiromesifen persistence in soil under okra after spraying at 120 and 240 g a.i./ha. Residues at either dose of treatment were below the quantitative limit of 0.01 µg/g in soil samples examined 20 days after the last spray. Spiromesifen was applied to cabbage by Lekha et al. (2016) at application rates of 125 and 250 g a.i. /ha and no residues were discovered in the soil.

During a period of two years, the spiromesifen dissipation pattern on cabbage field soil was assessed by Siddamallaiah and Mohapatra (2016). Spiromesifen was recovered in soil in amounts ranging from 85.44 to 103.37 per cent. The limits for measurement and detection were 0.003 g/ml and 0.01 mg/kg, respectively. At harvest (30 days later), the field soil analysis revealed no spiromesifen residues. Spiromesifen was applied on tomatoes by Siddamallaiah *et al.* (2017) at application rates of 125 and 250 g a.i./ha and they recorded the half-lives of 5.6 to 7.4 and 8.4 to 9.5 days in soil, respectively.

Residues of spiromesifen measured from soil at 0th (2 hr) day and 10th day were below the limit of quantification (LOQ) when persistence studies of spiromesifen in brinjal field soil was conducted by Singh et al. (2021).

5.2 Fenazaquin

5.2.1 Residue estimation

The okra sample was extracted with acetone and hexane mixture (1:1 v/v) and partitioned with ethyl acetate. A glass column packed with activated charcoal and florisil was used and final volume was made with n-hexane. The analysis of fenazaquin residues were done with GC-NPD with nitrogen, hydrogen and zero air as a carrier gases with a flow rates of 1.8, 1.5 ml/min and 130 ml/min. the retention time of fenazaquin under these conditions were found to be 5.66 min (Duhan et al. 2010).

The insecticide residues of fipronil, lambda- cyhalothrin, ethion, cypermethrin, fenpropathrin and fenazaquin in chilli fruits was extracted and analyzed by QuEChERS technique and further analysis of all the insecticides except fenazaquin were analyzed on GC-ECD and fenazaquin was analyzed on HPLC with Photo Diode Array. Recovery studies were carried out by fortifying the untreated sample of chilli at 0.1, 0.25 and 0.5 mg/kg with each pesticide. Average recoveries for fipronil (88.14, 91.10 and 95.58%), lambda-cyhalothrin

(90.40, 105.46 and 97.58%), ethion (80.70, 77.50 and 84.07%), cypermethrin (76.94, 80.01 and 74.65%), fenpropathrin (86.42, 110.32 and 106.54%) and fenazaquin (90.40, 105.46 and 97.36%), respectively (Patil et al. 2019).

5.2.2 Persistence studies on crop

According to a study by Nasr et al. (2009), the initial deposits of difenoconazole 25 EC, emamectin benzoate 5 SG and fenazaquin 20 SC on the tomato crop after one hour of spraying were 1.77, 0.22 and 0.52 mg/kg which further dissipated with 99.43, 95.45 and 96.15 per cent, respectively. The pre-harvest intervals for difenoconazole, emamectin benzoate and fenazaquin were suggested to be 8, 3 and 1 days, respectively.

In a study conducted by Duhan et al. (2010), the average initial deposits of fenazaquin on okra fruits after 1h of spray at single (125 g a.i./ha) and double (250 g a.i./ha) dose were found to be 0.119 and 0.242 mg/kg which dissipated to 0.015 and 0.027 mg/kg with 87.39 and 88.84 per cent dissipation after 90 days interval, respectively. The half-life of fenazaquin at single and double dose was found to be 3.13 and 4.43 days, respectively. Patil et al. (2019) conducted an experiment on persistence and dissipation of fipronil (25 mL a.i./ha), lambda-cyhalothrin (25 mL a.i./ha), ethion (444 mL a.i./ha), cypermethrin (55.5 mL a.i./ha), fenpropathrin (150 mL a.i./ha) and fenazaquin (50 mL a.i./ha) in/on chilli fruits. The initial residues were found to be 0.27, 0.33, 0.20, 0.55, 1.58 and 2.33 mg which further dissipated with a per cent dissipation of 65.81, 79.14, 100.00, 100.00, 77.33 and 91.80 per cent after last application. Singh (2021) also reported that average initial deposits of fenazaquin on tomato fruits when sprayed at the application rate of 125 g a.i./ha and 250 g a.i./ha were 0.431 mg/kg and 0.721 mg/kg which dissipated to 85.92 and 92.69 per cent after 5 and 7 days, respectively.

Kaur et al. (2022a) conducted an experiment to examine the persistence of fenazaquin 10 EC on okra fruits at three different doses (25, 50 and 125 g a.i./ha). Following two hours of spraying, the average initial fenazaquin deposits from three doses were 1.611, 2.299 and 3.100 mg/kg which decreased to 98.94, 98.26 and 97.58 per cent respectively after 10 days of spray. Two year study on persistence of fenazaquin on brinjal fruits were conducted by Kaur et al. (2022b) which revealed that the initial deposits of fenazaquin @ 25, 50 and 125 g a.i./ha were found to be 0.046, 0.098, 0.174 and 0.048, 0.102, 0.170 mg/kg with half lives ranged between 0.65 to 1.78 days during 1st and 2nd year, respectively.

5.2.3 Persistence studies in soil

Initial fenazaquin deposits from apple field soil from lower (100 g a.i./ha) and higher doses (200 g a.i./ha) were 0.13–0.20 mg/kg and 0.32–1.0 mg/kg, respectively (Sharma et al. 2006).

According to studies conducted by Yaqoob et al. (2021) on the persistence and dissipation of fenazaquin (0.004% and 0.008%) in soil under treated apple tree canopies of the Red Delicious variety, the pesticides left no initial deposit at zero day after application and the residues remained undetectable until harvest.

Persistence studies of fenazaquin in tomato cropped field soil revealed that at application rate of 125 and 250 g a.i./ha the residues of fenazaquin were found to be 0.103 and 0.197 mg/kg, respectively. The residues of dissipated to 55.76 per cent at 2X dose, respectively (Singh 2021).

5.3 Chlorantraniliprole

5.3.1 Residue estimation

The studies on residue estimation of chlorantraniliprole was conducted by Vijayasree et al. (2015) showed that extraction and cleanup was carried out using QuEChERS method and chromatographic separation of chlorantraniliprole in brinjal and okra samples was achieved using LC-MS/MS. The operation of the liquid chromatography (LC) gradient involved the following two eluent components: A, 10 % methanol in water + 0.1 % formic acid/50 mM ammonium acetate; B, 10 % water in methanol + 0.1 % formic acid/50 mM ammonium acetate. The flow rate remained constant at 0.8 ml/min and injection volume was 10 μ L. The column temperature was kept at 40 °C. The effluent from the LC system was introduced into triple quadrupole API 3200 tandem mass spectrometry (MS/MS) system equipped with an electro spray ionization interface (ESI), operating in the positive ion mode. Under these operating conditions, the retention time of chlorantraniliprole was found to be 3.15 min. The multiple reaction monitoring (MRM) transitions used for the quantitative and qualitative estimation were m/z 484→285.9 and 484→452.9, respectively.

Chilli fruit samples were extracted using the modified QuEChERS method. Hexane and dichloromethane were utilized for extraction pursued by cleanup with adsorbent blend of silica + activated charcoal (5 + 0.2 g) in the middle of the two layers of anhydrous sodium

sulphate. Analysis of chlorantraniliprole residues were done by using GC-MS/MS. The response of scan assessment of chlorantraniliprole revealed peak at m/z 278, 280, 243, 215. The product ion present at m/z 278 and 280 was taken as precursor ion during Multiple Reaction Monitoring (MRM). The GC-MS/MS was operated in the positive ion mode and m/z 249 and 251 with transitions m/z 278 > 249 and m/z 280 > 251 at collision energy 20 eV was selected at quantifier ion. The retention time was found to be 20.37 ± 0.02 min in these conditions (Ahlawat et al. 2019).

For performing extraction and clean-up, QuEChERS method was followed as given by Anastassiades et al. (2003). The residues of chlorantraniliprole in okra samples were quantified by HPLC equipped with reversed phase C18 column and photo diode array (PDA) detector. The mobile phase used was acetonitrile and water in the ratio of 60:40 with a flow rate of 0.3 ml/min. The run time for the sample was 30 min as the retention time (RT) for chlorantraniliprole, when detected at a wavelength of 229 nm was 21.975 min. The linearity range lied between 0-20 ng concentrations (Singla et al. 2020).

5.3.2 Persistence studies on crop

Kar et al. (2012) investigated the persistence of chlorantraniliprole (Coragen 18.5 SC) on cauliflower at recommended doses of 9.25 g a.i./ha and 18.50 g a.i./ha. Initial chlorantraniliprole deposits were detected as 0.18 mg/kg and 0.29 mg/kg at single and double dose, respectively. After 3 and 5 days at recommended and double the recommended dosages, respectively, residues disappeared below the limit of detection of 0.10 mg/kg. The calculated half-life of chlorantraniliprole after application at single dose was 1.36 days.

Vijayasree et al. (2015) examined the dissipation of chlorantraniliprole (Coragen 18.5 SC) in brinjal and okra fruits after field application at single and double doses of 30 and 60 g a.i./ha from which it was concluded that initial residues of chlorantraniliprole at single and double dosages were 0.72 and 1.48 mg/kg on brinjal fruit and 0.48 and 0.91 mg/kg on okra fruits, respectively. On the tenth day, the residues were below the detectable level of 0.01 mg/kg. Half-life of chlorantraniliprole at 30 and 60 g ai/ha on brinjal was 1.58 and 1.80 days with the calculated waiting period of 0.69 and 2.38 days, whereas on okra, the half life values were 1.60 and 1.70 with a safe harvesting of okra fruits at 1 and 1.20 days, respectively. Pathipati et al. (2017b) conducted a field trial on chlorantraniliprole in chilli under open field and polyhouse conditions which revealed that after application at 60 g a.i./ha

initial deposits of 0.36 and 1.31 mg/kg were found in capsicum which dissipated to BDL in 7 and 15 days of spray, respectively. The half life of chlorantraniliprole in open and polyhouse conditions were 2 and 2.17 days with a suggested waiting period of 7 and 15 days, respectively. Similar studies were carried out by Ahlawat et al. (2019) on dissipation pattern of chlorantraniliprole in chilli and revealed that at 30 and 60 g a.i./ha, initial deposits of 3.16 and 4.18 mg/kg were found which persisted for 7 and 15 days after last application.

Kabadad and Gali (2018) reported 0.81 and 2.00 mg/kg of initial residues of chlorantraniliprole in cabbage at 0.20 and 0.40 ml/L, respectively which further dissipated to 100 per cent within 3 days after spray. It was discovered that the waiting period for crop harvest was five days following the last spray, based on the insecticide complete dissipation. Lee et al. (2019b) also reported the initial deposit of same chemical in two fields of Kimchi cabbage and recorded 0.11 and 0.24 mg/kg residue at X and 2X dose, respectively, with half-lives of 10.0 and 15.2 days.

Singla et al. (2020) studied persistence of chlorantraniliprole on okra and concluded that the average initial deposits were 0.21 and 0.46 mg/kg at 25 and 50 g a.i./ha, respectively. The initial residues dissipated to BDL of 0.03 mg/kg after 7 and 10 days at single and double dose, respectively. The residues reduced to half in 2.27 and 2.45 days with a safe waiting period of 0 and 1 day, at the recommended and double the recommended dosages, respectively.

5.3.3 Persistence studies in soil

Malhat et al. (2012) evaluated the dissipation trend of chlorantraniliprole in tomato field soil at the application rate of 60 ml/feddan (1 feddan= 4200 m²). The research on the persistence pattern of chlorantraniliprole on sugarcane field soil after application of granule formulation was carried out by Sharma et al. (2014c). The average first deposits of chlorantraniliprole were observed to be 0.88 and 1.59 mg/kg after application of chlorantraniliprole at 100 and 200 g a.i./ha, respectively. After 56 days of applying pesticides at both dosages, these residues disappeared below the limit of quantification (LOQ) of 0.01 mg/kg. At recommended and double the recommended dosages, chlorantraniliprole half-life values ($t_{1/2}$) were calculated to be 8.36 and 8.25 days, respectively.

Ramasubramanian et al. (2016) revealed from their study that persistence of chlorantraniliprole in sugarcane soil resulted initial residue of 0.513 and 1.031 mg/kg for the

recommended (75 g a.i./ha) and double the recommended (150 g a.i./ha) doses, respectively. The residues persisted up to 30 days after treatment irrespective of the doses applied. Half-life ($t_{1/2}$) at X and 2X dose was 6.60 and 6.73 days, respectively.

Kansara et al. (2021) revealed from their study that residues of chlorantraniliprole and λ -cyhalothrin in pigeonpea cropped soil at 30th day and harvest time were below the limit of quantification (LOQ).

5.4 Fenvalerate

5.4.1 Residue estimation

Using an n-hexane: isopropanol combination (3:1), Gupta and Singh (2001) extracted the fenvalerate residue from the cauliflower samples. Further n-hexane was dried over anhydrous Na₂SO₄ after the isopropanol was removed from the extract, then it was concentrated and purified over a florisil column (60-100 mesh). The fenvalerate residues were examined using GC-ECD. While LOQ was 0.01 mg/kg, the average recovery of fenvalerate from the cauliflower head samples supplemented at two levels, 0.1 and 0.5 mg/kg, was 88 and 92 per cent, respectively.

The fenvalerate residues in *Amaranthus tricolour* L. were identified by Muralikrshna et al. (2019) using gas chromatography with an electron capture detector. In 2014, the experiment was carried out in three distinct Kerala districts. The fenvalerate residues were cleaned up using the QuEChERS method after being extracted in ACN (acetonitrile). The average recovery of fenvalerate with relative standard deviation values at LOQ (0.05 mg/kg), 5 times the LOQ (0.25 mg/kg) and 10 times the LOQ (0.5 mg/kg) were 74.12 (4.22%), 90.68 (3.63%) and 92.54 (3.22%) per cent, respectively.

5.4.2 Persistence studies on crop

The persistence patterns of three synthetic pyrethroids fenvalerate, tau-fluvalinate, lambda-cyhalothrin and an organophosphorus insecticide, monocrotophos, on eggplant (*Solanum melongena* L.) have been evaluated. The extractable residues ranged from 0.05 to 0.45, 0.01 to 0.40, 0.003 to 0.09 and 0.09 to 0.32 μ g/g for fenvalerate, tau-fluvalinate, lambda-cyhalothrin and monocrotophos, respectively. Fenvalerate was the most persistent among the four, followed by monocrotophos, lambda-cyhalothrin and tau-fluvalinate (Mukherjee and Gopal 1992).

The dissipation pattern of fenvalerate (20 EC) residues on cabbage heads was examined by Jaglan et al. (1995) where they found initial deposits of 2.91 and 2.94 ppm which reduced to 2.02 and 2.08 ppm after 3 days of spraying with proprietary and laboratory formulations, respectively. The RL_{50} and waiting period values were for proprietary and laboratory formulations found to be 3.14 and 3.68 days and 8.89 and 10.19 days, respectively. Chinese broccoli, chinese mustard and chinese cabbage were sprayed four times with fenvalerate (Belmark) at a rate of 97.5 g a.i./ha at weekly intervals. In all three crops, the mean initial residues ranged from 0.67 to 3.6 mg/kg with a half-life of 3.3 to 10.9 days. On 21st day after treatment, residual levels on the corresponding crops were 0.11, 0.10 and 0.14 mg/kg which showed that Chinese broccoli had a slightly higher fenvalerate content and lost it more quickly than the other crops (Ripley et al. 2001).

In the spring cabbage, Zhang et al. (2006) investigated the residue level of fenvalerate 20 EC administered at the recommended dose (45 g a.i./ha) which revealed that the initial fenvalerate residue of 1.358 mg/kg reduced to 0.071 mg/kg in 8 days after last application with RL_{50} value of 2.2 days. Ahmed et al. (2016) investigated the fenvalerate (Fenfen 20 EC) dissipation behaviour on tomato crops when administered at 1.0 ml/L. Initial residual levels of 1.938 mg/kg decreased to 0.042 mg/kg on 14th day following the last treatment.

The dissipation rate of fenvalerate 20 EC in okra crop at the Dr. Y.S.P. University of Horticulture and Forestry farm in Solan, Himachal Pradesh, was examined by Nath et al. (2018) who concluded that initial deposits of 0.330 and 0.540 mg/kg reduced to 0.045 and 0.44 mg/kg when applied at rates of 0.075 and 0.150 kg a.i./ha with a half-lives of 2.62 and 2.24 days, respectively. In tomatoes and capsicum vegetables that were gathered from several locations in the Tumakuru region of Karnataka, initial deposits of 0.057 and 0.168 mg/kg were found using GC-MS, respectively (Shylesha et al. 2021). According to Bansal (2022), the initial residues on broccoli heads at 60 g a.i./ha were 1.23 times lower than those at 75 g a.i./ha. The initial residues on broccoli heads decreased to 0.035 mg/kg and 0.029 mg/kg in 7 and 10 days, resulting in 89.86 and 93.14 per cent dissipation at X and 1.25X dose.

5.4.3 Persistence studies in soil

Raha et al. (1993) examined residues of fenvalerate (Agrofen 20 EC) in brinjal soil when sprayed at the recommended dose rate (0.015%) and double dose (0.030 per cent). Fenvalerate residues in the soil on the spraying day ranged from 0.20 to 0.48 mg/kg. With a half life of 1.88 and 2.00 days for the corresponding doses, the leftovers persisted for 10 days.

The longevity of pyrethroid (cypermethrin) residue in eggplant soil is determined by Rahman et al. (2015). Up to 5 days and 7 days after the single and double doses of spraying, residue observed in the soil sample was above the MRL, respectively, however, after 10 days, the residue dropped below the detection threshold. In another study conducted by Bansal (2022) on persistence of fenvalerate in broccoli cropped soil and found that residues of fenvalerate at 60 and 75 g a.i./ha were below limit of quantification (0.01 mg/kg) at harvest.

5.5 Chlorpyrifos

5.5.1 Residue estimation

The extraction and cleanup for estimation of chlorpyrifos residues in cucumber fruits was carried out by using QuEChERS method. Residues of chlorpyrifos were quantified by using GC-FPD. Nitrogen was used as a carrier gas and other gases used were hydrogen and zero air with a flow rate of 80.0 ml/min and 120.0 ml/min and injection volume was 1 μ L. Under these conditions, the retention time of chlorpyrifos was found to be 10.301 min. The limit of quantification was found to be 0.05 mg/kg (Singh et al. 2019b).

A technique based on liquid chromatography-mass spectrometry (LC-MS/MS) was used by Raju et al. (2012), to estimate residues of organophosphorus pesticides, namely quinalphos and chlorpyrifos. The procedure involves using 10ml of acetonitrile to extract 10g of homogenised okra samples which are then cleaned up using a dispersive solid phase extraction with a mixture of primary secondary amine (PSA), graphitized carbon black (GCB), C18 and anhydrous magnesium sulphate. Liquid chromatography-electro spray ionization-tandem mass spectrometry was used for the final analysis, operating in the multiple reactions monitoring (MRM) mode and collecting two distinct precursor-product transitions for each target chemical. The average recoveries assessed at 10 g/kg ranged from 81 to 106 per cent, with relative standard deviations under 14 per cent.

5.5.2 Persistence studies on crop

According to Peter et al. (2001), when chlorpyrifos was applied on tomato and aubergine at doses of 1.5 and 3.0 kg a.i./ha and 2.32 and 3.31 kg a.i./ha, the initial deposits ranged between 0.72-1.12 mg/kg with half-lives of 1.88 and 3.01 days on aubergine and 2.32 and 3.31 days on tomato, respectively. Within 3 days, the chlorpyrifos residues in both fruits decreased from 56 to 76%. When applied at 350 g a.i./ha and 700 g a.i./ha, Jha et al. (2006) evaluated the persistence of chlorpyrifos on eggplant fruits and discovered that the

initial residues were 0.253 and 0.546 mg/kg, which disappeared with a half-life of 7.34 and 7.56 days, respectively. In cauliflower curds, the residue behaviour of chlorpyrifos was investigated over a two-year period by Raina and Raina (2008) who found that initial residues of 0.56 and 1.29 mg/kg and 0.86 and 1.43 mg/kg were recorded when chlorpyrifos at rates of 500 and 1000 g/ha were applied in 1st and 2nd year, respectively which persisted for 7 and 10 days with a half life of 1.4 to 1.5 and 1.5 to 1.6 days, in respective years. The residues reached below the MRL of 0.05 mg/kg in 5.0-6.3 and 7.1-7.3 days at single and double dose, respectively. Aktar et al. (2009) discovered that when chlorpyrifos 20 EC @ 500 g a.i./ha was applied a half-life value of 8.75 days with safe waiting period of 45.29 days was found on cabbage heads. Similar study was conducted on cabbage by Reddy and Reddy (2011) for evaluating dissipation pattern of chlorpyrifos at the rate of 0.05 per cent which showed that initial deposits of 2.75 mg/kg dissipated more than 80 per cent on 7th day of spray with a half life of 1.76 days and a safe waiting period of 6.53 days. After second spray of same insecticide in tomato at 400 and 800 g a.i./ha, initial residues of 0.117 and 0.253 mg/kg were found with a half life of 2.9 and 3.3 days, respectively (Gupta et al. 2011).

Samriti et al. (2012) investigated dissipation pattern of chlorpyrifos in okra after being applied at single (275 g a.i./ha) and double doses (550 g a.i./ha) which resulted in initial residues of 0.07 mg/kg and 0.15 mg/kg, respectively, which further dissipated to 92% after 10 days at the corresponding doses. The observed half-life times were 0.6 days. Jyot et al. (2013) carried out a field experiment to investigate chlorpyrifos persistence on chilli crops with application rates of 500 and 1000 g a.i./ha and found initial deposits as 0.59 and 2.02 mg/kg. With a single dose and a double dose, the initial deposits half lives were 4.43 and 2.01 days, respectively. In brinjal fruits, field tests were done by Chandra et al. (2014) to examine chlorpyrifos dissipation after being applied at 100, 200 and 300 g a.i./ha. Initial deposits on brinjal were 0.362, 0.679 and 0.876 mg/kg, respectively.

Gupta et al. (2015a) reported average initial deposits of 0.604 and 0.805 µg/g on cabbage when chlorpyrifos was applied at 400 and 800 g a.i./ha, respectively. The computed half-life value and safe waiting times were 0.68-0.76 and 1 days for the corresponding doses. In another study conducted by Ramadan et al. (2016) on tomato found the initial residues of 4.280 mg/kg when chlorpyrifos was applied at 1140 g a.i. ha. The insecticide residues incorporated into the plants decreased with a half-life time around 2.5 days and an estimated PHI (Pre Harvest Interval) of 15 days was recorded. Kavitha et al.

(2016) investigated the dissipation of a single dosage of chlorpyrifos in both an open field and polyhouse conditions and found that initial chlorpyrifos deposits on capsicum ranged between 0.468 and 0.882 mg/kg. In both open field and poly house situations, chlorpyrifos residues that were discovered two hours after the previous spray had reduced to below determination levels (BDL) of 0.05 mg/kg by the 7th and 15th days, respectively. Similar studies on same crop with same conditions were conducted by Shukla et al. (2016b) where they reported initial residue of 0.28 and 0.22 mg/kg which reached the BDL in 20 days of spray with half lives of 3.14 and 5.40 days in greenhouse and open field condition, respectively. Katna et al. (2018) conducted a persistence study of chlorpyrifos on french bean in Himachal (Solan) conditions. Chlorpyrifos was applied thrice on beans at doses of 600 and 1200 g a.i./ha, respectively. Initial deposits of chlorpyrifos on pods were 3.083 and 6.017 mg/kg, respectively, with half-lives of 1.86 and 2.29 days. After 15 days after applying a double dosage of chlorpyrifos, residue levels in french beans dropped below the LOQ.

Brar (2018) who revealed that the initial residues of chlorpyrifos on brinjal were 1.096 mg/kg and 1.982 mg/kg with a per cent dissipation of 92.25 and 95.72 per cent at 7 and 10 days interval at application rate of 300 and 600 g a.i./ha, respectively.

5.5.3 Persistence studies in soil

Fang et al. (2006) investigated the dissipation of chlorpyrifos in pakchoi (*Brassica chinensis*) cropped soil. At the single dose, the dissipation half-lives (DT₅₀) were 0.6–1.2 days in a greenhouse and 0.4–1.0 days in the open field and at a double dose, the corresponding values were 1.2–2.1 days in a greenhouse and 0.5–1.3 days in an open field. When using Action 55 EC (chlorpyrifos 50%+cypermethrin 5%) @ 0.8 and 1.6 L/ha on tomato crops, Gupta et al. (2011) found no chlorpyrifos residues in the soil on the day of application for single dose and detected residues (0.012 mg/kg) at double dose that became below detection level after 3 days. According to Samriti et al. (2012), chlorpyrifos residues were determined to be 15 mg/kg at the single dose (275 g a.i./ha) and 36 mg/kg at the double dose (550 g a.i./ha) in the soil beneath the okra crop. There were no chlorpyrifos residues detected in soil samples taken on the 7th and 15th day following application. Mackay et al. (2014) reported DT₅₀ values for chlorpyrifos in soil ranging from 168 to 720 h (7 to 30 days).

Singh (2017) investigated the fate of acephate, chlorpyrifos, quinalphos and triazophos in cucumber soil. Examination of soil residue data revealed that initial deposits of

chlorpyrifos were 0.112 mg/kg for the recommended dose (300 g a.i./ha) and 0.198 mg/kg for the double dose (600 g a.i./ha) on the third day after spray. At 3 and 7 days after spray all pesticide residues in soil were below the detectable level.

According to Katna et al. (2018), bean cropped soil had chlorpyrifos residues below the limit of quantification (LOQ) at harvest (45 days). The residues of chlorpyrifos @ 400 and 800 g a.i./ha were found below LOQ (< 0.01 mg/kg) within 20 days in cabbage field soil (Sharma 2020a).

5.6 Cyantraniliprole

5.6.1 Residue estimation

On UPLC-MS/MS fitted with C₁₈ column and mobile phases A: acetonitrile/0.2% acetic acid; B: water/0.1% acetic acid, cyantraniliprole residues in pakchoi and soil were examined. At 0.2 ml/min, the flow rate remained constant with a injection volume of 10 µl. The column temperature was kept at 40°C. Electrospray ionisation (ESI) source in the positive ion mode was used to carry out MS/MS detection in the selected reaction monitoring (SRM) mode. It was discovered that cyantraniliprole had a retention time of 1.82 minutes (Sun et al. 2012).

The samples of soil and cabbage were extracted with acetonitrile and final supernatant was filtered through a 0.2-µm syringe filter for analysis. For estimation of cyantraniliprole residues HPLC with PDA detector was used. The mobile phase used for elution was a mixture of water and methanol in the ratio of 30:70 at a flow rate of 0.70 mL/min. The injection volume was fixed at 5 µl and absorbance was recorded at 280 nm. To determine the LOD and LOQ, a signal-to-noise (S/N) ratio greater than 3 and 10, respectively, in HPLC chromatograms was considered (Kumar et al. 2021).

5.6.2 Persistence studies on crop

Sun et al. (2012) conducted a study on dissipation patterns of cyantraniliprole in pakchoi under field conditions and recorded initial concentration of 1.58 and 0.95 mg/kg in 2009 and 1.43 and 0.70 mg/kg in 2010 from Guangdong and Shanghai. The half-life time of cyantraniliprole was 2.9 and 5.3 days during 2009 and 3.6 and 6.4 days during 2010, respectively. Hu et al. (2013) used ultra-performance LC (UPLC)/MS/MS to conduct cyantraniliprole dissipation pattern. At three concentrations (0.01, 0.1 and 0.5 mg/kg), the average recoveries of cyantraniliprole in watermelon ranged from 85.71 to 105.74 per cent,

with RSD of 0.90-6.34 per cent. The trial findings revealed that the half-lives of cyantraniliprole from Zhejiang and Hunan were 1.1 and 2.7 days, respectively.

When comparing the initial residues (7-14 days) to the final plot (30-40 days before harvest), there was a 91.1 and 89.1 per cent drop in cyantraniliprole in grain and straw, respectively. For grain and straw, the biological half-lives of total cyantraniliprole were 11.3 and 9.4 days, respectively (Lee et al. 2019a). Kumar et al. (2021) conducted a study on residue dissipation of cyantraniliprole in cabbage and revealed that the initial deposits in cabbage were 0.403 and 1.195 mg/kg at 60 and 120 g a.i./ha, respectively. The initial residue decreased to 0.087 and 0.384 mg/kg on the 7th day and 0.032 and 0.141 mg/kg on the 15th day after application at X and 2X, respectively. After second application the initial deposits of 0.798 and 1.286 mg/kg decreased to 0.039 and 0.081 mg/kg on the 15th day at respective doses. The calculated dissipation half-lives of cyantraniliprole in cabbage were 3.5–4.2 days at single dose and 3.9–4.8 days at double dose.

After two applications of Cyantraniliprole 7.3% w/w + Diafenthiuron 36.4% w/w SC @ 60 + 300 g a.i./ha, residual and dissipation investigations of diafenthiuron and cyantraniliprole were conducted on okra under field circumstances. In single and double doses, the initial total diafenthiuron and cyantraniliprole residues in okra fruit were 0.28 and 0.55 mg/kg and 0.23 and 0.42 mg/kg, respectively. Residues decreased to below the limit of quantification (LOQ) of 0.01 mg/kg at 10 days for diafenthiuron and 7 and 10 days in both dosages for cyantraniliprole. The recommended waiting period for safe intake of okra is ten days (Sharma et al. 2022).

5.6.3 Persistence studies in soil

A study on the cyantraniliprole dissipation patterns in pakchoi field soil was done by Sun et al. (2012). In soil samples from Guangdong and Shanghai, the initial values of cyantraniliprole were 0.03 and 0.05 mg/kg and 0.03 and 0.06 mg/kg with a half-life of cyantraniliprole as 8.7 and 8.8 days in 2009 and 2010, respectively. Hu et al. (2013) revealed from their trial results the half-lives of cyantraniliprole obtained after soil treatment was 4.1 days in Zhejiang and 2.6 days in Hunan, respectively. The average levels of cyantraniliprole residues soil was below detection limit at 14 days after treatment.

After the first treatment, the zero-day deposits in cabbage cropped soil at 60 and 120 g a.i./ha were 0.031 and 0.051 mg/kg and after the second application, they were 0.139 and

0.246 mg/kg at the rate of 60 and 120 g a.i./ha, respectively. After the second application, maximum concentrations of 0.819 and 1.061 mg/kg at single and double doses were recorded on the 5th day. These concentrations subsequently dropped to 0.212 and 0.372 mg/kg on the fifteenth day. The dissipation half-lives of cyantraniliprole in cabbage soil were determined to be 3.8–5.3 days at single dose and 4.1–4.7 days at double dose, respectively (Kumar et al. 2021)

5.7 Imidacloprid

5.7.1 Residue estimation

The extraction and cleanup of chilli fruit samples were prepared following the QuEChERS method for the determination of imidacloprid residues. The imidacloprid residues were quantified by using HPLC. The mobile phase used was acetonitrile and water (1:1) with a flow rate of 1 ml/min. The retention time was 4.05 minutes when detected at wavelength of 270 nm with an injection volume of 20 µl. Limit of quantification was recorded as 0.05 mg/kg (Mathew et al. 2012).

The estimation of imidacloprid residues in cucumber fruits was carried out by Nasr et al. (2014) by using a High Pressure Liquid Chromatography (HPLC) fitted with a diode array UV detector (wavelength of 270 nm). The column was C₁₈ and the mobile phase was (acetonitrile/water) (40/60 v/v). The injection volume was 20 µl and the flow rate utilised was 0.8 ml/min. The retention time of imidacloprid under these conditions was 3.2 minutes.

5.7.2 Persistence studies on crop

After spraying Confidor 200SL at 0.3 and 0.6 ml/l at the fruiting stage, Indumathi et al. (2001) examined the persistence of imidacloprid in okra. At the indicated dosage, imidacloprid had a half-life of 2 to 4 days. However, 10 days after treatment with the lower dose and 15 days after treatment with the greater concentration, the residues were no longer traceable. A similar observation was made by Sivaveerapandian et al. (2002) who studied the dissipation pattern of imidacloprid on okra fruits, which revealed that no residues of imidacloprid were found from treatment plots upon which seed and foliar spray was done. The residue of imidacloprid persisted up to 3rd and 5th day when applied at the rate of 20 and 40 g a.i./ha. Hassan et al. (2005) investigated the persistence of chlorpyrifos, imidacloprid and acephate on brinjal at application rate of 700, 700 and 300 ml/acre, respectively. The residues of the aforementioned pesticides varied from (max-min) 0.075-0.039, 0.030-0.015 and 0.067-0.040 ppm, respectively, over the three sampling periods of 3 hours, 3 days and 7

days. Romeh et al. (2009) conducted a study on imidacloprid in leaves and unwashed tomato fruits at the rate of 100 g a.i./feddan (1 feddan= 4200 m²) and found that the initial deposits of imidacloprid were found to be 4.22 and 1.95 mg/kg, respectively, which reduced to levels of 0.44 and 0.075 mg/kg with a dissipation of 89.57 and 96.15 per cent of initial residues after 14 days of spraying. Imidacloprid leaves and unwashed tomato fruits both had half-lives ($T_{1/2}$) of 61.92 and 60.00 hours, respectively.

After applying imidacloprid at rates of 60 and 120 g a.i./ha at 7 days interval, the dissipation pattern of imidacloprid in brinjal was investigated by Mandal et al. (2010). At a single application rate and a double application rate, the half-lives for imidacloprid deposits were 2.31 and 2.18 days, respectively. The residues of imidacloprid required 10 days from both the dosages to fall below the detection limit of 0.01 mg/kg. Another study on persistence of imidacloprid at two doses (@ 30 and 60 g a.i./ha) on greenhouse cucumbers was conducted by Hassanzadeh et al. (2012) which revealed that at X and 2X doses of imidacloprid the initial residues of 1.93 and 3.65 mg/kg was found with a dissipation of 94.80 and 99.18 per cent, respectively. At single and double dose of imidacloprid a half life of 3.40 and 2.70 days was found, respectively.

After three applications of the combination product Solomon (β -cyfluthrin 9% + imidacloprid 21%) @ 18 and 36 g a.i./ha and 42 and 84 g a.i./ha, respectively, Patel et al. (2012) conducted persistence experiments of β -cyfluthrin and imidacloprid on okra fruits. Initial deposits for imidacloprid and β -cyfluthrin were 0.18 and 0.56 μ g/g and 0.30 and 1.23 μ g/g at recommended and twice the recommended doses, respectively. On the third day, both pesticides at the indicated dose were below the BDL of 0.01 μ g/g. At the indicated dosage, the half-lives of β -cyfluthrin and imidacloprid were 0.60 and 0.49 days, respectively.

A field trial was conducted by Varghese et al. (2015) on persistence study of imidacloprid and acetamiprid @ 20 g a.i./ha on chilli fruits. The result showed that initial residue of imidacloprid and acetamiprid were found to be 1.27 and 2.44 mg/kg which persisted for 7 and 15 days, respectively. From the dissipation data, the half-life values and waiting period of acetamiprid and imidacloprid were 2.27 and 7.18 and 2.08 and 11.26 days, respectively. Nasr et al. (2014) conducted an experiment on dissipation studies of imidacloprid on cucumber which revealed that the residues of imidacloprid were found to be less than the MRL value of 1 mg/kg further dissipated with half life of 2.2 days.

In their study on imidacloprid dissipation on okra, Karthik et al. (2015) reported initial deposits of 0.15 and 0.26 µg/g, respectively. Five days after application, at both doses, the residues were below the detection limit (BDL) of 0.01 µg/g with half-lives varied between 1.04 and 1.13 days, respectively. Gupta et al. (2015b) conducted an experiment on persistence study of imidacloprid on brinjal and revealed that at the application rate of 20 g a.i./ha the initial deposits of imidacloprid were 0.652 mg/kg which dissipated to 93.17 per cent on 10th day with a half life and waiting period of 1.92 and 4.70 days, respectively.

Another study conducted by Pandit et al. (2016) revealed that imidacloprid residue in okra leaf dissipated from 38– 48 per cent analysis on okra leaf and in fruit from 31– 44 per cent when applied @ 24.5 g a.i./ ha and @ 49.0 g a.i./ha, respectively. The residues found to be below detection limit within 15-20 days in leaves and 7 days in fruits with a half life ranging between 2.66–3.28 days in leaves and 1.76–2.07 days in fruits, respectively.

In a study performed by Sharma et al. (2018) on imidacloprid (0.018%), indoxacarb (0.015%) and lambda-cyhalothrin (0.004%) in a tomato field revealed that the initial deposits of lambda-cyhalothrin, indoxacarb and imidacloprid were found to be 0.643, 0.401 and 0.550 mg/kg, respectively. On the 10th day after spraying residues were below detectable levels. Imidacloprid, indoxacarb and lambda-cyhalothrin each had a half-life of 2.91, 5.26 and 3.06 days, respectively. The safe preharvest time for lambda-cyhalothrin, indoxacarb and imidacloprid were 0.36, 0.46 and 1.03 days, respectively.

Initial imidacloprid deposits on cabbage heads were determined by Bhartiya (2018) and recorded residues as 0.392 and 0.795 mg/kg when applied at rates of 25 and 50 g a.i./ha, respectively. The residues persisted for 3 and 5 days with a dissipation of 72.96 and 87.92 per cent at X and 2X dosage, respectively.

5.7.3 Persistence studies in soil

After being applied at rates of 60 and 120 g a.i./ha, the soil under brinjal was examined to determine dissipation of imidacloprid and β-cyfluthrin. A soil sample collected at 15 days following the last application did not reveal the presence of imidacloprid or β-cyfluthrin (Mandal et al. 2010). In addition, the residual dissipation of imidacloprid on grapes was investigated by Mohapatra et al. (2011b). The data showed that both the standard dose (80 g a.i./ha) and the double the standard dose (160 g a.i./ha) of imidacloprid residues in soil at harvest (105 days after the last treatment) were found to be below the detectable limit (0.05 mg/kg).

Nath and Thomas (2013) examined the dissipation pattern of imidacloprid applied as termiticidal application @ 120, 240 and 480 g a.i./ha in cultivated soil during cardamom production. According to the study, residues might be found in the treated soil for up to 20 days. The insecticide dissipation followed first-order kinetics and its half-life ranged from 2.58 to 3.96 days.

Akoijam and Singh (2014) examined the metabolism degradation and persistence of imidacloprid in paddy field soil with two applications @ 20 and 80 g a.i./ha at a interval of 10 days. The initial deposits of total imidacloprid were 0.44 and 1.61 mg/kg and the half-life value were 12.04 and 11.14 days at corresponding doses. In West Bengal, Pandit et al. (2016) conducted a study on persistence of imidacloprid at two doses of 24.5 g a.i./ha and 49.0 g a.i./ha in okra field soil, along with an untreated control. The findings demonstrated that, on 1st and 3rd day of application residues in the soil of an okra crop approached BDL, respectively.

5.8 Spirotetramat

5.8.1 Residue estimation

The green chilli samples were extracted thrice with acetonitrile and partitioned with 25 ml hexane and concentrated extract was cleaned by activated florisil sandwiched between layers of anhydrous Na₂SO₄. The residues of spirotetramat was analyzed on HPLC equipped with Photodiode Array detector and C18 column with a mobile phase of acetonitrile:water (1:1) and injection volume of 20 µl with a flow rate of 1ml/min. spirotetramat was analyzed at wavelength of 245 nm with a retention time of 9.8 min. (Mathew et al. 2012).

Tomato samples were extracted and cleaned up by using modified QuChERS technique. The residues of spirotetramat in tomato samples were analyzed by using HPLC equipped with diode array detector and quaternary pump (LC-20 AT) with a mobile phase of acetonitrile:water (80:20) and injection volume of 20 µl and flow rate of 0.8 ml/min. The residues were detected at wavelength of 254 nm and retention time was 4.39 minute (Wasu et al. 2020).

5.8.2 Persistence studies on crop

Mathew et al. (2012) evaluated the dissipation pattern of combination mix (spirotetramat +imidacloprid) at two doses of 120+120 and 240+240 g a.i./ha. The mean

initial deposit of spirotetramat and imidacloprid in green chilli was 1.2 and 1.752 mg/kg and 2.53 and 3.15 mg/kg for X and 2X dose, respectively which further dissipated reached below quantification limit within 15 and 20 (spirotetramat) and 30 and 35 days (imidacloprid). The half life values of spirotetramat were 2.01 and 3.09 days and for imidacloprid it was 5.82 and 5.77 days at respective doses. Similar study was conducted by Chahil et al. (2015) who studied persistence and dissipation pattern of spirotetramat and imidacloprid on chilli at application rate of 120 and 240 g a.i./ha and concluded that initial residues of 0.55 and 1.22 mg/kg and 0.73 and 1.49 mg/kg were recorded at respective doses. After 5 and 7 days (spirotetramat) and 7 and 10 days (imidacloprid) at X and 2X doses, respectively, residues of both the insecticide were below its limit of quantification (LOQ) of 0.03 mg/kg (spirotetramat) and 0.01 mg/kg (imidacloprid). At recommended and double the recommended dosages, the half-lives of spirotetramat and imidacloprid were found to be 1.91 and 1.30 days and 1.41 and 1.65 days, respectively. Both the studies vary from each other this may be due to the varied weather conditions.

Dissipation pattern of spirotetramat on brinjal fruits was studied by Shukla et al. (2016a) following three applications @ 90 and 180 g a.i./ha. The initial residues at single dose were found below determination level ($< 0.05 \mu\text{g/g}$) and $0.08 \mu\text{g/g}$ at double dose, respectively. The half-life ($T_{1/2}$) of the spirotetramat on brinjal fruits was found to be 1.71 days for the double dose.

Patyal et al. (2018) conducted study of spirotetramat on apple and found that initial residues were in range of 0.799- 0.996 and 1.596-1.786 mg/kg when applied at 150 and 300 g a.i./ha on apple in Himachal and J&K with a half life of 1.90-2.02 and 2.00-2.32 days at respective doses.

Jankowska et al. (2020) conducted a study on dissipation pattern of spirotetramat in basil, peppermint and sage and found that their initial concentration decreased to 0.196 mg/kg, 0.030 mg/kg and 0.125 mg/kg, respectively, indicating that up to 99 per cent of the initial concentrations reduced within 21 days. The half-life of spirotetramat was 0.51, 0.52 and 0.83 days in basil, peppermint and sage, respectively. Wasu et al. (2020) studied the persistence of spirotetramat from the combi product spirotetramat 120 SC + imidacloprid 120 SC @ (75 and 150 g a.i./ha) at fruiting stage and revealed that initial deposit of spirotetramat on tomato at single dose were found to be 0.57 and 1.20 mg/kg at double dose, similarly, initial imidacloprid residue of 0.76 and 1.52 mg/kg were found at single and double dose

respectively. On 5th and 7th day the residues reached below quantification limit (BQL) for spirotetramat and imidacloprid with half life of 1.93, 1.37 and 1.40, 1.92 days, respectively. Sharma (2020a) found the initial residues of spirotetramat on cabbage heads as 0.327 and 0.726 mg/kg at application rates of 90 g a.i./ha and 180 g a.i./ha, respectively.

5.8.3 Persistence studies in soil

Mohapatra et al. (2012) revealed from their study that residues of spirotetramat in mango field soil were below the determination limit of 0.05 mg/kg at harvest. According to Vemuri et al. (2014), spirotetramat and imidacloprid concentrations in mature grape berries and soil samples taken at harvest from plots treated with the X (90 g a.i./ha) and 2X (180 g a.i./ha) doses of the pesticide were below the determination level in grape orchards. They also came to the conclusion that spirotetramat vanished quickly in soil.

Shukla et al. (2016a) revealed that soil samples collected at 15th day from brinjal field showed spirotetramat residues below determination level of 0.05 µg/g at 90 and 180 g a.i./ha.

Patyal et al. (2018) also found no residues of spirotetramat in apple tree basin soil at the LOQ level of 0.03 mg/kg at all the four locations (H.P. and J&K) at harvest. Sharma (2020a) found that spirotetramat residues in cabbage cropped soil were found below LOQ (0.05 mg/kg) within 20 days at X dose of 90 g a.i./ha and 2X dose of 180 g a.i./ha.

5.9 Flubendiamide

5.9.1 Residue estimation

Battu et al. (2008) standardized an analytical method for the estimation of residues of flubendiamide in various substrates like cabbage, tomato, pigeonpea grain, pigeonpea straw, pigeonpea shell, chilli and soil. Residues were estimated using HPLC equipped with a UV detector at 230λ and a C18 column. Acetonitrile: water (60:40 v/v) at 1 mL/min was used as mobile phase. Both flubendiamide and des-iodo flubendiamide presented distinct peaks at retention times of 11.07 and 7.99 min, respectively. Consistent recoveries ranging from 85 to 99% for both compounds were observed when samples were spiked at 0.10 and 0.20 mg/kg levels. The limit of quantification of the method was worked out to be 0.01 mg/kg.

In a study undertaken by Sharma and Parihar (2013) estimation was done on HPLC Shimadzu LC-20 AT equipped with PDA by using Chromolith RP-18 column, mobile phase

used acetonitrile:water (60:40, v/v) with flow 1.0 mL/min. Retention times were recorded as 3.77 and 1.79 minutes for flubendiamide and thiacloprid, respectively. Methods were validated by conducting recovery studies both in tomato and soil. Samples were fortified with flubendiamide and thiacloprid at 0.01 and 0.1 µg, respectively. Limit of quantitation (LOQ) was found to be 0.01 mg/kg.

5.9.2 Persistence studies on crop

Sahoo et al. (2009) conducted a study on persistence of flubendiamide on chilli and found initial residues of 1.06 and 2.00 mg/kg at application rate of 60 and 120 g a.i./ha at 10 days interval. Flubendiamide residues dissipated upto 80 per cent in 3 days of the last application at both the dosages and persisted for 7 and 10 days with a half life of 0.96 and 0.91 days respectively at single and double dosages. Dissipation pattern of flubendiamide was studied by Kooner et al. (2010) on tomato which revealed that at 48 g a.i./ha residues dissipated with a half life of 0.33 and 1.00 day and were below determination limit of 0.01 mg/kg after 3 days after spray. In a study by Mohapatra et al. (2010), flubendiamide residue in cabbage after two applications of flubendiamide 480 SC @ 24 and 48 g a.i./ha was evaluated and found that initial residue of 0.33 and 0.49 mg/kg persisted for 10 days with a half life of 3.9 and 4.45 days, respectively.

According to Chawla et al. (2011), flubendiamide 480 SC persisted for 3 and 7 days following the final spray at doses of 90 (standard dose) and 180 (double dosage) g a.i./ha, respectively on brinjal fruits. On the fifth and tenth days, the initial deposits of 0.17 and 0.42 µg/g with half-lives ranging from 2.68 to 2.55 days at standard and double dose, reached below determination level (BDL) of 0.05 µg/g, respectively. Following three applications of flubendiamide at 10 days interval at 60 and 120 g a.i./ ha, Parmar et al. (2012) reported average initial deposits of 0.22 and 0.31 mg/g on chilli fruits. Flubendiamide residues were below detectable levels (BDL) of 0.05 µg/g following 3 and 5 days of treatment for recommended and double the recommended dose, respectively. At single and double doses, the half-life of flubendiamide was found to be 1.12 and 1.76 days, respectively. Takkar et al. (2012) conducted a field study on persistence of flubendiamide on brinjal at 90 and 180 g a.i./ha and found that initial residues of 0.33 and 0.61 mg/kg dissipated to 76 and 79 per cent with a half life ranged from 0.62 and 0.54 days, respectively. The durability of flubendiamide in okra fruits after foliar application at 24 g a.i./ha and 48 g a.i./ha was assessed by Das et al. (2012). According to HPLC investigations, initial deposits of 0.28 and 0.53 µg/g in okra fruits were below the determination limit of 0.01µg/g on 7 and 10 days, respectively with a

half-life of 4.7 to 5.1 days. Similar to this, flubendiamide dissipation pattern at 60 g a.i./ha on okra fruits was investigated by Reddy et al. (2013) where they found that initial deposit of 1.49 mg/kg had dissipated by 98.88 per cent and were below detectable level (BDL) on 7th day with a half-life of 1.83 days.

Another study on tomatoes was performed by Sharma et al. (2014a) who evaluated the persistence data of flubendiamide at 48 and 96 g a.i./ha and revealed that residues of flubendiamide were below detection limit on 20th day after spray in both doses with half life ranged from 0.33 to 3.28 days and 1.21 to 3.00 days at X and 2X dose with a safe consumption period of 1 day.

Buddidathi et al. (2015) conducted a capsicum field study on flubendiamide @ 48 and 96 g a.i./ha and found initial deposits of 0.665 and 1.545 mg/kg with RL₅₀ values of 4.3 and 4.7 days, respectively. Dissipation studies of flubendiamide on okra was conducted by Meenambigai et al. (2017) who found that after two sprays, initial residue 1.16 µg/g were dissipated more than 80 per cent in 5 days after application of flubendiamide at 48 g a.i./ha. The residues persisted up to 7 days after treatment and further dissipated to below detectable limit (BDL < 0.05 µg/g) on 10th day after treatment. Half life of 1.64 days and waiting periods of 4.6 days was observed.

Akshima (2019) concluded that after application of flubendiamide in combi product @ 36 and 72 g a.i./ha, initial deposits of 0.423 mg/kg and 0.815 mg/kg were recorded in chilli. The half life values of flubendiamide deposits at single and double doses were 1.85 and 1.72 days with a safe waiting period of 5.71 and 6.94, respectively. Gautam (2019), who evaluated that the initial deposits (0.535 and 0.921 mg/kg) of flubendiamide on okra fruits at application rates of 36 and 72 g a.i./ha dissipated to 87.42 and 84.21 per cent after the 10th day of treatment, respectively. The flubendiamide deposits dissipated to half in 3.34 and 3.69 days with a safe waiting period of 4.74 and 8.13 days at X and 2X dose, respectively.

Reddy et al. (2020) conducted the experiment to study the dissipation pattern of flubendiamide @ 60 g a.i./ha on field bean and revealed that the initial deposits of 1.79 mg/kg were detected on bean pods with a dissipation per cent of 49.72, 71.51, 92.74 and 96.65 per cent recorded at 1, 3, 5 and 7th day, respectively.

5.9.3 Persistence studies in soil

Sahoo et al. (2009) performed a field trial on persistence of flubendiamide in chilli field soil and it was revealed that no residues of flubendiamide was found at application @ 60

and 120 g a.i./ha on the crop. According to Mohapatra et al. (2010), soil samples taken from cabbage field were free of any flubendiamide residues at doses of 24 and 48 g a.i./ha after 15 days of spray application. No residues of flubendiamide were found when tomato field soil was treated with flubendiamide @ 48 and 96 g a.i./ha, respectively at harvest (Mohapatra et al. 2011a).

Flubendiamide (Fame 480 SC) residues in brinjal cropped soil were at BDL (0.05 µg/g) at both dosages when taken after 15 days of last spray at 90 g a.i./ha (single dose) and 180 g a.i./ha (double dose) (Chawla et al. 2011).

Flubendiamide persistence in okra field soil was assessed by Das et al. (2012) following applications at 24 and 48 g a.i./ha. Flubendiamide residues at both doses were found below detection limit (0.05 µg/g) after 15th day following the last spray. Paramasivam and Banerjee (2011) also observed that soil residues of flubendiamide in tomato cropped soil were below detection level (0.01 µg/g) on 10th day after last spray at either dose of application.

Gautam (2019) conducted a study of persistence of flubendiamide in okra field soil and found that residues were found to be below determination level (0.05 mg/kg) after 20 days of application of combination product of flubendiamide + deltamethrin (Fame Quick) at standard (36 + 24 g a.i./ha) and double dose (72 + 48 g a.i./ha). Similar results were found by Akshima (2019) in chilli field soil.

Persistence studies on red chilli fruits

Sharma *et al.* (2011) revealed from their study that residues of flubendiamide and thiacloprid in red chilli at application rate of 60 and 120 g a.i./ha were below determination level of 0.05 mg/kg. When the combination mix (spirotetramat 120 + imidacloprid 120) - 240 w/v SC was applied at two doses of 120+120 and 240+240 g a.i./ha, no residues of imidacloprid and spirotetramat beyond the limit of quantification could be found in red chillies at harvest (Mathew et al. 2012). When treated at 1000 and 2000 ml/ha, red chilli samples taken 20 days following the last application failed to detect spirotetramat and imidacloprid at their respective detection limits (Chahil et al. 2015). After being applied at 60 and 120 g a.i./ha, red chillies collected after 20 days did not show the presence of flubendiamide (Parmar et al. 2012).

6. Risk assessment

To investigate the environmental behaviour and translocation of imidacloprid residues in three crops eggplant, cabbage and mustard, Mukherjee and Gopal (2000) undertook a field trial at IARI, New Delhi. In eggplant, cabbage and mustard leaves, the TMRC (Theoretical Maximum Residue Contribution) derived from residue data was discovered to be 0.265, 0.305 and 0.159 mg/kg, respectively. This was less than the MPI (Maximum Permissible Intake) (3.13 mg/kg/day), which was determined by toxicological information. Consequently, it was determined that using imidacloprid was safe. With TMRC values of 0.069 and 0.1497 mg/person/day at 20 and 40 g a.i./ha of imidacloprid, respectively, which were lower than the MPI (3.135 mg/person/day) it was concluded that the imidacloprid was safe for consumption on mustard crop (Kumar and Dikshit 2001). Similar findings came from a study conducted by Arora et al. (2009) who evaluated the risk associated with the usage of imidacloprid on grape fruit.

Sharma et al. (2014b) estimated MPI as 1.21 mg/person/day. The TMRC values on day 0 were found to be 0.033, 0.014, 0.044 and 0.042 mg/kg b.w./day, as TMRC value was less than MPI value, spiromesifen falls under the acceptable risk range based on data reflecting maximum residues that may occur under worst conditions on recommended dose (150 g a.i./ha). Based on the HQ values, the safety of spiromesifen has also been evaluated. The estimated average daily intake (EADI) and hazard index value for fenvalerate in maize were 1.71×10^{-3} mg/kg b.w./day and 0.086, respectively and for cowpea EADI (Estimated Average Daily Intake) and hazard index values were 1.71×10^{-4} mg/kg b.w./day and 0.006 respectively, which concluded safe use for both crops (Akoto et al. 2013). The EDI values of chlorpyrifos in brinjal, lady finger and tomato were 0.0059, 0.0008 and 0.0001 mg/kg/day with health risk index of 1.97, 0.27 and 0.023, respectively which show minimal health risk to the consumers (Hossain et al. 2015). According to Liu et al. (2016), the EDI value of fenvalerate in persimmon fruit was 5.28×10^{-4} mg/kg b.w./day and the HQ value was 2.64 per cent for adults, showing that there was little to no risk to health from usage of fenvalerate on persimmon at recommended doses. Chahil et al. (2015) calculated the dietary risk for spirotetramat and imidacloprid in chilli. From the data it was concluded that MPI value for spirotetramat and imidacloprid was 2750 and 3300 $\mu\text{g}/\text{person}/\text{day}$ and TMRC values on 0 day were found to be 1.375 and 3.050 $\mu\text{g}/\text{person}/\text{day}$ and 1.825 and 3.725 $\mu\text{g}/\text{person}/\text{day}$ at 120 and 240 g a.i./ha, respectively. The data concluded that the consumer health risks for both the insecticide are minimal at both the dosages on chilli. Using risk quotients, the citrus

risk assessment was assessed. When applying the recommended levels of spirotetramat in citrus, the danger to human health was found to be significantly <1 , indicating that the risk was minimal (Zhang et al. 2017).

Chawla et al. (2018) assess the dietary risk of beta-cyfluthrin and imidacloprid as parts of a combi product in/on chickpea. HQ for beta-cyfluthrin was 0.0010-0.0011 for standard dose and 0.0013-0.0015 for double dose while the corresponding values for imidacloprid were 0.0015-0.0018 and 0.0016-0.0018, respectively. The results showed that the use of beta-cyfluthrin and imidacloprid as a combi-product on chickpea was safe provided that proper PHI was followed. According to Kumar et al. (2021), cyantraniliprole in cabbage fruit poses an estimated dietary risk of 0.0001-0.0015 mg/kg b.w./day at single dose (60 g a.i./ha) and 0.0005-0.0043 mg/kg b.w./day at double dose (120 g a.i./ha). RQ (Risk Quotient) values ranged from 0.2902 to 0.0116 at X dose and from 0.4676 to 0.0295 at 2X dose. RQ values in every case were substantially lower than 1, demonstrating that even after two subsequent applications of cyantraniliprole on cabbage, there is virtually minimal danger of food exposure for people.

Paramasivam (2020) estimated the dietary risk of chlorantraniliprole in tomato fruit at 30 g a.i./ha on 0, 1, 3, 5 and 7 days interval, as its EDI value came out in the range of 0.0001-0.0034 mg/kg b.w./day and the HQ value in range of 0.00003-0.0021 for adult, indicating that chlorantraniliprole did not pose a significant health risk. The cumulative dietary risk quotient (RQ) calculated based on the collective pesticide residues for chlorantraniliprole present in the combi-product (Chlorantraniliprole 9.26 % + λ -cyhalothrin 4.63 % ZC) was less than 1 from 0 day (2hr) at single (30 g a.i./ha) and double dose (60 g a.i./ha) indicating no risk to consumer (Kansara et al. 2021).

The HQ was found to be 0.01, 0.004, 0.014 and 0.009 %, respectively, for the recommended dose (144 g a.i./ha) of spiromesifen in okra, chilli, capsicum and brinjal. Being below the 100% limit, this finding implies no danger or harmful effects related to dietary residue exposure to spiromesifen (Dubey et al. 2021). For different consumers, the chronic and acute dietary exposure assessment risk quotient (RQ) values of thiacloprid in cowpeas were 2.44–4.41 and 8.72–15.78 per cent, respectively and for spirotetramat, they were 1.03–1.87 per cent and 0.18–0.32 per cent, respectively. All of the RQ values were lower than 100%. Consumers were exposed to a greater dietary risk from thiacloprid through cowpeas than from spirotetramat (Li et al. 2022).

Chapter-3

MATERIALS AND METHODS

The current study entitled “**Bioefficacy and residue dynamics of some pesticides used against insect pests of brinjal and chilli**” was carried out in the Department of Entomology, Dr. Y. S. Parmar University of Horticulture and Forestry, Nauni, Solan (HP) during the year 2021 and 2022. Field trials were conducted at experimental farm and the residue analysis was done in the Pesticide Residue Laboratory (PRL) of the department. The analytical method was validated as per the requirements defined by SANTE (2021). This chapter presents the experimental information pertaining to materials utilized, study methods and observations made under given headings:

- 3.1 Location**
- 3.2 Raising of crop**
- 3.3 Treatments**
- 3.4 Bioefficacy studies**
- 3.5 Laboratory materials**
- 3.6 Cleaning of glassware**
- 3.7 Preparation of stock solutions**
- 3.8 Validation of analytical method**
- 3.9 Pesticides persistence studies**
- 3.10 Risk assessment studies of pesticides**

3.1 Location

The study area was located at Nauni, Solan, Himachal Pradesh, at an inclination of around 1200 metres above mean sea level, between 30°51'23" N latitude and 77°10'7" E longitude. The location is classified as zone II mid-hills agro climatically. The climate is sub-temperate, with annual rainfall ranging from 1100 to 1300 mm, the majority of which falls during the monsoon season (June-August).

3.2 Raising of crop

Seeds of brinjal *Solanum melongena*, variety Pusa Purple Long, and chilli *Capsicum annum* var. *annum*, variety DKC-8, were procured from the seed sale unit of Department of Seed Science and Technology, UHF Nauni, Solan. The fields were ploughed and a suitable

amount of fully decomposed farm yard manure and fertilisers were added to the soil before sowing the seeds. The plots were 2 m x 2 m in size. Plants were planted at a planting distance of 60 cm x 30 cm for brinjal and 45 cm x 45 cm for chilli, as per standard packages of practices of the university (Anonymous 2020). The experiment was laid out in Randomized Block Design (RBD) with 15 treatments for bioefficacy studies and 10 treatments for persistence studies including untreated control and was replicated thrice.

3.2.1 Climatic conditions

Table 3.1 Climatic parameters during spraying and sampling period of brinjal and chilli crop

Climatic conditions	Brinjal (March – September)		Chilli (March – October)	
	2021	2022	2021	2022
Average Maximum temperature (°C)	29.40	30.70	28.80	30.00
Average Minimum temperature (°C)	19.70	15.00	17.70	14.40
Average Relative Humidity Morning (%)	74.30	52.50	72.10	54.40
Rainfall (mm)	5.40	2.60	4.40	2.60

Source: Meteorological Observatory, Department of Environmental Science, Dr. Y.S. Parmar University of Horticulture and Forestry, Nauni, Solan (H.P.) 173 230

3.3 Treatments

Pesticides enlisted in Table 3.2 were applied for bioefficacy studies against major insect pests of chilli and brinjal at different doses i.e. less than recommended doses (x), recommended doses (X) and double the recommended doses (2X) and for persistence (fruit and soil) and risk assessment studies doses at recommended and double the recommended were taken for two consecutive seasons 2021 and 2022.

The pesticides were sprayed on both brinjal and chilli crop at the time of insect- pest population appearance with each pesticide dose and sprayed twice at an interval of 10 days for both bioefficacy and persistence studies. Control plots were sprayed with water only. Pesticides were sprayed with a knapsack sprayer fitted with a hollow cone nozzle. Both brinjal and chilli plants were thoroughly covered with spray fluid to run-off stage. Spraying was done on a clear day with little wind and all required steps were followed to avoid pesticide drift to adjacent plots. To eliminate pesticide carryover from one treatment to the next, the sprayer and measurement cylinder were carefully cleaned after each spray.

Table 3.2 Pesticides and their different doses applied

Crop	Treat ment	Pesticides		Dosage (g a.i./ha)	Source Company
		Common Name	Trade Name		
Brinjal	T ₀	Control			
	T ₁	Spiromesifen 22.9% SC (x)	Oberon	72	Bayer Crop Science Ltd.
	T ₂	Spiromesifen 22.9% SC (X)		96	
	T ₃	Spiromesifen 22.9% SC (2X)		192	
	T ₄	Fenazaquin 10 % EC (x)	Magister	94	DuPont FMC Insecticide
	T ₅	Fenazaquin 10 % EC (X)		125	
	T ₆	Fenazaquin 10% EC (2X)		250	
	T ₇	Chlorantraniliprole 18.5% SC (x)	Coragen	30	DuPont FMC Insecticide
	T ₈	Chlorantraniliprole 18.5% SC (X)		40	
	T ₉	Chlorantraniliprole 18.5% SC (2X)		80	
	T ₁₀	Fenvalerate 20% EC (x)	Sumicidin	60	Sumitomo Chemical India Pvt. Ltd.
	T ₁₁	Fenvalerate 20% EC (X)		75	
	T ₁₂	Fenvalerate 20% EC (2X)		150	
	T ₁₃	Chlorpyrifos 20%EC (x)	Vardan	150	HPM Chemicals and Fertilizers Ltd.
	T ₁₄	Chlorpyrifos 20% EC (X)		200	
T ₁₅	Chlorpyrifos 20% EC (2X)	400			
Chilli	T ₀	Control		-	
	T ₁	Cyantraniliprole 10.26% OD (x)	Benevia	45	DuPont FMC Insecticide
	T ₂	Cyantraniliprole 10.26% OD (X)		60	
	T ₃	Cyantraniliprole 10.26% OD (2X)		120	
	T ₄	Imidacloprid 17.8% SL (x)	Confidor	19	Bayer Crop Science Ltd.
	T ₅	Imidacloprid 17.8% SL (X)		25	
	T ₆	Imidacloprid 17.8% SL (2X)		50	
	T ₇	Spirotetramat 15.31% OD (x)	Movento	45	Bayer Crop Science Ltd.
	T ₈	Spirotetramat 15.31% OD (X)		60	
	T ₉	Spirotetramat 15.31% OD (2X)		120	
	T ₁₀	Flubendiamide 20% WG (x)	Takumi	38	Rallis India Ltd.
	T ₁₁	Flubendiamide 20% WG (X)		50	
	T ₁₂	Flubendiamide 20% WG (2X)		100	
	T ₁₃	Fenazaquin 10 % EC (x)	Magister	94	DuPont FMC Insecticide
	T ₁₄	Fenazaquin 10 % EC (X)		125	
T ₁₅	Fenazaquin 10% EC (2X)	250			

3.4 Bioefficacy studies

As a pre-treatment count, observations of insect incidence and number were made one day before spraying. After each pesticide spray, a post-treatment count was performed at 1, 3, 5, 7 and 10 days for jassids and thrips and for shoot and fruit borer after 5th and 10th day for shoot infestation. All the counts were taken during the morning hours. The data on fruit damage was also taken at the time of harvest through counting of total number of fruits and number of damaged fruits, plot wise.

3.4.1 Jassids

Five brinjal plants were selected randomly from each plot/replication and divided into three main strata: upper, middle and lower leaves and from each stratum, number of nymphs and adults were counted.

3.4.2 Thrips

Five chilli plants were selected randomly from each plot. Thrips population on each plant were estimated by counting thrips population on 10 randomly selected leaves and 10 flowers and mean number of thrips per plant was calculated. Thrips population on the chilli leaf surface and in the flower was estimated according to Bacci et al. (2008). The leaf was turned carefully in a way to avoid disturbance of the thrips and number of thrips were counted. Chilli flowers were detached from plant and shaken on white piece of paper and number of thrips (adults and nymph) was counted.

3.4.3 Shoot and fruit borer

Pre and post treatment counts (5 and 10 days after application) of infested shoots were made on five randomly selected plants and numbers of damaged shoots were observed. Beside this the fruits from five randomly selected plants per plot were harvested after each spray and number of healthy and damaged fruits were recorded treatment wise separately.

3.4.4 Statistical analysis

3.4.4.1 Jassids and Thrips

The per cent reduction of jassids and thrips population in all the treatments was calculated by using Henderson-Tilton's formula (Henderson and Tilton 1955) as under:

$$\text{Per cent reduction in population} = 100\left(1 - \frac{T_a}{T_b} \times \frac{C_b}{C_a}\right)$$

Where, T_a = Number of insects after treatment

T_b = Number of insects before treatment

C_a = Number of insects in untreated control after treatment

C_b = Number of insects in untreated control before treatment.

Post-treatment counts were made after 1, 3, 5, 7 and 10 days of pesticide application. The per cent reduction in population was calculated at different days interval. The data



Plate 1. Experimental view of brinjal in field



Plate 2. Experimental view of chilli in field



Plate 3a. Attack of jassids (*Amrasca biguttula biguttula*) on brinjal

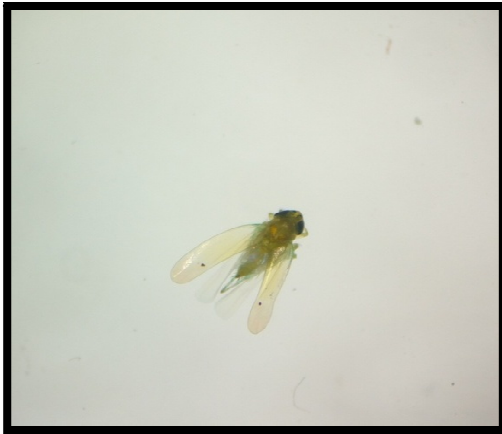


Plate 3b. Adult and nymph of jassids under microscope



Plate 4a. Toppling of shoot due to attack of shoot and fruit borer



Plate 4b. Larva of shoot and fruit borer in shoot



Plate 4c. Fruit with a bore hole caused by larvae of brinjal



Plate 4d. Larva of shoot and fruit borer



Plate 5a. Adult and nymph of thrips on chilli flower



Plate 5b. Chilli leaf curl due to thrips attack



Plate 5c. Adults of thrips under microscope



Plate 6a. Adult of *Coccinella septempunctata* on brinjal



Plate 7a. Adult of *Coccinella septempunctata* on chilli



Plate 7b. Adult of *Hippodamia variegata* on chilli

obtained were assigned to angular transformations, analysed statistically by applying RBD as suggested by Gomez and Gomez (1984).

3.4.4.2 Shoot and Fruit borer

Shoot infestation due to shoot and fruit borer was recorded in the form of toppled shoots from 5 randomly selected plants per plot before and after (5 and 10 days) each spray. The fruits from five randomly selected plants per plot were harvested after each spray and number of healthy and damaged fruits (observations based on insertion holes present on damaged fruit) was recorded treatment wise separately and per cent fruit infestation/damage was worked out. The per cent shoot and fruit damage was calculated by using the following formula (Guru and Patil 2018).

$$\text{Per cent shoot infestation} = \frac{\text{Number of infested shoots}}{\text{Total number of shoots}} \times 100$$

$$\text{Per cent fruit infestation} = \frac{\text{Number of infested fruits}}{\text{Total number of fruits}} \times 100$$

The data obtained were assigned to square root transformation, analysed statistically by applying RBD as suggested by Gomez and Gomez (1984).

3.4.5 Phytotoxicity studies

Phytotoxicity was observed on brinjal and chilli plants due to the application of treatments for yellowing, stunting, necrosis, chlorosis, vein clearing, epinasty and hyponasty at an interval of 1, 3, 5, 7 and 10 days as per the rating scale (0-10) as mentioned in Table 3.3.

Table 3.3: Phytotoxicity rating scale (PRS)

Crop response/ Crop injury	Rating
0	0
1-10%	1
11-20%	2
21-30%	3
31-40%	4
41-50%	5
51-60%	6
61-70%	7
71-80%	8
81-90%	9
91-100%	10

3.4.6 Effect of pesticides on beneficial insects

The presence of beneficial insects was observed on 5 plants per replication in the pesticide treated plots compared with the untreated control plot population at an interval of 1, 3, 5, 7 and 10 days in both the crops. The data obtained were assigned to square root transformation, analysed statistically by applying RBD as suggested by Gomez and Gomez (1984).

3.4.7 Benefit cost ratio

The benefit cost ratio measures the relationship between the profits made from an experiment's costs, which are both expressed in monetary terms. Agriculture involves a variety of risks at different stages of plant growth due to both biotic and abiotic factors and the relative importance of these factors determines final yield (Verma et al. 2018). The procedure for calculating benefit cost ratio of the different treatments is given under:

1. **Fruit yield/ha (q):** Fruit yield per hectare was worked out on the basis of fruits harvested per plot

$$\text{Fruit yield/ha (q)} = \frac{\text{Fruit yield/plot (kg)} \times 10000 \times 0.80}{\text{Area of plot (m}^2\text{)} \times 100}$$

2. **Total cost of cultivation :** Fixed cost + Variable cost
3. **Gross income :** Yield (q/ha) × Sale rate (Rs.)
4. **Net income :** Gross income – Total cost of cultivation
5. **Benefit cost ratio :** $\frac{\text{Net income}}{\text{Total cost of cultivation}}$

Table 3.4 Cost incurred in purchase of pesticides in brinjal

Sr. No.	Pesticides	Price
1	Chlorantraniliprole 18.5% SC	Rs. 1097/60 ml
2	Spiromesifen 22.9% SC	Rs. 650/ 100 ml
3	Fenazaquin 10% EC	Rs. 820/ 250 ml
4	Chlorpyriphos 20% EC	Rs. 146/ 250 ml
5	Fenvalerate 20% EC	Rs. 85/ 100 ml

Table 3.5 Cost incurred in purchase of pesticides in chilli

Sr. No.	Pesticides	Price
1	Cyantraniliprole 10.26% OD	Rs. 1013/90 ml
2	Flubendiamide 20% WG	Rs. 207/ 25 g
3	Imidacloprid 17.8% SL	Rs. 400/ 100 ml
4	Spirotetramat 15.31% OD	Rs. 2175/ 500 ml
5	Fenazaquin 10% EC	Rs. 820/ 250 ml

3.5 Laboratory materials used for research work

The following chemicals (analytical grade), glassware and instruments were used to carry out the study:

3.5.1 Chemicals

1. Acetone (C_3H_6O), Merck Specialities Pvt. Ltd. Worli, Mumbai
2. Ammonium formate (NH_4HCO_2), Sigma-Aldrich, Merck KGaA, Germany
3. Acetonitrile (CH_3CN), Aventor Performance Material India Ltd. Thane, Maharashtra
4. Acetonitrile (CH_3CN) LC-MS/MS grade, Merck KGaA, Germany
5. Formic acid (CH_2O_2), Merck KGaA, Germany
6. Magnesium Sulphate ($MgSO_4$), Merck Specialities Pvt. Ltd. Worli, Mumbai
7. Methanol (CH_3OH) LC-MS/MS grade, Merck KGaA, Germany
8. n-Hexane (C_6H_{14}), Merck Specialities Pvt. Ltd. Worli, Mumbai
9. Potassium dichromate ($K_2Cr_2O_7$), Merck Specialities Pvt. Ltd. Worli, Mumbai
10. Primary Secondary Amines (PSA), Agilent Technology, USA
11. Reference standards, Dr. Ehrenstorfer, Augsburg, Germany
12. Sodium Chloride ($NaCl$), Merck Specialities Pvt. Ltd. Worli, Mumbai
13. Sodium Sulphate (Na_2SO_4), Merck Specialities Pvt. Ltd. Worli, Mumbai
14. Sulphuric acid (H_2SO_4), Merck Specialities Pvt. Ltd. Worli, Mumbai
15. Teepol, Merck Specialities Pvt. Ltd. Worli, Mumbai

3.5.2 Glassware and plastic wares

1. Beakers of 50 and 100 ml capacity, Borosil Glassworks Ltd., Delhi
2. Graduated test tubes with stoppers of 5 ml capacity, Borosil Glassworks Ltd., Delhi
3. Injection vials (1.5ml), Agilent Technologies, USA
4. Ivory PTFE/ red silicone rubber septa, Agilent Technologies, USA
5. Plastic stands for holding tubes, Tarson Products Pvt. Ltd., Kolkota
6. Polypropylene centrifuge tubes (50 and 15 ml), Tarson Products Pvt. Ltd., Kolkota
7. Tips of 1 and 5 ml capacity, Tarson Products Pvt. Ltd., Kolkota
8. Turbo tubes of 30 ml capacity, Borosil Glassworks Ltd., Delhi

3.5.3 Instruments

1. Air Generator, PCI Analytics Pvt. Ltd.
2. Auto Pipettes (1 and 5 ml): Tarson Products Pvt. Ltd., Subhash Road, Kolkota
3. Centrifuge: Eppendorf India Ltd., Chandigarh
4. Electronic balance: Mettler Toledo India Pvt. Ltd. Mumbai

5. GC-MS/MS: M/s Shimadzu corporation, Japan
6. LC-MS/MS: M/s Agilent Technologies, USA
7. High volume homogenizer: Heidolph, Germany
8. Low volume high speed homogenizer: Heidolph, Germany
9. Refrigerator: Godrej India Ltd., Mumbai
10. Rotospin mixer: Tarson Products Pvt. Ltd., Subhash Road, Kolkata
11. Spinex test tube shaker: Tarson Products Pvt. Ltd., Subhash Road, Kolkata
12. Turbo evaporator: Turbo Vap® LV. Caliper Life Service

3.5.4 Gases

Helium and agron air 99.99 % purity: M/s Linde India Ltd., Mumbai

3.6 Cleaning of glassware

The EPA (1980) procedure for cleaning of glassware was adopted to eliminate any kind of interfering substances/contaminants. The glassware was soaked in hot water followed by rinsing with organic solvent in order to remove the contaminants if any. The deep penetrant and oxidizing agent, chromic acid 20 per cent [potassium dichromate (20 g) in sulphuric acid (100 ml) w/v] was used to remove traces of organic contaminants. The glassware was dipped in chromic acid for 4-5 hours and thereafter, the same was washed with 'Teepol' followed under running tap water to remove chromic acid. The glassware was further washed with soap solution and tap water rinsed with distilled water and finally with acetone to flush out the traces of organic contaminants.

3.7 Preparation of stock solutions

Dr. Ehrenstorfer, Augsburg, Germany certified reference materials (CRMs) of pesticide standards under study were procured from their manufacture/supplier to prepare the respective stock solution of 400 ppm each by applying the formula:

$$\text{Concentration of stock solution } (\mu\text{g/ml}) = \frac{\text{Wt. (g)} \times 10^6 \times \text{Purity } (\%)}{\text{V (ml)}} \times 100$$

Where,

Wt = weight of the CRM (g)

V = Volume of the CRM to be prepared (ml)

From each stock solution, respective working solutions of 40 ppm, 10 ppm and 1 ppm were prepared by serial dilutions. To calculate the volume of a definite solution required to prepare solutions of other concentration, the following equation is used:

$$C_1V_1=C_2V_2$$

Where,

C_1 = Known concentration

V_1 = Volume to be taken from known stock solution

C_2 = Required concentration

V_2 = Required volume

Similarly, prepared lower concentrations with n-hexane and with methanol for analysis in GC-MS/MS and LC-MS/MS, respectively.

3.8 Validation of analytical method

Each analytical measurement goal is to get reliable, accurate data which is consistent. Validated analytical techniques are crucial in reaching this objective. Any good analytical approach should include evaluating the quality, consistency and reliability of analytical data using the findings from method validation. Analytical procedures must be validated to comply with laws and quality requirements that affect analytical laboratories.

The AOAC official method 2007.01 (QuEChERS method) was modified for analysis of pesticides in the laboratory. The analytical method has been validated as per the guidelines issued by SANTE (French words Sante for Health and Consummators for Consumers) vide their document SANTE/XXXX/2013 (SANTE 2021) for system precision, specificity /selectivity, matrix effect, linearity, repeatability, reproducibility and ruggedness. The validation process was performed for the estimation of chlorantraniliprole, fenazaquin, spiromesifen, chlorpyriphos and fenvalerate residues in brinjal and cyantraniliprole, imidacloprid, fenazaquin, spirotetramat and flubendiamide residues in chilli.

3.8.1 Preparation of sample

3.8.1.1 Extraction

About 1 kg brinjal and 500 g chilli fruits were homogenized in high volume and low speed homogenizer and 15 g representative homogenized sample was placed in 50 ml polypropylene centrifuge tube containing 30 ml acetonitrile. Material was homogenized at 15000 rpm for 2 minutes in low volume high speed homogenizer. Anhydrous sodium chloride (3 g) was added into the tube, shaken at 50 rpm for 5 minutes with Rotospin shaker and then centrifuged at 3000 rpm for 3 minutes in eppendorf centrifuge. Upper layer fraction of 18 ml was transferred to another 50 ml centrifuge tube containing 9 g anhydrous sodium sulphate and was shaken for 5 minutes at 50 rpm.

3.8.1.2 Cleanup

Anhydrous magnesium sulphate (1150 mg) and PSA (400 mg) were taken in 15 ml polypropylene centrifuge tube. The tube was capped and shaken for one minute on Spinix test tube shaker. Approximately 11 ml fractions from 18 ml extract was added into the centrifuge tube, shaken for one minute at 50 rpm in Rotospin shaker and centrifuged in eppendorf centrifuge at 3000 rpm for 5 minutes. The 6 ml fraction was transferred to the 30 ml turbo tube and evaporated the solvent to dryness in turbo evaporator at 45° C in the presence of gentle air stream. The residues of fenazaquin, chlorpyriphos, fenvalerate and spiromesifen were dissolved in 3 ml of n-hexane and were injected (1 µl) in to GC-MS/MS whereas, residues of cyantraniliprole, chlorantraniliprole, flubendiamide, spirotetramat and imidacloprid were dissolved in methanol for injection (2 µl) into LC-MS/MS.

3.8.2 Determination of residues

Table 3.6 Parameters of GC-MS/MS for residue analysis

Instrument	Shimadzu Nexis GC 2030 TQ 8040 NX	
Detector	MS TQ 8040 NX	
Detector voltage	0.6 KV	
Software	GCMS solution version 4.5	
Carrier gas	Helium	
Gas flow	1 ml min ⁻¹	
Column	Capillary gas column, SH-RXI-5 Sil MS	
Injection port temperature	250° C	
Interface temperature	280° C	
Ion source temperature	200° C	
Collision gas	Argon	
Solvent delay	3 min	
MRM mode	Fenvalerate (peak I and peak II)	225.10 > 119.10 225.10 > 147.10 419.10 > 225.10
	Chlorpyriphos	196.90 > 168.90 313.90 > 257.90 313.90 > 285.90
	Spiromesifen	272 > 254 272 > 209 272 > 231
	Fenazaquin	160.20 > 145.10 145.20 > 115.10 145.20 > 91.10
Retention time (min)	Fenvalerate (Peak I +Peak II)	36.77+37.30
	Chlorpyriphos	19.54
	Spiromesifen	28.58
	Fenazaquin	29.98

Oven temperature programming: Initial temperature 80° C was held for 4 minutes then increased to 200° C at the rate of 12° C per minutes and kept for 5 minutes then again raised to 280° C at the rate of 5° C per minutes with a hold time of 10 minutes. The chromatographic

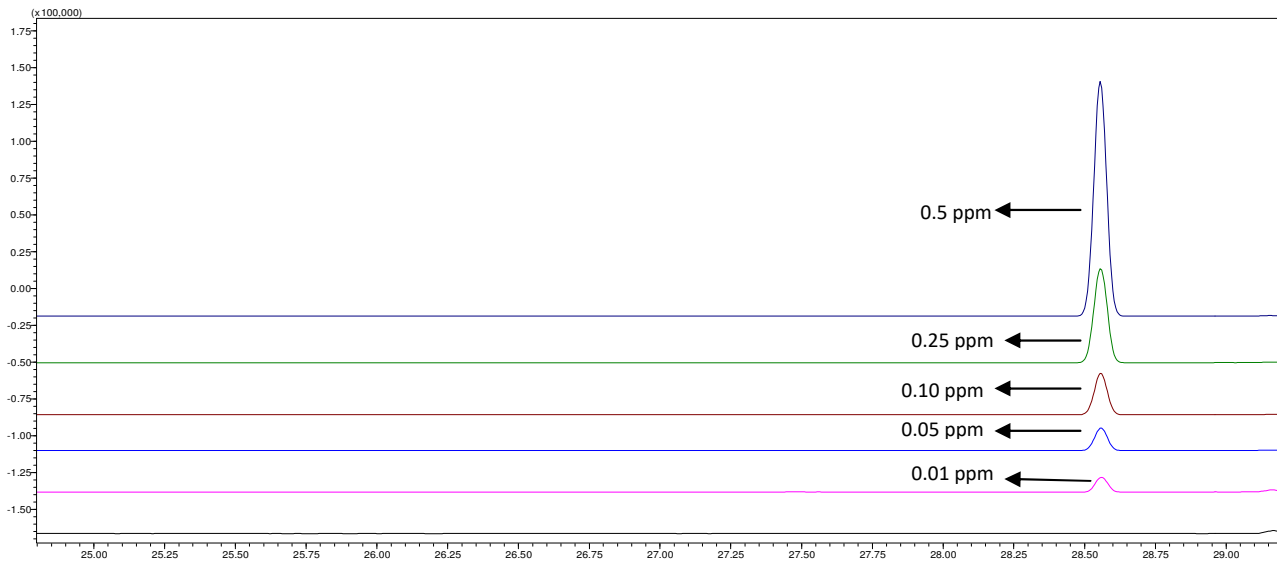


Fig. 3.1 Chromatographic response of different concentrations of spiromesifen in GC-MS/MS

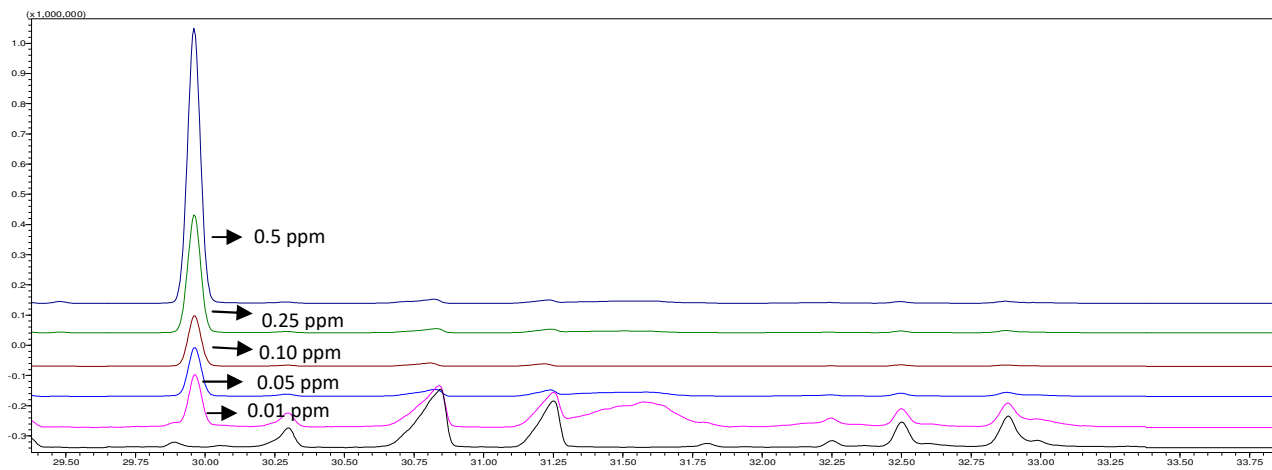


Fig. 3.2 Chromatographic response of different concentrations of fenazaquin in GC-MS/MS

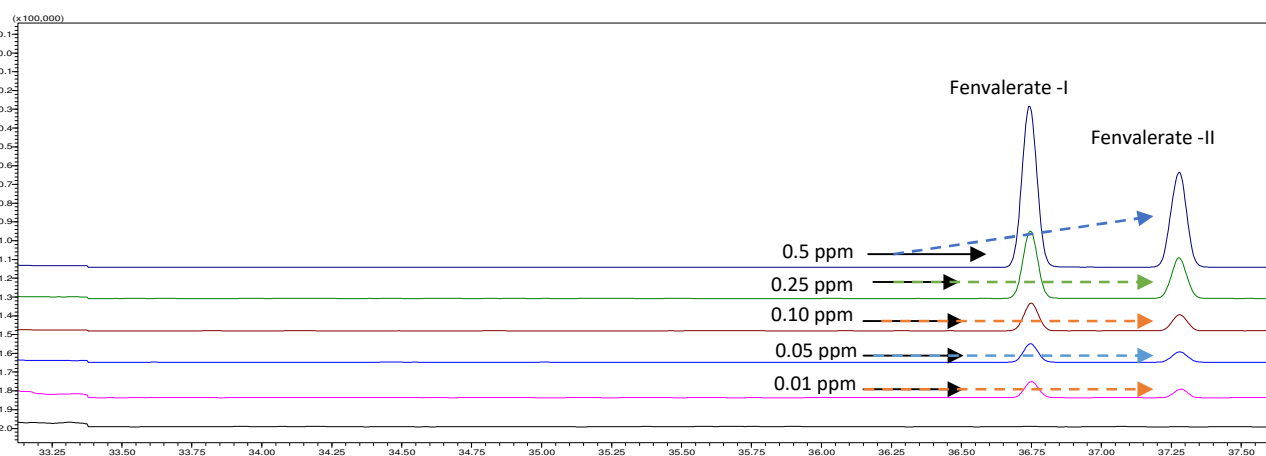


Fig. 3.3 Chromatographic response of different concentrations of fenvalerate in GC-MS/MS

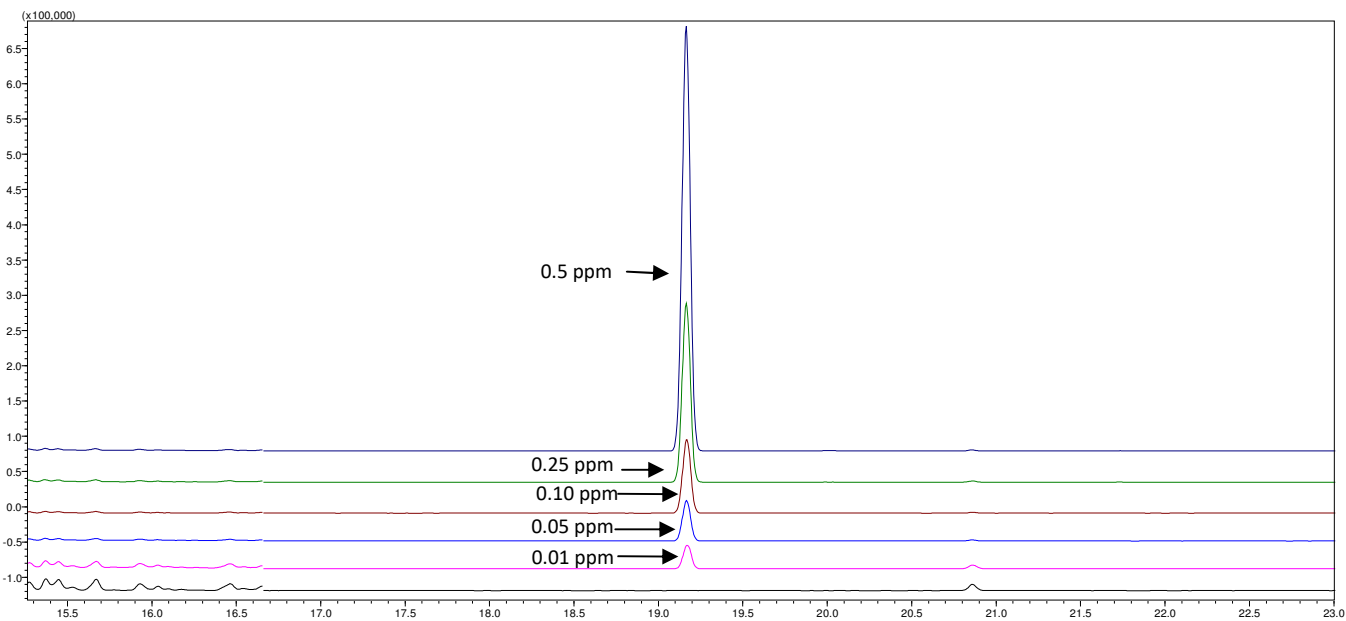


Fig. 3.4 Chromatographic response of different concentrations of chlorpyrifos in GC-MS/MS

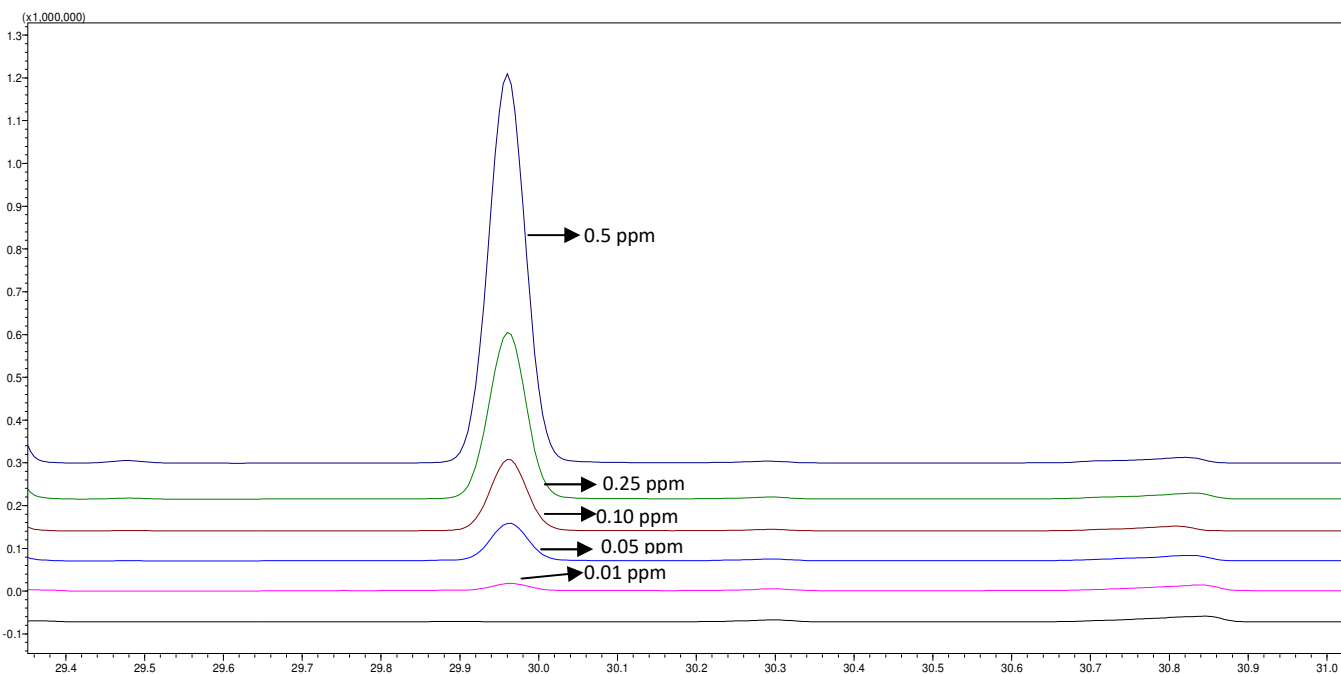


Fig. 3.5 Chromatographic response of different concentrations of fenazaquin in GC-MS/MS

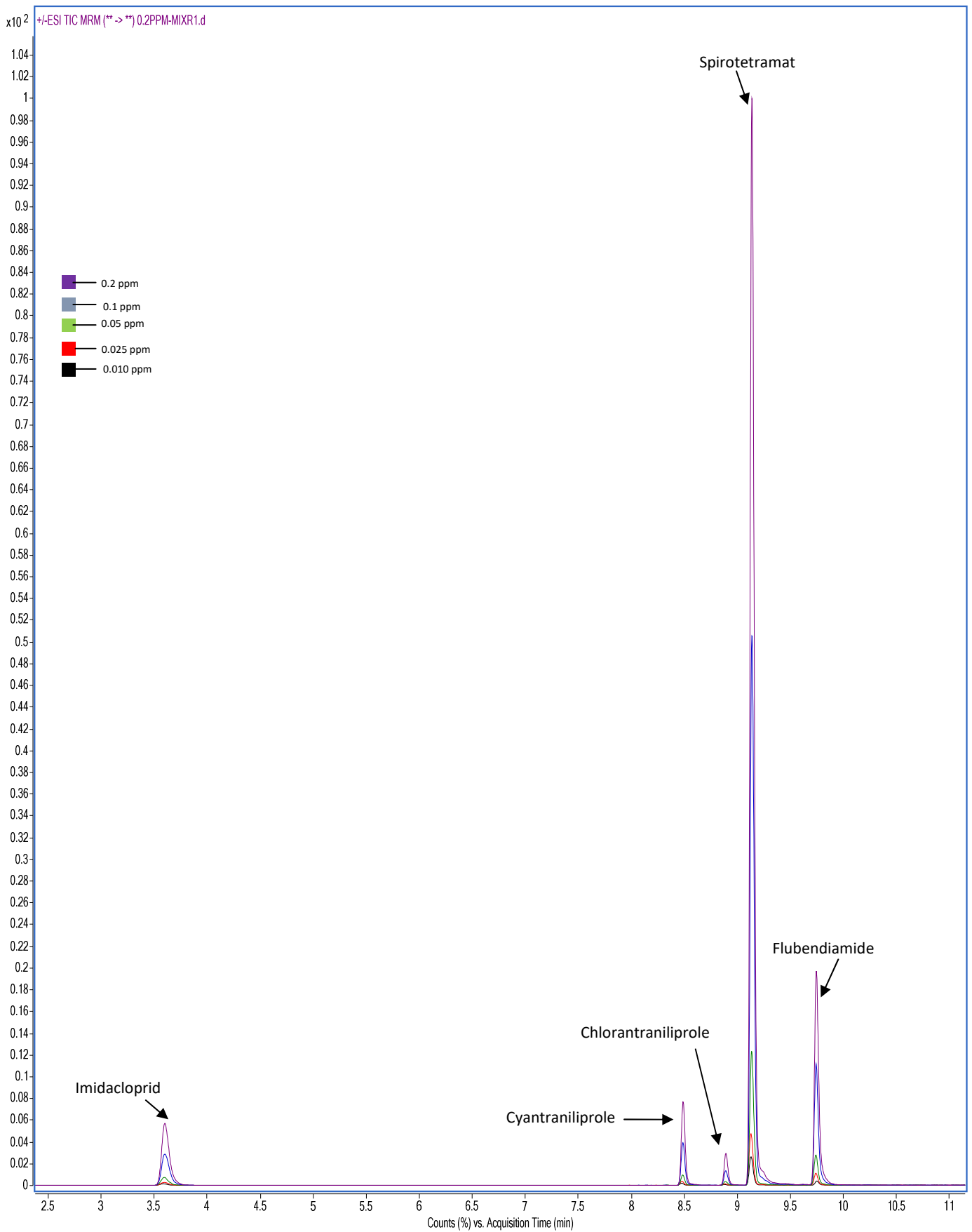


Fig. 3.6 Chromatographic response of different concentrations of imidacloprid, cyantraniliprole, spirotetramat, flubendiamide and chlorantraniliprole in LC-MS/MS

response of different concentrations of spiromesifen, fenazaquin, fenvalerate and chlorpyrifos (GC-MS/MS) are given in Fig. 3.1, 3.2, 3.3, 3.4 and 3.5.

Table 3.7: Parameters of LC-MS/MS for residue analysis

LC parameters	Value			
Instrument	Agilent 1260 Infinity II Ultivo LC/TQ			
Analytical column	Agilent Infinity LabPoroshell 120 EC-C18, 3.0 x 150mm, 2.7 μ m			
Guard Column	Agilent Infinity LabPoroshell 120 EC-C18, 3.0 x 5mm, 2.7 μ m			
Software	Agilent MassHunter			
Column temperature	40 $^{\circ}$ C			
Mobile phase A	Water + 2.5mM ammonium formate + 0.25% formic acid			
Mobile phase B	Acetonitrile + 0.25% formic acid			
Flow rate	0.4 ml/min			
Injection volume	2 μ l			
Binary pump gradient	Time (min)	A (%)	B (%)	Flow (ml/min)
	3.00	70.00	30.00	0.40
	6.00	5.00	95.00	
	10.00	5.00	95.00	
	10.10	70.00	30.00	
12.00	70.00	30.00		
MS/MS Parameters				
Ionization mode/Source	Positive and negative Electron spray ionization (ESI)			
Scan type	MRM			
Drying gas temperature	325 $^{\circ}$ C			
Drying gas flow	12 L/min			
Nebulizer pressure	45 psi			
Capillary voltage	(\pm ESI) 3500 V			

Table 3.8 MRM conditions for different pesticides

Compound name	Retention time (min)	Precursor ion (m/z)	Product ion (m/z)	Fragmentor (V)	Collision Energy (V)	Polarity
Chlorantranilprole	8.88	482.00	283.20	84	12	+
		482.00	111.60	84	60	+
Cyantranilprole	8.48	475.00	444.00	85	10	+
		475.00	286.00	85	15	+
Imidacloprid	3.60	256.00	209.10	70	16	+
		256.00	175.10	70	28	+
Flubendiamide	9.72	681.00	274.00	50	12	-
		681.00	254.00	50	28	-
Spirotetramat	9.12	374.20	330.20	84	12	+
		374.20	216.20	84	36	+

The chromatographic response of imidacloprid, cyantranilprole, chlorantranilprole, spirotetramat and flubendiamide (LC-MS/MS) is given in Fig. 3.6

3.8.3 System Precision

The precision of the method is defined as the degree of scatter of individual test results of multiple measurements of a homogenous sample. A system (analytical instrument) needs to be tested in order to assess sensitivity and precision before putting it into use.

Solvent standard of 0.1 mg/kg concentration were prepared in n-hexane (fenazaquin, spiromesifen, chlorpyrifos and fenvalerate) and injected into GC-MS/MS and standard of 0.1 mg/kg of chlorantraniliprole, imidacloprid, cyantraniliprole, spirotetramat and flubendiamide were prepared in methanol and injected into LC-MS/MS and were replicated five times. Retention time and area of an individual analyte was recorded. Mean, standard deviation and % RSD were calculated for retention time and area for each pesticide. % RSD was compared with acceptance criteria of < 20% (SANTE 2021) to proceed further for the method validation.

$$\% \text{ RSD} = \left[\frac{\text{SD}}{\text{mean}} \right] * 100$$

3.8.4 Specificity (Matrix match):

Although matrix elements might interfere with the signal and cause a rise or decrease in the signal, matrix effects are frequently observed in GC-MS/MS and LC-MS/MS and must be evaluated during the initial validation stage. Each pesticide was added to the sample matrix extract at a fortification level of 0.1 mg/kg. Each pesticide solvent standard was also prepared at the same concentration. Standards for the sample matrix and solvent were injected five times. Peak area in the sample matrix and the matching area in the solvent standard of each pesticide were noted. Matrix effect (ME) was calculated as per the method used by Tiryaki (2016):

$$\text{ME (\%)} = \frac{\text{Peak area of matrix standard} - \text{Peak area of solvent standard}}{\text{Peak area of solvent standard}} \times 100$$

The statistical significance of difference in the area was calculated by using the student t test as per EURACHEM guide (EURACHEM 2012). If t calculated was found to be less than t table value at 95 % confidence interval and n-1 (where n is number of observations) degrees of freedom the matrix effect was considered to be non-significant.

$$t_{\text{cal.}} = \frac{d\sqrt{n}}{\text{SD}}$$

Where d is the mean of differences (d_i) and SD is the standard deviation of differences (d_i) and n is number of observations

3.8.5 Linearity

The pesticides *viz.*, fenazaquin, spiromesifen, fenvalerate and chlorpyrifos were taken at concentration levels of 0.005, 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg and chlorantraniliprole,

flubendiamide, imidacloprid, cyantraniliprole and spirotetramat at 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg, respectively. For each pesticide, derivation of back calculated concentration from true concentration was worked out with acceptance criteria of $\leq 20\%$ as per SANTE guidelines (SANTE 2021). Also, calibration curves for each pesticide were drawn by plotting the average peak area across five replicates versus the concentration.

$$\text{Derivation of back calculated concentration} = \frac{(C_{\text{measured}} - C_{\text{true}})}{(C_{\text{true}})} \times 100$$

Where, C_{measured} = concentration measured from equipment

C_{true} = actual concentration

3.8.6 Determination of LOQ (Limit of Quantification) and LOD (Limit of Detection):

LOD and LOQ were calculated according to Anonymous (2009). Limit of detection (LOD) is the lowest concentration of analyte that can be reliably detected using the method but not necessarily quantified. The LOQ is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated conditions of test. To calculate LOD and LOQ, brinjal matrix was spiked individually with fenazaquin, spiromesifen, fenvalerate and chlorpyrifos at concentrations 0.005, 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg and chlorantraniliprole at 0.005, 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg. In case of chilli, sample matrix was spiked with flubendiamide, imidacloprid, cyantraniliprole, spirotetramat at 0.005, 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg. After fortification, 1 and 2 μl were injected into GC-MS/MS and LC-MS/MS, respectively and peak area was recorded. A signal-to-noise ratio (S/N) of three is generally accepted for estimating LOD and signal-to-noise ratio of ten is used for estimating LOQ (Shrivastava and Gupta 2011). The limit of detection (LOD) and limit of quantification (LOQ) were determined by subjecting concentration and area to regression equation $Y = a + bX$, where Y = area, X = insecticide concentration, a = intercept and b = slope. The LOD was calculated by the formula $3 \times \text{SD} / \text{slope}$, whereas the LOQ was equaled to $10 \times \text{SD} / \text{slope}$ where, SD = Standard deviation.

3.8.7 Accuracy/Recovery

To determine the accuracy of pesticides, the brinjal and chilli fruit samples were spiked at LOQ, 5X LOQ and 10X LOQ level with different analyte in five replications in the beginning of the analytical procedure and termed as pre-extraction spiked matrix standards (PrEMS). Per cent recovery and % RSD was calculated for all tested pesticides. Per cent

recovery in the range of 70 to 120 per cent and per cent RSD for recovery to be less than 20 per cent was kept as the acceptance criteria for recovery as per SANTE guidelines.

3.8.8 Precision of the method

The precision of the method was determined by repeatability, reproducibility and ruggedness of the method. For determination of precision of the method, the repeatability, reproducibility and ruggedness was done at three fortification levels of LOQ, 5X LOQ and 10X LOQ. Brinjal samples were spiked with fenazaquin, chlorantraniliprole, fenvalerate, spiromesifen and chlorpyrifos whereas, chilli fruit matrix samples were spiked with cyantraniliprole, imidacloprid, flubendiamide, spirotetramat and fenazaquin. Sample matrix were fortified in the beginning of the analytical procedure and termed as pre-extraction spiked matrix standards.

3.8.8.1 Repeatability was studied by repeating the processing of pre-extraction spiked matrix standards (PrEMS) of each insecticide on two different days by the same person. Per cent recovery and % RSD were calculated.

3.8.8.2 Reproducibility was studied by processing the pre-extraction spiked matrix standards (PrEMS) of each insecticide by another person. Per cent recovery and % RSD were calculated.

3.8.8.3 Ruggedness of an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters. In order to check the ruggedness of validated method, matrix of the other commodity representative the same group as per SANTE guidelines was used along with the deliberate changes in the two steps of the procedure. The following changes were made:

- i) Brinjal matrix was used as PrEMS instead of chilli and chilli matrix was used as PrEMS instead of brinjal.
 - ii) Low volume homogenizer time was changed to 3 minutes instead of 2 minutes.
 - iii) In dispersive solid phase cleanup, 15 ml tube containing 0.4 g PSA sorbent and 1.15 g anhydrous magnesium sulphate was centrifuged for 2 minutes instead of 3 minutes.
- Per cent recovery and % RSD were calculated.

Table 3.9 Acceptance criteria for different parameters of validation

Parameter	Criterion
Sensitivity/linearity	Deviation of back- calculated concentration from true concentration $\leq 20\%$
Matrix effect	-
LOQ	\leq MRL
Accuracy	70-120%
Precision (RSDr) (Repeatability)	$\leq 20\%$
Precision (RSDwR) (Reproducibility)	$\leq 20\%$
Ruggedness	$\leq 20\%$
Retention time	± 0.1 min.

3.8.9 Estimation of uncertainty of measurement

Uncertainty is “a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand”. Uncertainty is associated with each measurement result. A complete measurement result typically includes an indication of the uncertainty in the form $x \pm U$, where x is the measurement result and U is an indication of the uncertainty. Calculation of uncertainty is important step for method development process. The standard uncertainty was determined at LOQ level for all the insecticides taken under study as per the statistical procedure of the EURACHEM/CITAC Guide CG 4 (EURACHEM 2012). The main sources of uncertainty in the method validation procedure were as follows:

3.8.9.1 Uncertainty associated with precision: The random errors due to extraction, clean up, and GC-MS/MS and LC-MS/MS analyses steps were approximated by standard deviations which were calculated from 5 time repeated observation recorded at LOQ level after injecting pesticides in solvent (n-hexane and methanol) after fortifying brinjal and chilli samples.

a. Standard uncertainty during determination of area of standard of pesticide in solvent (n-hexane and methanol):

Chlorantraniliprole, spiromesifen, fenvalerate, fenazaquin, chlorpyrifos cyantraniliprole, flubendiamide, spirotetramat and imidacloprid solution of 0.01 mg/kg were prepared. The area under each pesticide was recorded. Uncertainty of pesticides area was calculated after working out mean area and standard deviation due to solvent.

$$\text{Mean area } \bar{X} = \text{Sum} / n \quad (n = \text{no. of observations})$$

$$\text{Standard deviation} = N1$$

$$U_{\text{area}} = \frac{\text{Std. deviation (N1)}}{\sqrt{n}}$$

$$\begin{aligned} \text{Regression equation (Calibration)} &= 0.99 \\ &= 0.01 \text{ uncertainty} \end{aligned}$$

$$\text{Instrument specification} = \frac{\text{Instrument sensitivity (LOQ)}}{\sqrt{3}} \quad (\sqrt{3} = \text{value for rectangular distribution})$$

$\frac{U_{\text{std area}}}{0.01} = \sqrt{\left[\frac{\text{Std. deviation (N1)}}{\text{Mean } (\bar{X})} \right]^2 + \left[\frac{\text{Instrument specification}}{\text{LOQ}} \right]^2}$ <p style="text-align: center;">(Uncertainty RE Calib)</p>
--

$$\begin{aligned} \frac{U_{\text{std area}}}{0.01} &= A \\ U_{\text{std area}} &= A \times 0.01 = B \end{aligned}$$

b. Uncertainty of standard at fortification level in brinjal and chilli sample:

Brinjal fruit samples were fortified with chlorantranilprole, spiromesifen, fenvalerate, fenazaquin, chlorpyriphos at 0.01 mg/kg fortification level. Chilli fruit samples were fortified with cyantranilprole, flubendiamide, spirotetramat, imidacloprid and fenazaquin at 0.01 mg/kg. After extraction, cleanup and GC-MS/MS and LC-MS/MS analysis, the amount of pesticide recovered was recorded to calculate the uncertainty associated with potential interferences in the concentration mean amount recovered and standard deviation.

Mean amount recovered $X = \text{Sum} / n$ (n= no. of observations)

Standard deviation = N2

$$U_{\text{(reap)}} = \frac{\text{Std. deviation (N2)}}{\sqrt{n}}$$

c. Uncertainty due to area of brinjal and chilli sample:

Brinjal fruit samples were fortified with chlorantranilprole, spiromesifen, fenvalerate, fenazaquin, chlorpyriphos at 0.01 mg/kg fortification level. Chilli fruit samples were fortified with cyantranilprole, flubendiamide, spirotetramat, imidacloprid and fenazaquin at 0.01 mg/kg. After extraction and cleanup, samples were injected into GC-MS/MS and LC-MS/MS

and recorded area under each pesticide. Since the area has not a perfect geometric shape, there is also an uncertainty in any area calculation which was calculated as:

$$\text{Mean area } \bar{X} = \text{Sum} / n \quad (n = \text{no. of observations})$$

$$\text{Standard deviation} = N3$$

$$S_{(\text{sample area})} = \frac{\text{Std. Deviation (N3)}}{\sqrt{n}}$$

$$\frac{U_{\text{sample area}}}{0.01} = \sqrt{\left[\frac{S_{(\text{sample area})}}{\text{Mean}} \right]^2 + \left[\frac{\text{Instrument Specification}}{\text{LOQ}} \right]^2}$$

$$\frac{U_{\text{sample area}}}{0.01} = M$$

$$U_{\text{sample area}} = M \times 0.01 = N$$

3.8.9.2 Measurement of uncertainty due to standard preparation:

The uncertainties in the preparation of standard solutions were calculated from estimates of standards, volumetric glassware, pipettes and temperature effects etc. All the uncertainty sources for each of the parameters were measured as:

a) % purity of standard = 98.3 % (say)

$$\begin{aligned} \text{Uncertainty} &= 100 - \text{df} + \% \text{ purity} \\ &= 100 - 98.3 \\ &= 1.7\% \\ &= \frac{1.7}{100} = 0.017 \end{aligned}$$

$$U_{\text{purity of std}} = \frac{\text{Uncertainty}}{\sqrt{3}} \quad (\sqrt{3} \text{ is value for rectangular distribution})$$

b) Volume makeup

$$\text{Temp} = 27^\circ \text{C} \pm 2^\circ$$

$$\text{Water expansion coefficient} = 2.14 \times 10^{-4}$$

i)
$$U_{\text{centrifuge tube (50 ml)}} = \frac{\text{Uncertainty from certificate}}{k \text{ value for 95\% confidence (= 2)}}$$

$$U_{\text{calibration volume}} = \frac{0.05}{2} = 0.025$$

ii) Temperature effect = Volume of centrifuge tube × uncertainty in temperature × water expansion coefficient

$$= 50 \times 2 \times 2.14 \times 10^{-4}$$

$$= 0.0214$$

$$U_{(\text{calibration volume})} = \sqrt{U_{\text{volumetric flask}} + \text{temp effect}}$$

c) Pipetting

i) Pipette calibration (5 ml) = $\frac{\text{Uncertainty from certificate (0.05)}}{\text{k value for 95\% confidence (= 2)}} = 0.025$

ii) Temperature effect = Volume of pipette × uncertainty in temperature × water expansion coefficient

$$= 5 \times 2 \times 2.14 \times 10^{-4}$$

$$= 0.00214$$

$$U_{\text{Pipetting}} = \sqrt{\text{Pipette calibration} + \text{temp effect}}$$

$$= \sqrt{0.025 + 0.00214} = \sqrt{0.02714} = 0.16474$$

$\frac{U_{\text{std}}}{0.01\text{ppm}} = \sqrt{\left[\frac{U_{(\text{purity of std})}}{100 - \text{purity}}\right]^2 + \left[\frac{U_{(\text{calibration volume})}}{\text{Vol of flask}}\right]^2 + \left[\frac{U_{\text{Pipetting}}}{\text{Vol of pipette}}\right]^2}$ <p>(Conc. of std from 1)</p>
--

$$\frac{U_{\text{std}}}{0.01\text{ppm}} = G$$

$$U_{\text{std}} = G \times 0.01 = H$$

$$\text{Temperature} = 2 \times 23 = 46 / \sqrt{3} = 26.5589$$

$$U_{\text{temp}} = 26.5589 \times \text{water expansion coefficient} = 0.0056836$$

3.8.9.3 Uncertainty due to compounds used: The uncertainty due to compounds used during extraction end cleanup of the sample was calculated on the basis of the purity of the compound as:

a) **NaCl** Purity = 99.5%
 Uncertainty = 0.5%
 = 0.5/100 = 0.005

$U_{\text{purity NaCl}} = 0.005/\sqrt{3} = 0.0029$ ($\sqrt{3}$ is value for rectangular distribution)

b) **Na₂SO₄** Purity = 99.5%
 Uncertainty = 0.5%
 = 0.5/100 = 0.005

$U_{\text{purity Na}_2\text{SO}_4} = 0.005/\sqrt{3} = 0.0029$ ($\sqrt{3}$ is value for rectangular distribution)

c) **MgSO₄** Purity = 98%
 Uncertainty = 2%
 = 2/100 = 0.02

$U_{\text{purity MgSO}_4} = 0.02/\sqrt{3} = 0.0115$ ($\sqrt{3}$ is value for rectangular distribution)

d) **Uncertainty due to Bottle top dispenser (100 ml)**

i) $U_{\text{Bottle top dispenser (100 ml)}} = \frac{\text{Uncertainty from certificate}}{\text{k value for 95\% confidence (= 2)}}$

= $\frac{0.05}{2}$
 $U_{\text{Bottle top dispenser}} = 0.025$

ii) Temperature effect = Volume of cylinder × uncertainty in temperature × water expansion coefficient
 = $100 \times 2 \times 2.14 \times 10^{-4}$
 = 0.0428

$U_{\text{(volume)}} = \sqrt{(U_{\text{measuring cylinder}})^2 + (\text{temp effect})^2}$
 = $\sqrt{(0.025)^2 + (0.0214)^2}$
 = $\sqrt{0.00625 + 0.00458}$
 = $\sqrt{0.01083}$
 = 0.0329

e) **Uncertainty due to Bottle top dispenser (10 ml)**

Bottle top dispenser = 3ml from dispenser of 10 ml

i) Bottle top dispenser calibration (10 ml) = $\frac{\text{Uncertainty from certificate (0.01)}}{\text{k value for 95\% confidence (= 2)}} = 0.005$

ii) Temperature effect = Volume dispensed × uncertainty in temperature × water expansion coefficient

$$= 10 \times 2 \times 2.14 \times 10^{-4}$$

$$= 0.00428$$

$$U_{\text{final volume}} = \text{BTD calibration} + \text{temp effect}$$

$$= 0.005 + 0.00428 = 0.00928$$

$$\frac{U_{\text{sample}}}{3 \text{ ml (Final volume)}} = \sqrt{\left[\frac{U_{\text{purity NaCl}}}{100\text{-purity}} \right]^2 + \left[\frac{U_{\text{purity Na}_2\text{SO}_4}}{100\text{-purity}} \right]^2 + \left[\frac{U_{\text{purity Mg SO}_4}}{100\text{-purity}} \right]^2 + \left[\frac{U_{\text{final volume}}}{\text{Vol. of pipette}} \right]^2 + \left[\frac{U_{\text{volume}}}{\text{Final volume (30 ml)}} \right]^2}$$

$$\frac{U_{\text{sample}}}{3} = L$$

$$U_{\text{sample}} = L \times 3$$

$$U_c \text{ Av value of fortification level of sample (AA)} = \sqrt{\left[\frac{U_{\text{std Area}}}{\text{Mean of standard area}} \right]^2 + \left[\frac{U_{\text{sample area}}}{\text{Mean of standard area}} \right]^2 + \left[\frac{U_{\text{reap}}}{\text{Mean of reap}} \right]^2 + \left[\frac{U_{\text{sample}}}{\text{Vol. of pipette}} \right]^2 + \left[\frac{U_{\text{std Std Concentration}}}{\text{Concentration}} \right]^2}$$

Therefore say Uncertainty calculated = Q mg/kg

3.9 Pesticides persistence studies

The persistence of pesticides such as chlorantraniliprole, spiromesifen, fenvalerate, fenazaquin and chlorpyrifos was studied in brinjal. On the other hand, persistence of cyantraniliprole, flubendiamide, spirotetramat, imidacloprid and fenazaquin was done in chilli fruits. Persistence of pesticides was also studied in the red chilli fruits and field soil (at harvest).

3.9.1 Treatments

Each pesticide was applied twice at an interval of 10 days at two concentrations i.e. single (X) and double doses (2X) (Table 3.10). The experiment was laid in randomized block design (RBD), with each treatment replicated three times. The control plots were treated with water only.

Table 3.10 Pesticides and their different doses applied on brinjal and chilli crop

Crop	Treatment	Pesticides	Dosage/ha	
			g a.i.	Formulation (g or ml)
Brinjal	T ₀	Control	-	-
	T ₂	Spiromesifen (X) (22.9% SC)	96	400
	T ₃	Spiromesifen (2X) (22.9% SC)	192	800
	T ₅	Fenazaquin (X) (10% EC)	125	1250
	T ₆	Fenazaquin (2X) (10% EC)	250	2500
	T ₈	Chlorantraniliprole (X) (18.5% SC)	40	200
	T ₉	Chlorantraniliprole (2X) (18.5% SC)	80	400
	T ₁₁	Fenvalerate (X) (20% EC)	75	375
	T ₁₂	Fenvalerate (2X) (20% EC)	150	750
	T ₁₄	Chlorpyrifos (X) (20% EC)	200	1000
	T ₁₅	Chlorpyrifos (2X) (20% EC)	400	2000
Chilli	T ₀	Control	-	-
	T ₂	Cyantraniliprole (X) (10.26% OD)	60	600
	T ₃	Cyantraniliprole (2X) (10.26% OD)	120	1200
	T ₅	Imidacloprid (X) (17.8% SL)	25	125
	T ₆	Imidacloprid (2X) (17.8% SL)	50	250
	T ₈	Spirotetramat (X) (15.31% OD)	60	400
	T ₉	Spirotetramat (2X) (15.31% OD)	120	800
	T ₁₁	Flubendiamide (X) (20% WG)	50	250
	T ₁₂	Flubendiamide (2X) (20% WG)	100	500
	T ₁₄	Fenazaquin (X) (10% EC)	125	1250
	T ₁₅	Fenazaquin (2X) (10% EC)	250	2500

3.9.2 Sampling

3.9.2.1 Fruits

Brinjal (1kg) and chilli (500 g) fruit samples were collected from each replication at an interval of 0, 1, 3, 5, 7, 10, 15, 20 and 25 days, and red chilli samples at harvest (48 days) after second spray of each pesticide. The samples were packed in polyethylene bags, labeled well and brought to laboratory for pesticide residue analysis. Each sample was chopped into small pieces and mixed thoroughly. After quartering and sub-quartering, a representative sample was taken in blender for homogenization at a high speed to get the fine homogenate without any large particles or segregated material. The samples were analyzed for residue estimation by the validated QuEChERS technique as mentioned in 3.8.1.1 and 3.8.1.2.

3.9.2.2 Soil

Soil samples (500 g) from the sprayed field were collected at harvest. Pesticides residues were normally confined to the top layers of the soil. Drive the auger to a plough depth of 15 cm and draw the soil sample. Reduce the bulk to 1 kg by quartering and

compartmentalization. Quartering was done by dividing the thoroughly mixed sample into four equal parts. The two equal opposite quarters were discarded and the remaining quarters were remixed and the process was repeated until the desired sample size was obtained. The samples were placed on blotting paper and allowed to shade dry at room temperature in the PRL. The air dried samples were ground and sieved through a No. 20 mm brass soil sieve.

3.9.2.2.1 Soil analysis

Soil was analyzed by another QuEChERS technique, modified for analysis of soil (Asensio-Ramos et al. 2010). A representative 10 g sieved ground dry soil sample was taken in a 50 ml polypropylene centrifuge tube, to which 20 ml acetonitrile was added and allowed for shaking up to 1 minute using a Rotospin shaker. To this 4 g of magnesium sulphate and 1 g of sodium chloride was added and centrifuged at 3300 rpm for 3 minutes. After centrifugation, a 10 ml of supernatant was taken in another centrifuge tube of 15 ml containing 1.5 g of magnesium sulphate and 0.250 g of PSA, thereafter allowed for 3 minutes shaking. After shaking, the tube was sonicated for 3 minutes and then centrifuged for 10 minute at 4400 rpm. From this tube 4 ml aliquot of the supernatant was taken in a turbo tube and evaporated to dryness in presence of nitrogen current at 45° C. The dried residues of fenazaquin, chlorpyriphos, fenvalerate, spiromesifen were dissolved in 2 ml of n-hexane for injection (1 µl) in to GC-MS/MS and residues of cyantraniliprole, chlorantraniliprole, flubendiamide, spirotetramat and imidacloprid were dissolved in methanol for injection (2 µl) into LC-MS/MS.

3.9.3 Recovery studies

3.9.3.1 Recovery studies in brinjal fruits and soil

Recovery experiment was conducted by spiking the untreated brinjal fruits and field soil at 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg (fenazaquin, spiromesifen, chlorpyriphos and fenvalerate) and at 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg (chlorantraniliprole) levels. Fortified samples were processed as per the procedure described under 3.8.1.1, 3.8.1.2, 3.9.2.2 and 3.9.2.2.1 for analysis of samples, respectively. The percent recovery was calculated as follows:

$$\text{Per cent Recovery} = \frac{\text{Amount recovered}}{\text{Amount added}} \times 100$$

3.9.3.2 Recovery studies in green and red chilli fruits and soil

Recovery experiment was conducted by spiking the untreated green and red chilli fruits and soil at 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg (fenazaquin) and at 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg (cyantraniliprole, flubendiamide, spirotetramat and imidacloprid) levels. Fortified samples were processed as per the procedure described under 3.8.1.1, 3.8.1.2, 3.9.2.2 and 3.9.2.2.1 for analysis of samples, respectively. The percent recovery was calculated as follows:

$$\text{Per cent Recovery} = \frac{\text{Amount recovered}}{\text{Amount added}} \times 100$$

3.9.4 Dissipation studies

3.9.4.1 Calculation of Residue Half Life (RL₅₀) Values

The RL₅₀ values were calculated as per Hoskins (1961) formula, which is as follows:

$$t_{1/2} = \frac{\log 2}{k_1} = \frac{0.301}{k_1} = \frac{0.301}{b}$$

Where,

$t_{1/2}$ = half-life value (RL₅₀) of residues in days

k_1 = slope of regression equation of the log residues determined in mg kg⁻¹ or ppm (y) on the time elapsed in days (x)

3.9.4.2 Calculation for Safe Waiting Period

The MRL (Maximum residue limit) recommended by FSSAI (FSSAI 2020) were used as tolerance limit for calculating safe waiting period of pesticides (Table 3.11).

Table 3.11 MRL and waiting period of pesticides

Crop	Pesticides	FSSAI MRL (ppm)
Brinjal	Chlorantraniliprole	0.6
	Fenazaquin	0.01
	Chlorpyrifos	0.2
	Spiromesifen	0.5
	Fenvalerate	2
Chilli	Cyantraniliprole	0.5
	Fenazaquin	0.5
	Flubendiamide	0.02
	Spirotetramat	2
	Imidacloprid	0.3

The waiting period values were calculated as per Hoskins (1961) formula, which is as follows:

$$T_{si} = \frac{\log k_2 - \log tol}{k_1} = \frac{\log k_2 - \log tol}{b}$$

Where,

T_{si} = time taken in days by the insecticide to reach tolerance limit

$\log k_2$ = log of initial deposit

$\log tol$ = log of proposed tolerance limit

k_1 = b = slope of regression equation

3.9.4.3 Residues Dissipation Rate

The dissipation follows first phase of kinetics (fast phase of removal of pesticide) whereas persistence follows second phase of kinetics (slow phase of removal of pesticide). The per cent dissipation of the residue over the initial deposit was calculated for various sampling interval as per the following mathematical formula:

$$\text{Per cent dissipation} = 100 - \frac{\text{Residue (mg/kg)}}{\text{Initial deposit}} \times 100$$

3.10 Risk assessment studies of pesticides

Food consumption behavior for rural and urban community mainly depends upon agricultural production in India. The dietary risk assessment was carried out for different age groups suggested by ICMR (2010).

Brinjal and chilli national capita intake was taken from the NSSO (2014). For each group national capita intake was calculated by dividing the average body weight (60 kg) and multiplying the weight of the specified age group. The value of consumption of commodity was obtained by dividing daily intake of the commodity by weight of specified age group.

Calculation of dietary risk assessment was done using hazard quotient (HQ) (Lozowieka et al. 2014; Fu et al. 2016). For calculating hazard quotient, at first estimated daily intake (EDI) was calculated for chlorantraniliprole, spiromesifen, fenazaquin, chlorpyrifos and fenvalerate in brinjal and cyantraniliprole, imidacloprid, spirotetramat, fenazaquin and flubendiamide in chilli at pre-harvest interval of crop (PHI) as follows:

Hazard quotient (HQ) was calculated as:

$$\text{HQ} = \frac{\text{EDI (Estimated daily intake)}}{\text{ADI (Acceptable daily intake)}}$$

Where,

ADI = acceptable daily intake expressed as mg/kg body weight/ day

Estimated daily intake (EDI) was calculated as:

$$\text{EDI} = \frac{\text{Highest residues} \times \text{Daily consumption of food commodity}}{\text{Body weight}}$$

Where,

EDI was expressed as mg/kg body weight/ day (Lozowieka et al. 2014)

The HQ (Hazard Quotient) was determined to know the acceptable risk in rural and urban community. If the HQ worked out for given pesticide is < 1, then the dietary risk considered to be within the acceptable risk; however, if value observed > 1, it will represent the higher risk to consumer (Malhat et al. 2014; Ludwicki et al. 2015).

To evaluate overall dietary risk assessment of insecticides, analysis of the consumer's total diet was worked out using theoretical maximum dietary intake (TMDI) for all the commodities in the Indian diet in a single day for which daily consumption data (NSSO 2014) and MRL (maximum residue limit) values. TMDI was calculated as product of MRL and per capita consumption per day.

$$\text{TMDI} = \text{MRL} \times \text{per capita consumption per day}$$

Calculated TMDI values were then compared with maximum permissible intake (MPI) and MRL values assigned to the chlorantraniliprole, spiromesifen, fenazaquin, chlorpyrifos and fenvalerate in brinjal and cyantraniliprole, imidacloprid, spirotetramat, fenazaquin and flubendiamide in chilli. MPI was worked out by multiplying acceptable daily intake (ADI) with average body weight (ICMR 2010).

$$\text{MPI} = \text{ADI} \times \text{Average body weight}$$

MPI is expressed as mg residue per person/day. If TMDI < MPI and MRL, then pesticides will be considered as safe and pose least risk to humans.

Chapter-4

RESULTS AND DISCUSSION

The present investigations were carried out in order to study “**Bio-efficacy and residue dynamics of some pesticides used against insect pests of brinjal and chilli**”. All the pesticides were analysed for their bio-efficacy and residue dynamics on treated brinjal and chilli crop during the two consecutive cropping seasons of 2021 and 2022. The data obtained from the bio-efficacy trial was recorded from the field trials conducted in the farm of Department of Entomology and residue analysis was carried out in Pesticide residue laboratory. The results, thus obtained have been described for each objective under the following heads:

- 4.1 Bioefficacy studies on brinjal**
- 4.2 Bioefficacy studies on chilli**
- 4.3 Validation of the analytical method (QuEChERS) for determination of pesticides in brinjal and chilli**
- 4.4 Persistence study of pesticides in brinjal fruits**
- 4.5 Persistence study of pesticides in chilli fruits**
- 4.6 Statistical constants of pesticides**
- 4.7 Persistence study of pesticides in soil**
- 4.8 Risk assessment**

4.1 Bioefficacy studies on brinjal

The bioefficacy of five pesticides *viz.*, chlorantraniliprole, fenazaquin, spiromesifen, fenvalerate and chlorpyrifos at three different doses i.e. lesser than single dose (x), single dose (X) and double dose (2X) were evaluated against jassids (*Amrasca biguttula biguttula*) and shoot and fruit borer (*Leucinodes orbonalis*) on brinjal crop in the two consecutive years 2021 and 2022.

4.1.1 Bioefficacy of pesticides against jassids (*A. biguttula biguttula*)

4.1.1.1 Per cent reduction of jassids after first spray application of pesticides on brinjal during 2021

The data presented in Table 4.1 showed that all treatments significantly reduced the number of jassids on 1, 3, 5, 7 and 10 days after spraying (DAS). According to observations made a day before spray, there were 5.43 to 7.18 jassids per plant and they were evenly distributed over the field.

Table 4.1 Bioefficacy of pesticides against jassids on brinjal after first spray during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	Pre-count (No. of jassids/plant)	Per cent reduction of jassids per plant***					
				1DAS	3DAS	5DAS	7DAS	10 DAS	Mean
T ₀	Untreated control	-	6.63 (2.76)**	-	-	-	-	-	
T ₁	Spiromesifen (22.9 % SC) (x)	72	7.18 (2.86)	53.56 (47.02)*	65.85 (54.25)	73.70 (59.13)	71.78 (57.91)	60.94 (51.52)	65.17 (53.93) ^{d, e}
T ₂	Spiromesifen (22.9 % SC) (X)	96	6.32 (2.70)	59.68 (50.58)	75.97 (60.65)	78.52 (62.46)	74.10 (59.40)	63.27 (52.74)	70.31 (57.17) ^c
T ₃	Spiromesifen (22.9 % SC) (2X)	192	6.79 (2.79)	62.52 (52.24)	81.46 (64.53)	86.90 (68.79)	76.05 (60.73)	66.70 (54.77)	74.73 (60.21) ^b
T ₄	Fenazaquin (10 % EC) (x)	94	6.62 (2.76)	65.15 (53.80)	77.32 (61.55)	73.61 (59.13)	67.36 (55.19)	61.66 (51.75)	69.02 (56.28) ^c
T ₅	Fenazaquin (10 % EC) (X)	125	6.44 (2.73)	73.94 (59.33)	84.98 (67.24)	82.32 (65.11)	74.30 (59.53)	69.38 (56.42)	76.99 (61.53) ^b
T ₆	Fenazaquin (10 % EC) (2X)	250	6.13 (2.67)	75.42 (60.32)	88.55 (70.26)	84.77 (67.07)	78.27 (62.27)	70.29 (56.97)	79.46 (63.38) ^a
T ₇	Chlorantraniliprole (18.5 %SC) (x)	30	6.07 (2.66)	52.72 (46.55)	49.35 (44.61)	53.66 (47.09)	50.23 (45.12)	45.59 (42.45)	50.31 (45.16) ^g
T ₈	Chlorantraniliprole (18.5 %SC) (X)	40	6.80 (2.79)	62.35 (52.14)	59.15 (50.26)	57.97 (49.57)	59.83 (50.67)	53.33 (46.90)	58.53 (49.91) ^f
T ₉	Chlorantraniliprole (18.5 %SC) (2X)	80	6.21 (2.68)	67.23 (55.11)	64.94 (53.69)	61.02 (51.36)	59.96 (50.74)	52.34 (46.32)	61.10 (51.44) ^{e, f}
T ₁₀	Fenvalerate (20 % EC) (x)	60	5.43 (2.53)	38.98 (38.61)	34.91 (36.16)	34.38 (35.82)	31.86 (34.28)	24.74 (29.68)	32.97 (34.91) ^k
T ₁₁	Fenvalerate (20 % EC) (X)	75	5.70 (2.58)	39.95 (39.18)	37.67 (37.85)	36.69 (37.26)	34.47 (35.94)	31.87 (34.33)	36.13 (36.91) ^j
T ₁₂	Fenvalerate (20 % EC) (2X)	150	6.50 (2.74)	41.74 (40.23)	40.95 (39.77)	42.18 (40.49)	43.52 (41.26)	41.66 (40.18)	42.01 (40.38) ^h
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	5.76 (2.60)	57.96 (49.56)	66.54 (54.68)	61.65 (51.72)	54.94 (47.82)	48.34 (44.03)	57.89 (49.56) ^f
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	5.52 (2.55)	60.42 (51.01)	72.03 (58.14)	64.36 (53.35)	59.48 (50.45)	56.14 (48.51)	62.49 (52.29) ^e
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	6.10 (2.66)	62.99 (52.53)	70.16 (56.99)	67.96 (55.56)	66.67 (54.73)	61.98 (51.91)	65.95 (54.34) ^d
	Mean		NS	58.31 (49.88) ^c	64.66 (54.04) ^a	63.98 (53.59) ^a	60.19 (51.07) ^b	53.88 (47.22) ^d	

*Figure in parentheses are arc sine transformed values, **Figure in parentheses are square root transformed values

***Mean of 3 replications DAS- Days after spray NS- Non significant

CD_{0.05} (Days): 1.04

(Treatments): 1.79

(Days × Treatments): 4.02

The findings shown in Table 4.1 revealed that all treatments treated with various pesticides significantly reduced the number of jassids. After first spray of application, highest significant mean per cent reduction was found in the plots treated with fenazaquin (79.46 %) @ 250 g a.i./ha (T₆) which was followed by fenazaquin @ 125 g a.i./ha (T₅) with 76.99 % reduction. Lowest per cent reduction of 32.97 per cent was observed in the plot treated with fenvalerate @ 60 a.i./ha. In treatment T₁ (spiromesifen @ 72 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha) and T₃ (spiromesifen @ 192 g a.i./ha) jassids population significantly reduced upto 5th day. In the treatments like T₄ (fenazaquin @ 94 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha), T₁₄ (chlorpyrifos @ 200 g a.i./ha) and T₁₅ (chlorpyrifos @ 400 g a.i./ha) per cent reduction of jassids was increased

upto 3rd day of spray. Variation was noticed in the plots of T₇ (chlorantraniliprole @ 30 g a.i./ha), T₈ (chlorantraniliprole @ 40 g a.i./ha) and T₁₂ (fenvalerate @ 150 g a.i./ha) where slight increase and decrease of jassids population was noticed at different days of observations. This variation can be due to pesticide pressure or changing weather conditions on different days. In treatment T₉ (chlorantraniliprole @ 80 g a.i./ha), T₁₀ (fenvalerate @ 60 g a.i./ha) and T₁₁ (fenvalerate @ 75 g a.i./ha) increasing trend in jassids population was noticed at all days after spray (Table 4.1).

Overall comparison of different treatments revealed that treatment T₆ (fenazaquin @ 250 g a.i./ha) was the most effective against jassids on brinjal providing 79.46 per cent reduction (Table 4.1). The next best treatment was T₅ (fenazaquin @ 125 g a.i./ha) with 76.99 per cent reduction which was statistically at par with treatment T₃ (spiromesifen @ 192 g a.i./ha) with a reduction of 74.73 per cent. The next best treatment in the series was treatment T₂ (Spiromesifen @ 96 g a.i./ha) with overall 70.31 per cent reduction in the population of jassids which was statistically at par with treatment T₄ (fenazaquin @ 94 g a.i./ha). Treatment T₁₄ (chlorpyrifos @ 200 g a.i./ha) and T₁₅ (chlorpyrifos @ 400 g a.i./ha) with a reduction of 62.49 and 65.95 per cent, respectively were statistically at par with treatment T₁ (spiromesifen @ 72 g a.i./ha). Treatment T₁₄ (chlorpyrifos @ 200 g a.i./ha) (62.49 %) and T₈ (chlorantraniliprole @ 40 g a.i./ha) (58.53 %) were statistically at par with treatment T₉ (chlorantraniliprole @ 80 g a.i./ha) (61.10 %) also, T₈ (chlorantraniliprole @ 40 g a.i./ha) was statistically at par with T₁₃ (chlorpyrifos @ 150 g a.i./ha) (57.89%). Lowest per cent reduction was observed in the plot T₁₀ (fenvalerate @ 60 g a.i./ha) followed by T₁₁ (fenvalerate @ 75 g a.i./ha), T₁₂ (fenvalerate @ 150 g a.i./ha) and T₇ (chlorantraniliprole @ 30 g a.i./ha) with per cent reduction of 32.97, 36.13, 42.01 and 50.31 per cent, respectively.

4.1.1.2 Per cent reduction of jassids after second spray application of pesticides on brinjal during 2021

After second spray, again treatment T₆ (fenazaquin @ 250 g a.i./ha) caused the highest per cent reduction (86.01 %) of jassid population on 1DAS followed by T₅ (fenazaquin @ 125 g a.i./ha) (75.47 %) and again lowest per cent reduction (41.95 %) was recorded in the treatment T₁₀ (fenvalerate @ 60 g a.i./ha) after 1DAS. Treatment from T₁ to T₅ showed similar decreasing trend of jassid population upto 7th DAS. However, except T₁₀ and T₁₁ where an increasing trend was noticed on all days, all other treatments showed similar increasing trend from 5th DAS.

Mean reduction after 10 DAS revealed highest control of jassid population with double dose of fenazaquin (@ 250 g a.i./ha) giving a control of 84.50 per cent which was statistically superior to all other treatments. The second best treatment was T₅ (fenazaquin @ 125 g a.i./ha) with 81.78 per cent reduction of jassids over control. The next best treatment in series was T₃ (spiromesifen @ 192 g a.i./ha) (75.61 %) which was statistically at par with T₄ (fenazaquin @ 94 g a.i./ha) and T₂ (spiromesifen @ 96 g a.i./ha) showing a 73.99 and 73.60 per cent reduction, respectively. T₁ (spiromesifen @ 72 g a.i./ha) showed 68.21 per cent of reduction in jassid population which was statistically at par with T₁₄ (chlorpyrifos @ 200 g a.i./ha) (66.88 %) and T₁₅ (chlorpyrifos @ 400 g a.i./ha) (68.00 %), T₁₄ was also statistically at par with T₉ (chlorantraniliprole @ 80 g a.i./ha) and T₁₃ (chlorpyrifos @ 150 g a.i./ha) with per cent reduction 63.61 and 63.88, respectively. Again the lowest per cent reduction of jassids was noticed in plots treated with fenvalerate (Table 4.2).

Table 4.2 Bioefficacy of pesticides against jassids on brinjal after second spray during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	Per cent reduction of jassids per plant**					Mean
			1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	-	-	-	-	-	-
T ₁	Spiromesifen (22.9 % SC) (x)	72	59.85 (50.66)*	69.52 (56.51)	77.33 (61.57)	70.67 (57.21)	63.67 (52.93)	68.21 (55.77) ^d
T ₂	Spiromesifen (22.9 % SC) (X)	96	63.47 (52.80)	77.30 (61.64)	84.67 (66.94)	74.47 (59.70)	68.10 (55.61)	73.60 (59.34) ^c
T ₃	Spiromesifen (22.9 % SC) (2X)	192	64.85 (53.63)	79.60 (63.28)	84.87 (67.22)	79.37 (63.13)	69.37 (56.39)	75.61 (60.73) ^c
T ₄	Fenazaquin (10 % EC) (x)	94	68.08 (55.60)	81.43 (64.52)	75.85 (60.57)	72.95 (58.64)	71.63 (57.80)	73.99 (59.42) ^c
T ₅	Fenazaquin (10 % EC) (X)	125	75.47 (60.42)	88.34 (70.03)	85.07 (67.24)	81.08 (64.25)	78.92 (62.77)	81.78 (64.94) ^b
T ₆	Fenazaquin (10 % EC) (2X)	250	86.01 (68.12)	91.75 (73.38)	87.90 (69.73)	80.92 (64.15)	75.92 (60.65)	84.50 (67.20) ^a
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	56.94 (48.99)	57.67 (49.42)	52.05 (46.16)	48.39 (44.06)	47.03 (43.28)	52.42 (46.38) ^h
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	65.55 (54.05)	71.26 (57.57)	65.68 (54.12)	52.15 (46.29)	48.56 (44.17)	60.64 (51.24) ^g
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	67.68 (55.35)	69.97 (56.76)	63.80 (53.00)	61.64 (51.72)	54.96 (47.84)	63.61 (52.93) ^{f, g}
T ₁₀	Fenvalerate (20 % EC) (x)	60	41.95 (40.35)	38.66 (38.42)	34.29 (35.80)	33.68 (35.41)	29.82 (32.99)	35.68 (36.59) ^j
T ₁₁	Fenvalerate (20 % EC) (X)	75	45.15 (42.19)	38.01 (38.02)	36.61 (37.21)	35.83 (36.74)	34.47 (35.91)	38.01 (38.01) ^j
T ₁₂	Fenvalerate (20 % EC) (2X)	150	45.08 (42.14)	49.66 (44.77)	48.94 (44.37)	41.21 (39.91)	37.37 (37.66)	44.45 (41.77) ⁱ
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	60.75 (51.21)	71.89 (57.98)	67.11 (55.00)	62.39 (52.16)	57.24 (49.15)	63.88 (53.10) ^{e, f, g}
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	63.68 (52.93)	78.43 (62.35)	70.23 (56.98)	62.73 (52.48)	59.30 (50.38)	66.88 (55.02) ^{d, e, f}
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	69.52 (56.66)	78.90 (62.76)	72.23 (58.18)	61.60 (51.69)	57.77 (49.46)	68.00 (55.75) ^d
	Mean		62.27 (52.34) ^c	69.49 (57.16) ^a	67.11 (55.61) ^b	61.27 (51.83) ^c	56.94 (49.13) ^d	

*Figure in parentheses is arc sine transformed values, ** Mean of 3 replications DAS- Days after spray

CD_{0.05} (Days): 1.25

(Treatments): 2.17

(Days × Treatments): 4.85

4.1.1.3 Per cent reduction of jassids after first spray application of pesticides on brinjal during 2022

The data presented in Table 4.3 revealed that all the treatments applied on brinjal crop were statistically superior over control. One day before the application of pesticides the number of jassids varied from 6.34-7.78 jassids per plant.

Table 4.3 Bioefficacy of pesticides against jassids on brinjal after first spray during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	Pre-count (No. of jassids/plant)	Per cent reduction of jassids per plant***					
				1DAS	3DAS	5DAS	7DAS	10 DAS	Mean
T ₀	Untreated control	-	6.85 (2.80)**	-	-	-	-	-	
T ₁	Spiromesifen (22.9 % SC) (x)	72	7.36 (2.89)	57.18 (49.11)*	71.61 (57.79)	70.73 (57.23)	68.80 (56.04)	63.23 (52.67)	66.31 (54.57) ^d
T ₂	Spiromesifen (22.9 % SC) (X)	96	6.90 (2.81)	66.93 (54.91)	76.01 (60.68)	78.81 (62.68)	75.39 (60.28)	72.54 (58.38)	73.94 (59.38) ^b
T ₃	Spiromesifen (22.9 % SC) (2X)	192	7.26 (2.87)	71.47 (57.70)	79.95 (63.41)	82.35 (65.15)	83.61 (66.15)	76.50 (60.99)	78.78 (62.68) ^a
T ₄	Fenazaquin (10 % EC) (x)	94	6.78 (2.79)	67.08 (54.97)	76.09 (60.73)	74.43 (59.62)	72.15 (58.15)	69.54 (56.50)	71.86 (57.99) ^{b,c}
T ₅	Fenazaquin (10 % EC) (X)	125	6.34 (2.71)	74.73 (59.87)	80.59 (63.86)	85.60 (67.67)	79.71 (63.23)	71.18 (57.53)	78.36 (62.43) ^a
T ₆	Fenazaquin (10 % EC) (2X)	250	7.05 (2.84)	73.53 (59.07)	82.34 (65.13)	86.36 (68.31)	82.64 (65.37)	75.27 (60.17)	80.03 (63.61) ^a
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	6.55 (2.75)	53.41 (46.94)	64.76 (53.57)	59.58 (50.52)	54.40 (47.51)	49.97 (44.97)	56.43 (48.70) ^f
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	6.56 (2.75)	55.03 (47.88)	68.83 (56.05)	63.13 (52.60)	63.00 (52.58)	59.10 (50.22)	61.91 (51.91) ^e
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	7.14 (2.85)	58.69 (50.00)	69.20 (56.29)	74.38 (59.59)	69.67 (56.60)	61.29 (51.52)	66.65 (54.80) ^d
T ₁₀	Fenvalerate (20 % EC) (x)	60	6.43 (2.73)	39.21 (38.74)	39.59 (38.96)	37.44 (37.69)	34.67 (36.05)	32.01 (34.44)	36.59 (37.18) ^h
T ₁₁	Fenvalerate (20 % EC) (X)	75	6.96 (2.82)	41.44 (40.04)	41.99 (40.36)	37.63 (37.81)	35.74 (36.67)	31.14 (33.89)	37.59 (37.75) ^h
T ₁₂	Fenvalerate (20 % EC) (2X)	150	7.44 (2.91)	43.84 (41.44)	46.90 (43.20)	44.23 (41.65)	38.35 (38.23)	36.08 (36.87)	41.88 (40.28) ^g
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	6.76 (2.76)	56.10 (48.50)	59.03 (50.19)	68.87 (56.07)	64.90 (53.66)	59.59 (50.51)	61.70 (51.79) ^e
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	7.78 (2.96)	65.13 (53.80)	79.05 (62.79)	75.32 (60.33)	69.38 (56.52)	59.49 (50.51)	69.67 (56.79) ^c
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	7.26 (2.87)	68.17 (55.64)	72.86 (58.58)	78.80 (62.57)	72.28 (58.23)	66.45 (54.60)	71.71 (57.92) ^{b,c}
	Mean		NS	59.46 (50.57) ^c	67.26 (55.44) ^a	67.84 (55.97) ^a	64.34 (53.70) ^b	58.89 (50.25) ^c	

*Figure in parentheses is arc sine transformed values, **Figure in parentheses is square root transformed values

***Mean of 3 replications DAS- Days after spray NS- Non significant

CD_{0.05} (Days): 0.87

(Treatments): 1.51

(Days × Treatments): 3.37

During second year, again the plots treated with fenazaquin showed less number of jassid population in which treatment T₆ (fenazaquin @ 250 g a.i./ha) showed maximum mean per cent reduction of 80.03 per cent and was most effective after 5 days (86.36 %) of spray and was at par with T₃ (spiromesifen @ 192 g a.i./ha) and T₅ (fenazaquin @ 125 g a.i./ha) which showed 78.78 and 78.36 per cent reduction, respectively. The next best treatment was T₂

(spiromesifen @ 96 g a.i./ha) which showed highest reduction after 5 days of spray and was at par with T₄ (fenazaquin @ 94 g a.i./ha) and T₁₅ (chlorpyrifos @ 400 g a.i./ha) with the reduction of 71.86 and 71.71 per cent, respectively, also the two of the treatments were found at par with T₁₄ (chlorpyrifos @ 200 g a.i./ha) with the reduction of 69.67 per cent. The plots received treatments T₉ (chlorantraniliprole @ 80 g a.i./ha) (66.65 %) and T₁ (spiromesifen @ 72 g a.i./ha) (66.31 %) were at par with each other. The treatment T₈ (chlorantraniliprole @ 40 g a.i./ha) and T₁₃ (chlorpyrifos @ 150 g a.i./ha) were at par with each other with per cent reduction of 61.91 and 61.70 per cent, respectively. Other treatments i.e. T₁₀ (fenvalerate @ 60 g a.i./ha), T₁₁ (fenvalerate @ 75 g a.i./ha), T₁₂ (fenvalerate @ 150 g a.i./ha) and T₇ (chlorantraniliprole @ 30 g a.i./ha) showed least reduction of jassids i.e. 36.59, 37.59, 41.88 and 56.43 per cent, respectively (Table 4.3)

Treatment T₁ (spiromesifen @ 72 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha), T₇ (chlorantraniliprole @ 30 g a.i./ha), T₈ (chlorantraniliprole @ 40 g a.i./ha) and T₁₄ (chlorpyrifos @ 200 g a.i./ha) showed an increase in jassid population after 3rd day of spray, whereas T₂ (spiromesifen @ 96 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha), T₉ (chlorantraniliprole @ 80 g a.i./ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha) and T₁₅ (chlorpyrifos @ 400 g a.i./ha) showed a decreasing trend upto 5th day of spray. Treatments T₁₀ (fenvalerate @ 60 g a.i./ha), T₁₁ (fenvalerate @ 75 g a.i./ha) and T₁₂ (fenvalerate @ 150 g a.i./ha) with lowest per cent reduction showed a increasing trend after 3rd day of spray.

4.1.1.4 Per cent reduction of jassids after second spray application of pesticides on brinjal during 2022

After second spray in 2022, the plots treated with treatment T₆ (fenazaquin @ 250 g a.i./ha) showed highest effectiveness in reducing jassid population with 85.57 per cent reduction (Table 4.4). The second most effective treatment was T₅ (fenazaquin @ 125 g a.i./ha) with 82.00 per cent reduction which was followed by T₃ (spiromesifen @ 192 g a.i./ha) . The next best applied treatment was T₄ (fenazaquin @ 94 g a.i./ha) (76.25 %) which was at par with T₂ (spiromesifen @ 96 g a.i./ha) (76.06 %) and T₁₅ (chlorpyrifos @ 400 g a.i./ha) (73.91 %). Treatments T₁₄ (chlorpyrifos @ 200 g a.i./ha) (70.00 %), T₉ (chlorantraniliprole @ 80 g a.i./ha) (69.87 %) and T₁ (spiromesifen @ 72 g a.i./ha) (69.51 %) were statistically at par with one another with each other. Treatment T₈ (chlorantraniliprole @ 40 g a.i./ha) and T₁₃ (chlorpyrifos @ 150 g a.i./ha) proved to be next best applied treatments with 64.72 and 62.99

per cent reduction which were statistically at par with each other. Lowest number of reduction was in the treatments T₁₀ (fenvalerate @ 60 g a.i./ha), T₁₁ (fenvalerate @ 75 g a.i./ha), T₁₂ (fenvalerate @ 150 g a.i./ha) and T₇ (chlorantraniliprole @ 30 g a.i./ha), provided 38.71, 40.54, 42.79 and 59.41 per cent reduction in the population of jassids, respectively (Table 4.4)

Table 4.4 Bioefficacy of pesticides against jassids on brinjal after second spray in 2022

Treatments	Pesticides	Dosage (g a.i./ha)	Per cent reduction of jassids per plant**					Mean
			1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	-	-	-	-	-	-
T ₁	Spiromesifen (22.9 % SC) (x)	72	60.82 (51.24)*	73.80 (59.20)	75.26 (60.19)	70.65 (57.19)	67.04 (54.96)	69.51 (56.56) ^c
T ₂	Spiromesifen (22.9 % SC) (X)	96	69.55 (56.54)	77.29 (61.55)	79.99 (63.42)	80.48 (63.86)	72.99 (58.69)	76.06 (60.81) ^d
T ₃	Spiromesifen (22.9 % SC) (2X)	192	73.54 (59.06)	81.41 (64.56)	80.29 (63.64)	85.07 (67.45)	76.73 (61.18)	79.41 (63.18) ^c
T ₄	Fenazaquin (10 % EC) (x)	94	68.26 (55.72)	78.01 (62.01)	82.46 (65.25)	79.69 (63.36)	72.83 (58.59)	76.25 (60.99) ^d
T ₅	Fenazaquin (10 % EC) (X)	125	78.18 (62.21)	85.42 (67.58)	86.75 (68.68)	83.28 (65.98)	76.38 (60.91)	82.00 (65.07) ^b
T ₆	Fenazaquin (10 % EC) (2X)	250	77.62 (61.86)	89.42 (71.00)	91.81 (73.44)	86.98 (68.98)	82.01 (64.94)	85.57 (68.04) ^a
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	58.05 (49.62)	61.63 (51.72)	64.94 (53.67)	58.43 (49.84)	54.01 (47.28)	59.41 (50.43) ^g
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	56.73 (48.85)	68.76 (56.00)	72.06 (58.10)	67.54 (55.27)	58.51 (49.89)	64.72 (53.62) ^f
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	60.91 (51.32)	70.06 (56.85)	75.20 (60.18)	77.22 (61.51)	65.95 (54.28)	69.87 (56.83) ^c
T ₁₀	Fenvalerate (20 % EC) (x)	60	43.51 (41.24)	40.47 (39.49)	37.59 (37.79)	36.14 (36.92)	35.82 (36.74)	38.71 (38.44) ⁱ
T ₁₁	Fenvalerate (20 % EC) (X)	75	41.89 (40.31)	41.18 (39.90)	39.26 (38.78)	40.53 (39.53)	39.83 (39.12)	40.54 (39.53) ^{hi}
T ₁₂	Fenvalerate (20 % EC) (2X)	150	46.11 (42.75)	45.74 (42.53)	43.78 (41.41)	40.35 (39.41)	37.98 (38.01)	42.79 (40.82) ^h
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	56.82 (48.90)	67.74 (55.42)	65.74 (54.18)	63.01 (52.53)	61.65 (51.72)	62.99 (52.55) ^f
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	66.29 (54.52)	80.83 (64.05)	76.81 (61.20)	64.81 (53.60)	61.27 (51.50)	70.00 (56.97) ^c
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	69.89 (56.73)	71.09 (57.48)	77.92 (61.99)	80.33 (63.65)	70.35 (57.02)	73.91 (59.37) ^d
	Mean		61.88 (52.06) ^c	68.86 (56.62) ^a	69.99 (57.46) ^a	67.63 (55.94) ^b	62.22 (52.32) ^c	

*Figure in parentheses is arc sine transformed values, ** Mean of 3 replications DAS- Days after spray

CD_{0.05} (Days): 0.97

(Treatments): 1.68

(Days × Treatments): 3.74

4.1.1.5 Average per cent reduction of jassids following two applications of pesticides during 2021 and 2022

Throughout the two years, all insecticides exhibited identical patterns in all sprays. In each spray, it was discovered that the applied treatments were superior to the control. The results of all pesticide applications showed that treatment T₆ (fenazaquin @ 250 g a.i./ha) was the most successful of all treatments and treatment T₁₀ (fenvalerate @ 60 g a.i./ha) was prove to be less effective than all other treatments (Fig. 4.1 and 4.2).

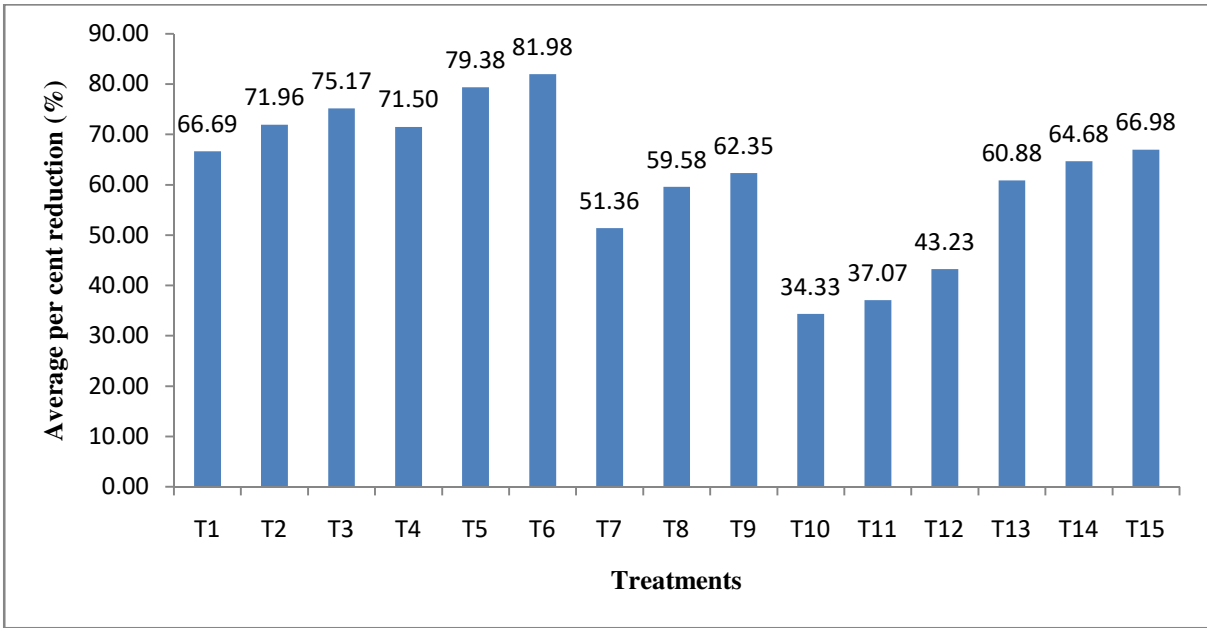


Fig. 4.1 Average per cent reduction of jassids in brinjal after two sprays during 2021

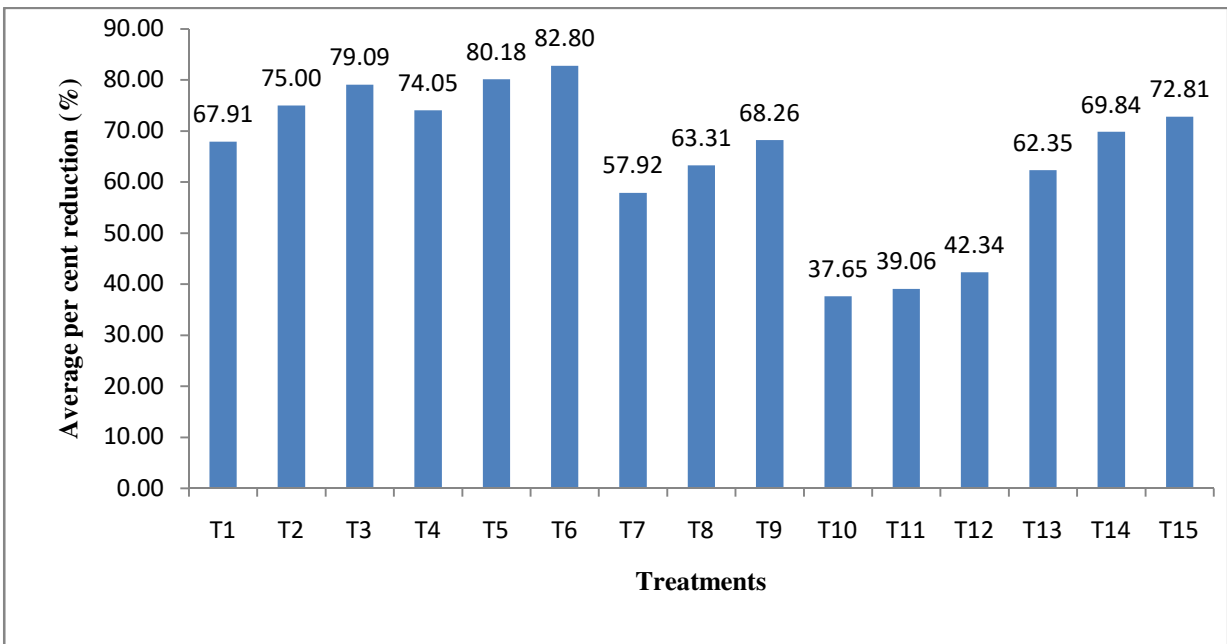


Fig. 4.2 Average per cent reduction of jassids in brinjal after two sprays during 2022

The bioefficacy of chlorantraniliprole, spiromesifen, fenazaquin, chlorpyrifos and fenvalerate against jassids in brinjal has not been studied by much workers hence very less data are available. The present studies were conducted on mentioned pesticides under mid hill conditions of Himachal Pradesh. The results of our study showed that fenazaquin @ 250 g a.i./ha was most effective among all other treatments and was followed by the spiromesifen @ 192 g a.i./ha treated plots in both the years.

Our findings were in close proximity with the experiment conducted by Surwase et al. (2017) who found that after application of spiromesifen @ 96 g a.i./ha against jassids in cotton per cent reduction of 64.31 and 74.41 per cent was recorded after 2nd and 3rd spray, respectively. The dissimilarity in our results can be due to the different crop physiology, rate of application and the climatic conditions of that place. Vikas (2020) conducted a study on bioefficacy of different pesticides against jassids in brinjal and revealed that the plots treated with chlorpyrifos @ 200 g a.i./ha recorded 62.63, 69.84 and 76.30 per cent reduction in the population of jassids after 1st, 2nd and 3rd spray, respectively which was in close proximity to our results.

4.1.2 Bioefficacy of pesticides against brinjal shoot and fruit borer (*Leucinodes orbonalis*) in brinjal

The different pesticides viz., spiromesifen, fenazaquin, chlorantraniliprole, fenvalerate and chlorpyrifos were evaluated at three concentrations i.e. less than single dose (x), single dose (X) and double dose (2X), for the management of brinjal shoot and fruit borer. Pre-treatment observations on shoot infestation were recorded a day prior to the treatment and there after observations were recorded at 5 and 10 days after each spray. In case of fruit infestation observations were recorded after each spray (10 days).

4.1.2.1 Effect of pesticides on per cent shoot damage by shoot and fruit borer after first spray in brinjal during 2021

The shoot infestation one day before spray ranged between 14.99 to 17.39 per cent (Table 4.5). There was no significant difference in the shoot infestation among all treatments before spray, indicating that the pest was more or less uniformly present throughout the crop.

At five days after first spray significantly lowest shoot infestation (3.86 %) was recorded in T₉ (chlorantraniliprole @ 80 g a.i./ha) which was significantly at par with T₈ (chlorantraniliprole @ 40 g a.i./ha) (3.94 %) followed by T₇ (chlorantraniliprole @ 30 g a.i./ha) with the shoot infestation of 5.57 per cent which was further at par with the T₁₅ (chlorpyrifos @ 400 g a.i./ha) (7.00 %). The next best treatment was T₁₂ (fenvalerate @ 150 g a.i./ha) (7.69 %) which was statistically at par with T₁₄ (chlorpyrifos @ 200 g a.i./ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha), T₁₁ (fenvalerate @ 75 g a.i./ha) and T₁₀ (fenvalerate @ 60 g a.i./ha) with per cent infestation of 8.36, 8.91, 9.20 and 9.40 per cent, respectively. Treatment T₆ (fenazaquin @ 250 g a.i./ha) (10.41 %) was statistically at par with T₃ (spiromesifen @ 192 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha) and T₄

(fenazaquin @ 94 g a.i./ha) with per cent infestation of 10.66, 10.90, 12.12 and 12.46 per cent, respectively and among treated plots the maximum shoot infestation was recorded in T₁ (spiromesifen @ 72 g a.i./ha) (13.85 %). The order of lowest to highest shoot infestation was T₉> T₈>T₇>T₁₅>T₁₂>T₁₄>T₁₃>T₁₁>T₁₀>T₆>T₃>T₅>T₂>T₄>T₁>T₀.

Ten days after treatment, the mean shoot infestation was recorded between 2.74-14.93 per cent when compared to untreated control (20.10 %). Minimum mean per cent shoot infestation of 2.74 per cent was recorded in the treatment T₉ (chlorantraniliprole @ 80 g a.i./ha) which was statistically at par with T₈ (chlorantraniliprole @ 80 g a.i./ha) (3.64 %). Next best treatment was T₇ (chlorantraniliprole @ 30 g a.i./ha) (4.78 %) which was statistically at par with T₁₅ (chlorpyrifos @ 400 g a.i./ha) (5.10 %), T₁₄ (chlorpyrifos @ 200 g a.i./ha) (6.55 %) and T₁₃ (chlorpyrifos @ 150 g a.i./ha) (6.62 %). Treatment T₁₂ (fenvalerate @ 150 g a.i./ha) was at par with T₁₁ (fenvalerate @ 75 g a.i./ha), T₁₀ (fenvalerate @ 60 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha) and T₅ (fenazaquin @ 125 g a.i./ha) with shoot infestation in the range of 9.03-9.70 per cent. Treatments T₃ (spiromesifen @ 192 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha) and T₁ (spiromesifen @ 72 g a.i./ha), and showed an increasing trend of per cent shoot infestation by borer i.e. 11.12, 13.39, 14.69 and 14.93 per cent, respectively. The order of lowest to highest shoot infestation was T₉>T₈>T₇>T₁₅>T₁₄>T₁₃>T₁₂>T₁₁>T₁₀>T₆>T₅>T₃>T₄>T₂>T₁>T₀.

4.1.2.2 Effect of pesticides on per cent shoot damage by shoot and fruit borer after second spray in brinjal during 2021

The data presented in Table 4.5, showed that, all tested pesticides were significantly superior over the control in reducing the shoot damage by shoot and fruit borer on brinjal. On 5th day after spray, the damage varied from 1.30 per cent (chlorantraniliprole @ 80 g a.i./ha) to 22.15 per cent (in control). The application of T₉ (chlorantraniliprole @ 80 g a.i./ha) was significantly superior to other treatments. The next best treatment in series was treatment T₈ (chlorantraniliprole @ 40 g a.i./ha) (2.97 %) which was at par with T₇ (chlorantraniliprole @ 30 g a.i./ha) with per cent infestation of 4.03 per cent. Next best treatment in series was T₁₅ (chlorpyrifos @ 400 g a.i./ha) (7.44 %) which was statistically at par with T₁₄ (chlorpyrifos @ 200 g a.i./ha), T₁₂ (fenvalerate @ 150 g a.i./ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha) and T₁₁ (fenvalerate @ 75 g a.i./ha) with per cent infestation in the range of 7.94-9.20 per cent. Other treatments T₁₀ (fenvalerate @ 60 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha), T₃ (spiromesifen @ 192 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), T₄

(fenazaquin @ 94 g a.i./ha) and T₁ (spiromesifen @ 72 g a.i./ha) showed per cent infestation of 9.40, 10.17, 10.87, 11.04, 12.63, 13.82 and 15.32 per cent, respectively. The efficacy of the pesticides was T₉> T₈> T₇> T₁₅> T₁₄> T₁₂> T₁₃> T₁₁> T₁₀> T₆> T₃> T₅>T₂>T₄>T₁>T₀.

Table 4.5: Effect of different pesticides treatments on shoot infestation by shoot and fruit borer of brinjal during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	Precount (% shoot infestation)	Per cent shoot infestation**			
				After 1 st spray		After 2 nd spray	
				5 th day	10 th day	5 th day	10 th day
T ₀	Untreated control	-	16.55 (4.19)*	18.42 (4.41) ^f	20.10 (4.59) ^f	22.15 (4.81) ^g	23.34 (4.93) ^g
T ₁	Spiromesifen (22.9 % SC) (x)	72	17.39 (4.29)	13.85 (3.85) ^c	14.93 (3.99) ^c	15.32 (4.04) ^f	12.59 (3.69) ^f
T ₂	Spiromesifen (22.9 % SC) (X)	96	17.23 (4.27)	12.12 (3.62) ^d	14.69 (3.96) ^e	12.63 (3.69) ^e	10.88 (3.45) ^e
T ₃	Spiromesifen (22.9 % SC) (2X)	192	15.60 (4.07)	10.66 (3.41) ^d	11.12 (3.48) ^d	10.87 (3.45) ^d	10.31 (3.36) ^c
T ₄	Fenazaquin (10 % EC) (x)	94	16.04 (4.13)	12.46 (3.67) ^d	13.39 (3.79) ^d	13.82 (3.85) ^e	14.11 (3.89) ^f
T ₅	Fenazaquin (10 % EC) (X)	125	15.83 (4.10)	10.90 (3.45) ^d	9.70 (3.27) ^c	11.04 (3.47) ^d	11.86 (3.59) ^c
T ₆	Fenazaquin (10 % EC) (2X)	250	16.34 (4.16)	10.41 (3.38) ^d	9.46 (3.23) ^c	10.17 (3.34) ^d	11.30 (3.51) ^e
T ₇	Chlorantraniliprole(18.5 % SC) (x)	30	16.35 (4.17)	5.57 (2.56) ^b	4.78 (2.40) ^b	4.03 (2.24) ^b	3.41 (2.10) ^b
T ₈	Chlorantraniliprole(18.5 % SC) (X)	40	15.08 (4.01)	3.94 (2.22) ^a	3.64 (2.15) ^a	2.97 (1.99) ^b	1.37 (1.54) ^a
T ₉	Chlorantraniliprole(18.5 % SC) (2X)	80	15.44 (4.05)	3.86 (2.20) ^a	2.74 (1.93) ^a	1.30 (1.52) ^a	1.00 (1.41) ^a
T ₁₀	Fenvalerate (20 % EC) (x)	60	16.57 (4.19)	9.40 (3.22) ^c	9.03 (3.17) ^c	9.40 (3.22) ^d	9.55 (3.25) ^c
T ₁₁	Fenvalerate (20 % EC) (X)	75	16.54 (4.19)	9.20 (3.19) ^c	9.03 (3.17) ^c	9.20 (3.19) ^c	9.03 (3.17) ^d
T ₁₂	Fenvalerate (20 % EC) (2X)	150	14.99 (4.00)	7.69 (2.95) ^c	8.10 (3.02) ^c	8.73 (3.12) ^c	7.43 (2.90) ^d
T ₁₃	Chlorpyriphos (20 % EC) (x)	150	16.30 (4.16)	8.91 (3.15) ^c	6.62 (2.76) ^b	8.99 (3.16) ^c	8.37 (3.06) ^d
T ₁₄	Chlorpyriphos (20 % EC) (X)	200	16.43 (4.17)	8.36 (3.06) ^c	6.55 (2.75) ^b	7.94 (2.99) ^c	5.37 (2.52) ^c
T ₁₅	Chlorpyriphos (20 % EC) (2X)	400	16.32 (4.16)	7.00 (2.83) ^b	5.10 (2.47) ^b	7.44 (2.91) ^c	4.48 (2.34) ^b
	C.D _{0.05}		NS	0.32	0.45	0.29	0.34

*Figure in parentheses is square root transformed values **Mean of 3 replications NS- Non significant

After ten days of spray, the shoot damage varied from 1.00 (chlorantraniliprole @ 80 g a.i./ha) to 23.34 (control) per cent. The minimum infestation was found in T₉

(chlorantraniliprole @ 80 g a.i./ha) which was statistically at par with T₈ (chlorantraniliprole @ 40 g a.i./ha) (1.37 %). Next best treatment was T₇ (chlorantraniliprole @ 30 g a.i./ha) (3.41 %) which was statistically at par with T₁₅ (chlorpyrifos @ 400 g a.i./ha) with 4.48 per cent shoot infestation. Treatment T₁₄ (chlorpyrifos @ 200 g a.i./ha) with 5.37 per cent infestation was third best treatment in series. Treatment T₁₂ (fenvalerate @ 150 g a.i./ha) was statistically at par with treatment T₁₃ (chlorpyrifos @ 150 g a.i./ha) and T₁₁ (fenvalerate @ 75 g a.i./ha) showing per cent infestation of 8.37 and 9.03 per cent, respectively. Other treatments *viz.*, T₁₀ (fenvalerate @ 60 g a.i./ha), T₃ (spiromesifen @ 192 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₁ (spiromesifen @ 72 g a.i./ha) and T₄ (fenazaquin @ 94 g a.i./ha) showed per cent infestation in the range of 9.55-14.11 per cent. The trend of effectiveness of insecticides was almost same as observed on 5th day after the spray. The efficacy of the pesticides were T₉>T₈ >T₇>T₁₅>T₁₄> T₁₂>T₁₃>T₁₁>T₁₀>T₃>T₂>T₆>T₅>T₁>T₄>T₀.

4.1.2.3 Effect of pesticides on per cent shoot damage by shoot and fruit borer after first spray in brinjal during 2022

The data on infestation by shoot and fruit borer on shoots after first and second spray during 2022 was presented in Table 4.6. All the pesticides were found to be significantly superior over untreated control in minimizing incidence of brinjal shoot borer after first application of pesticides. The post treatment observations recorded on 5th day after spraying indicated that the minimum shoot damage was recorded in the treatment T₉ (chlorantraniliprole @ 80 g a.i./ha) (3.97 %) which was statistically at par with T₈ (chlorantraniliprole @ 40 g a.i./ha) (4.63 %) and T₇ (chlorantraniliprole @ 30 g a.i./ha) (4.92 %). The next best treatment was T₁₂ (fenvalerate @ 150 g a.i./ha) (7.25 %) which was statistically at par with T₁₅ (chlorpyrifos @ 400 g a.i./ha), T₁₁ (fenvalerate @ 75 g a.i./ha) and T₁₄ (chlorpyrifos @ 200 g a.i./ha) with per cent shoot infestation of 7.96, 8.33 and 8.51 per cent, respectively. Shoot infestation of other treatments *viz.*, T₁₀ (fenvalerate @ 60 g a.i./ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha), T₃ (spiromesifen @ 192 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha) were in the range of 10.38-11.21 per cent. Among all the treatments the maximum shoot infestation was recorded in T₁ (spiromesifen @ 72 g a.i./ha) i.e. 12.40 per cent. The efficacy of the pesticides was T₉>T₈>T₇>T₁₂>T₁₅>T₁₁>T₁₄>T₁₀>T₁₃>T₆>T₃>T₅>T₂>T₄>T₁>T₀.

Similarly, after ten days after first spray, again plots treated with T₉ (chlorantraniliprole @ 80 g a.i./ha) (1.38 %) showed lowest shoot damage among all the other treated ones. The next best treatment was T₈ (chlorantraniliprole @ 40 g a.i./ha) (3.54 %) which was statistically at par with T₇ (chlorantraniliprole @ 30 g a.i./ha) with per cent infestation of 3.72 per cent. Treatment T₁₂ (fenvalerate @ 150 g a.i./ha) (5.45 %) was statistically at par with T₁₅ (chlorpyriphos @ 400 g a.i./ha) (6.04 %). Treatments T₁₄ (chlorpyriphos @ 200 g a.i./ha), T₁₃ (chlorpyriphos @ 150 g a.i./ha), T₁₁ (fenvalerate @ 75 g a.i./ha), T₁₀ (fenvalerate @ 60 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha), T₃ (spiromesifen @ 192 g a.i./ha) and T₂ (spiromesifen @ 96 g a.i./ha) showed per cent infestation in the range of 6.95-13.10 per cent. Treatment T₁ (spiromesifen @ 72 g a.i./ha) (14.37 %) and untreated control (14.44 %) was statistically at par with each other and showed maximum shoot infestation. In overall comparison the efficacy of the pesticides were T₉>T₈>T₇>T₁₂>T₁₅>T₁₄>T₁₃>T₁₁>T₁₀> T₆>T₅>T₄>T₃>T₂>T₁>T₀.

After second spray during 2022, the shoot damage varied from 2.89 per cent to 17.37 per cent. Plot treated with T₉ (chlorantraniliprole @ 80 g a.i./ha) (2.89 %) showed minimum shoot damage and was statistically at par with T₈ (chlorantraniliprole @ 40 g a.i./ha) and T₇ (chlorantraniliprole @ 30 g a.i./ha) with per cent infestation of 3.16 and 3.88 per cent, respectively. The next best treatment in series was T₁₅ (chlorpyriphos @ 400 g a.i./ha) (5.79 %) which was statistically at par with T₁₂ (fenvalerate @ 150 g a.i./ha), T₁₁ (fenvalerate @ 75 g a.i./ha) and T₁₄ (chlorpyriphos @ 200 g a.i./ha) with per cent infestation ranging between 6.38 to 6.94 per cent. Treatment T₁₀ (fenvalerate @ 60 g a.i./ha) (8.21 %) was statistically at par with T₁₃ (chlorpyriphos @ 150 g a.i./ha) (8.54 %) and T₆ (fenazaquin @ 250 g a.i./ha) (9.57 %). Treatments T₃ (spiromesifen @ 192 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha) and T₄ (fenazaquin @ 94 g a.i./ha) showed high per cent of shoot infestation in the range of 10.59-12.33 per cent. The maximum shoot infestation was in treatment T₁ (spiromesifen @ 72 g a.i./ha) and untreated control which were at par with each other. The efficacy of the pesticides was T₉> T₈> T₇>T₁₅> T₁₂> T₁₁> T₁₄> T₁₀> T₁₃> T₆>T₃> T₅> T₂> T₄> T₁>T₀ (Table 4.6).

Similarly, after ten days of spray again the minimum infestation was found in T₉ (chlorantraniliprole @ 80 g a.i./ha) (1.56 %) which was at par with T₈ (chlorantraniliprole @ 40 g a.i./ha) with 1.85 per cent of shoot infestation. Next best treatment was T₇ (chlorantraniliprole @ 30 g a.i./ha) (2.85 %) which was at par with T₁₅ (chlorpyriphos @ 400 g a.i./ha) (3.00 %) and T₁₄ (chlorpyriphos @ 200 g a.i./ha) (3.95 %). Treatment T₁₂ (fenvalerate

@ 150 g a.i./ha) which was proved to be third best treatment in the series with 4.35 per cent of shoot infestation. Treatment T₁₃ (chlorpyrifos @ 150 g a.i./ha) was statistically at par with treatments T₁₁ (fenvalerate @ 75 g a.i./ha), T₁₀ (fenvalerate @ 60 g a.i./ha) and T₆ (fenazaquin @ 250 g a.i./ha) with the shoot infestation of 6.56, 7.59 and 8.06 per cent, respectively. Treatments T₃ (spiromesifen @ 192 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₁ (spiromesifen @ 72 g a.i./ha) and T₄ (fenazaquin @ 94 g a.i./ha) showed shoot infestation in the range of 8.49-12.96 per cent. The efficacy of the pesticides were T₉>T₈>T₇>T₁₅>T₁₄>T₁₂>T₁₃>T₁₁>T₁₀>T₆>T₃>T₂>T₅>T₁>T₄>T₀.

Table 4.6: Effect of different pesticides treatments on shoot infestation by shoot and fruit borer of brinjal during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	Precount (% shoot infestation)	Per cent shoot infestation**			
				After 1 st spray		After 2 nd spray	
				5 th day	10 th day	5 th day	10 th day
T ₀	Untreated control	-	13.04 (3.75)*	13.40 (3.79) ^e	14.44 (3.93) ^g	17.37 (4.29) ^e	19.99 (4.58) ^g
T ₁	Spiromesifen (22.9 % SC) (x)	72	12.60 (3.69)	12.40 (3.66) ^d	14.37 (3.92) ^g	15.39 (4.05) ^c	11.49 (3.53) ^f
T ₂	Spiromesifen (22.9 % SC) (X)	96	13.57 (3.82)	10.04 (3.32) ^c	13.10 (3.75) ^f	11.50 (3.54) ^d	9.94 (3.31) ^e
T ₃	Spiromesifen (22.9 % SC) (2X)	192	13.93 (3.86)	9.88 (3.30) ^c	12.55 (3.68) ^f	10.59 (3.40) ^d	8.49 (3.08) ^e
T ₄	Fenazaquin (10 % EC) (x)	94	14.37 (3.92)	11.21 (3.49) ^d	12.24 (3.64) ^f	12.33 (3.65) ^d	12.96 (3.74) ^f
T ₅	Fenazaquin (10 % EC) (X)	125	14.69 (3.96)	10.78 (3.43) ^c	10.33 (3.37) ^e	11.28 (3.50) ^d	10.04 (3.32) ^e
T ₆	Fenazaquin (10 % EC) (2X)	250	12.62 (3.69)	10.18 (3.34) ^c	9.36 (3.22) ^e	9.57 (3.25) ^c	8.06 (3.01) ^d
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	14.12 (3.89)	4.92 (2.43) ^a	3.72 (2.17) ^b	3.88 (2.21) ^a	2.85 (1.96) ^b
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	14.20 (3.90)	4.63 (2.37) ^a	3.54 (2.13) ^b	3.16 (2.04) ^a	1.85 (1.69) ^a
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	12.70 (3.70)	3.97 (2.23) ^a	1.38 (1.54) ^a	2.89 (1.97) ^a	1.56 (1.60) ^a
T ₁₀	Fenvalerate (20 % EC) (x)	60	13.26 (3.78)	10.38 (3.37) ^c	8.95 (3.15) ^e	8.21 (3.03) ^c	7.59 (2.93) ^d
T ₁₁	Fenvalerate (20 % EC) (X)	75	14.99 (4.00)	8.33 (3.05) ^b	8.33 (3.05) ^d	6.71 (2.78) ^b	6.56 (2.75) ^d
T ₁₂	Fenvalerate (20 % EC) (2X)	150	13.81 (3.85)	7.25 (2.87) ^b	5.45 (2.54) ^c	6.38 (2.72) ^b	4.35 (2.31) ^c
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	13.39 (3.79)	9.20 (3.19) ^c	7.76 (2.96) ^d	8.54 (3.09) ^c	6.33 (2.71) ^d
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	13.33 (3.79)	8.51 (3.08) ^b	6.95 (2.82) ^d	6.94 (2.82) ^b	3.95 (2.22) ^b
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	14.72 (3.96)	7.96 (2.99) ^b	6.04 (2.65) ^c	5.79 (2.61) ^b	3.00 (2.00) ^b
	C.D _{0.05}		NS	0.25	0.26	0.32	0.33

*Figure in parentheses is square root transformed values **Mean of 3 replications NS- Non significant

4.1.2.4 Average per cent shoot infestation by shoot and fruit borer following two applications of pesticides during 2021 and 2022

In both years, the data showed that treatment T₉ (chlorantraniliprole @ 80 g a.i./ha) was the most effective against shoot and fruit borer in brinjal whereas, T₁ (spiromesifen @ 72 g a.i./ha) showed the highest infestation when compared with untreated control (Fig. 4.3 and 4.4).

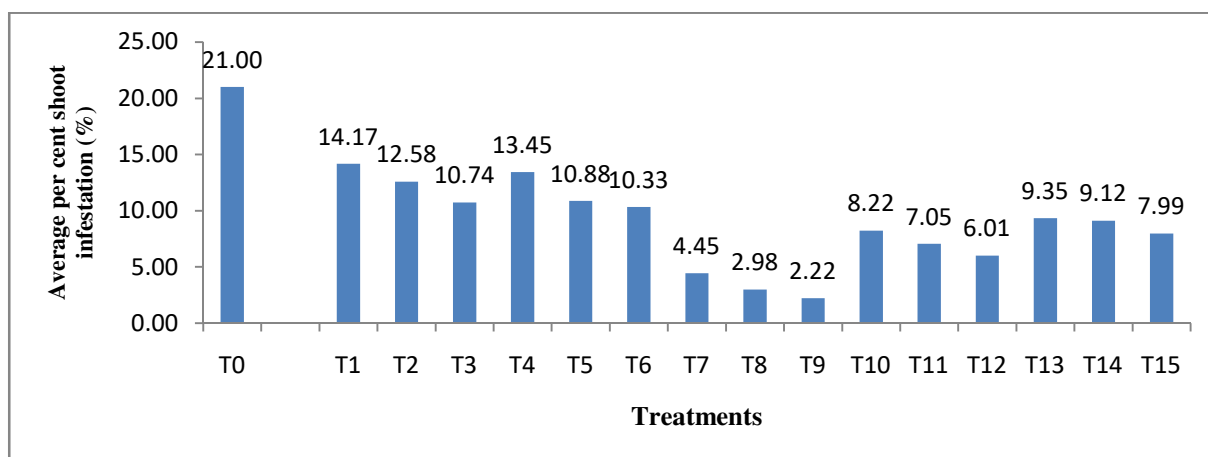


Fig. 4.3 Average per cent shoot infestation by shoot and fruit borer in brinjal after two sprays during 2021

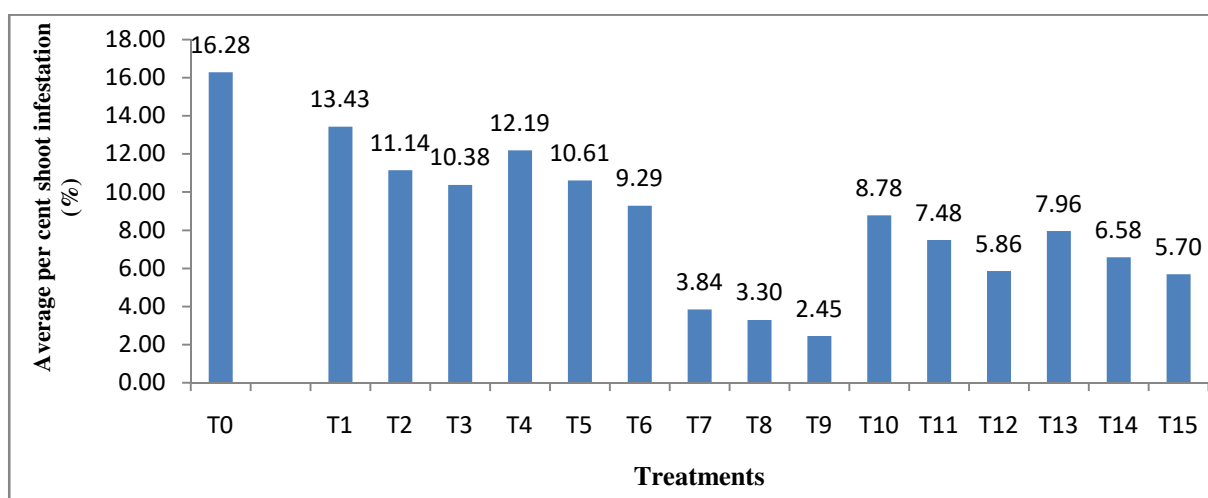


Fig. 4.4 Average per cent shoot infestation by shoot and fruit borer in brinjal after two sprays during 2022

4.1.2.5 Effect of pesticides on per cent fruit damage by shoot and fruit borer after first and second spray in brinjal during 2021

After first spray, observations on fruit damage due to shoot and fruit borer were also recorded during the experimental period. Results presented in Table 4.7 indicated that per cent fruit damage was significantly suppressed in all the insecticidal treatments over the untreated control. Minimum fruit damage (8.29 %) was recorded in treatment T₉ (chlorantraniliprole @

80 g a.i./ha) (1.56 %) at 10 days after first spray which was statistically at par with T₈ (chlorantraniliprole @ 40 g a.i./ha) with 10.63 per cent fruit damage followed by T₁₅ (chlorpyriphos @ 400 g a.i./ha) (15.25 %), which was statistically at par with T₇ (chlorantraniliprole @ 30 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha) and T₁₄ (chlorpyriphos @ 200 g a.i./ha) causing 15.87, 17.61 and 18.54 per cent fruit damage, respectively. Whereas, plots treated with T₁₃ (chlorpyriphos @ 150 g a.i./ha) were noticed with 19.80 per cent fruit damage and were statistically at par with T₁₂ (fenvalerate @ 150 g a.i./ha) (20.15 %), T₁₁ (fenvalerate @ 75 g a.i./ha) (20.72 %) and T₅ (fenazaquin @ 125 g a.i./ha) (22.65 %). Treatments T₁₀ (fenvalerate @ 60 g a.i./ha), T₃ (spiromesifen @ 192 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), showed fruit damage in the range of 24.72-28.24 per cent. Among all treatments T₁ (spiromesifen @ 72 g a.i./ha) showed the highest per cent fruit damage by the borer i.e. 30.22 per cent.

Table 4.7: Effect of different pesticides treatments on fruit infestation by shoot and fruit borer of brinjal during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	Per cent fruit infestation**	
			After 1 st spray	After 2 nd spray
T ₀	Untreated control	-	34.33(5.94) ^{c *}	37.62(6.21) ^h
T ₁	Spiromesifen (22.9 % SC) (x)	72	30.22 (5.59) ^c	32.06 (5.75) ^g
T ₂	Spiromesifen (22.9 % SC) (X)	96	28.24 (5.41) ^d	27.67 (5.35) ^f
T ₃	Spiromesifen (22.9 % SC) (2X)	192	24.86 (5.09) ^d	21.97 (4.79) ^e
T ₄	Fenazaquin (10 % EC) (x)	94	25.64 (5.16) ^d	28.11 (5.40) ^f
T ₅	Fenazaquin (10 % EC) (X)	125	22.65 (4.86) ^c	23.56 (4.96) ^e
T ₆	Fenazaquin (10 % EC) (2X)	250	17.61 (4.31) ^b	16.90 (4.23) ^d
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	15.87 (4.11) ^b	12.95 (3.73) ^c
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	10.63 (3.41) ^a	7.92 (2.99) ^b
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	8.29 (3.05) ^a	5.27 (2.50) ^a
T ₁₀	Fenvalerate (20 % EC) (x)	60	24.72 (5.07) ^d	23.59 (4.96) ^e
T ₁₁	Fenvalerate (20 % EC) (X)	75	20.72 (4.66) ^c	18.70 (4.44) ^d
T ₁₂	Fenvalerate (20 % EC) (2X)	150	20.15 (4.60) ^c	16.36 (4.17) ^d
T ₁₃	Chlorpyriphos (20 % EC) (x)	150	19.80 (4.56) ^c	17.85 (4.34) ^d
T ₁₄	Chlorpyriphos (20 % EC) (X)	200	18.54 (4.42) ^b	14.91 (3.99) ^c
T ₁₅	Chlorpyriphos (20 % EC) (2X)	400	15.25 (4.03) ^b	12.74 (3.71) ^c
	CD _{0.05}		0.40	0.36

*Figure in parentheses is square root transformed values **Mean of 3 replications

Data presented in Table 4.7 revealed that after second spray all the insecticidal treatments significantly reduced the fruit damage due to borer over the control. Minimum fruit damage (5.27 %) was recorded in treatment T₉ (chlorantraniliprole @ 80 g a.i./ha) which

resulted in most superior one in all the treatments. The next best treatment was T₈ (chlorantraniliprole @ 40 g a.i./ha) with 7.29 per cent fruit damage followed by T₁₅ (chlorpyriphos @ 400 g a.i./ha) (12.74 %) which was statistically at par with T₇ (chlorantraniliprole @ 30 g a.i./ha) (12.95 %) and T₁₄ (chlorpyriphos @ 200 g a.i./ha) (14.91 %). Treatment T₁₂ (fenvalerate @ 150 g a.i./ha) (16.36 %) was statistically at par with T₆ (fenazaquin @ 250 g a.i./ha), T₁₃ (chlorpyriphos @ 150 g a.i./ha) and T₁₁ (fenvalerate @ 75 g a.i./ha) with fruit damage of 16.90, 17.85 and 18.70 per cent. However, fruit damage ranged between 21.97-32.06 per cent in the fruits harvested from the plots treated with T₃ (spiromesifen @ 192 g a.i./ha), T₁₀ (fenvalerate @ 60 g a.i./ha), T₅ (fenazaquin @ 125 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha) and T₁ (spiromesifen @ 72 g a.i./ha). In control plots (T₀), 37.62 per cent fruit damage was noticed.

4.1.2.6 Effect of pesticides on per cent fruit damage by shoot and fruit borer after first and second spray in brinjal during 2022

The data in the Table 4.8 demonstrated that all insecticidal treatments considerably reduced fruit damage over the untreated control in the second season. After first spray minimum fruit damage was recorded in the plots treated with T₉ (chlorantraniliprole @ 80 g a.i./ha) with 6.80 per cent fruit damage which was followed by T₈ (chlorantraniliprole @ 40 g a.i./ha) (11.77 %) which was further statistically at par with T₁₅ (chlorpyriphos @ 400 g a.i./ha), T₇ (chlorantraniliprole @ 30 g a.i./ha), T₁₄ (chlorpyriphos @ 200 g a.i./ha) and T₁₂ (fenvalerate @ 150 g a.i./ha) with per cent fruit damage of 12.65, 13.97, 14.89 and 15.16 per cent, respectively. Next best treatment was T₆ (fenazaquin @ 250 g a.i./ha) (17.07 %) which was further statistically at par with T₁₃ (chlorpyriphos @ 150 g a.i./ha) (18.40 %), T₃ (spiromesifen @ 192 g a.i./ha) (19.30 %), T₂ (spiromesifen @ 96 g a.i./ha) (21.08 %) and T₁₁ (fenvalerate @ 75 g a.i./ha) (21.81 %). In other treatments i.e. T₅ (fenazaquin @ 125 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha) and T₁₀ (fenvalerate @ 60 g a.i./ha) fruit damage caused by the borer was in range of 22.94-23.83 per cent. T₁ (spiromesifen @ 72 g a.i./ha) (29.79 %) and T₀ (untreated control) (31.01 %) were statistically at par with each other and showed maximum fruit damage in the fruits which were harvested on 10th day of the spray.

After second spray almost similar trend was found in the treatments where the minimum fruit damage was again recorded in the plots treated with T₉ (chlorantraniliprole @ 80 g a.i./ha) (5.46 %) which was further statistically at par with T₈ (chlorantraniliprole @ 40 g a.i./ha) with 7.70 per cent of fruit damage. The next best treatment was found in the plots

treated with treatment T₇ (chlorantraniliprole @ 30 g a.i./ha) (9.54 %) which was statistically at par with T₁₅ (chlorpyrifos @ 400 g a.i./ha) (11.69 %) followed by T₁₄ (chlorpyrifos @ 200 g a.i./ha) (14.20 %) which showed similarity with the plots treated with T₆ (fenazaquin @ 250 g a.i./ha), T₃ (spiromesifen @ 192 g a.i./ha) and T₁₂ (fenvalerate @ 150 g a.i./ha) with 14.75, 17.24 and 17.39, respectively. Treatment T₁₃ (chlorpyrifos @ 150 g a.i./ha) (18.19 %) was statistically equivalent to T₅ (fenazaquin @ 125 g a.i./ha), T₁₁ (fenvalerate @ 75 g a.i./ha) and T₂ (spiromesifen @ 96 g a.i./ha) with a fruit damage in the range of 18.65-21.98 per cent. Fruit damage found in the plots treated with T₄ (fenazaquin @ 94 g a.i./ha), T₁₀ (fenvalerate @ 60 g a.i./ha) and T₁ (spiromesifen @ 72 g a.i./ha) were in the range of 24.51-28.77 per cent (Table 4.8).

Table 4.8: Effect of different pesticides treatments on fruit infestation by shoot and fruit borer of brinjal during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	Per cent fruit infestation**	
			After 1 st spray	After 2 nd spray
T ₀	Untreated control	-	31.01(5.66) ^{e*}	35.62(6.05) ^f
T ₁	Spiromesifen (22.9 % SC) (x)	72	29.79 (5.55) ^e	28.77 (5.46) ^e
T ₂	Spiromesifen (22.9 % SC) (X)	96	21.08 (4.70) ^c	21.98 (4.79) ^d
T ₃	Spiromesifen (22.9 % SC) (2X)	192	19.30 (4.51) ^c	17.24 (4.27) ^c
T ₄	Fenazaquin (10 % EC) (x)	94	23.58 (4.96) ^d	24.51 (5.05) ^e
T ₅	Fenazaquin (10 % EC) (X)	125	22.94 (4.89) ^d	18.65 (4.43) ^d
T ₆	Fenazaquin (10 % EC) (2X)	250	17.07 (4.25) ^c	14.75 (3.97) ^c
T ₇	Chlorantraniliprole(18.5 % SC)(x)	30	13.97 (3.87) ^b	9.54 (3.25) ^b
T ₈	Chlorantraniliprole(18.5 % SC)(X)	40	11.77 (3.57) ^b	7.70 (2.95) ^a
T ₉	Chlorantraniliprole(18.5 % SC)(2X)	80	6.80 (2.79) ^a	5.46 (2.54) ^a
T ₁₀	Fenvalerate (20 % EC) (x)	60	23.83 (4.98) ^d	26.76 (5.27) ^e
T ₁₁	Fenvalerate (20 % EC) (X)	75	21.81 (4.78) ^c	21.60 (4.75) ^d
T ₁₂	Fenvalerate (20 % EC) (2X)	150	15.16 (4.02) ^b	17.39 (4.29) ^c
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	18.40 (4.40) ^c	18.19 (4.38) ^d
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	14.89 (3.99) ^b	14.20 (3.90) ^c
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	12.65 (3.69) ^b	11.69 (3.56) ^b
	CD _{0.05}		0.54	0.41

*Figure in parentheses is square root transformed values **Mean of 3 replications

4.1.2.7 Average per cent fruit infestation by shoot and fruit borer following two applications of pesticides during 2021 and 2022

The data shown that treatment T₉ (chlorantraniliprole @ 80 g a.i./ha) was the most successful against in reducing fruit damage by shoot and fruit borer in brinjal whereas, T₁ (spiromesifen @ 72 g a.i./ha) (Fig. 4.5 and 4.6).

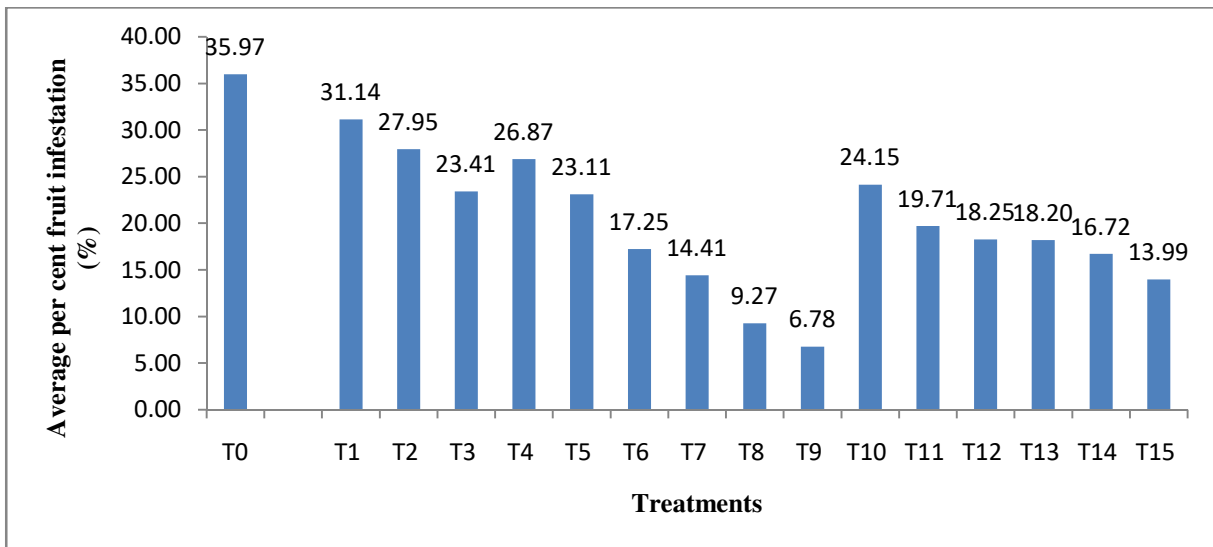


Fig. 4.5 Average per cent fruit infestation by shoot and fruit borer in brinjal after two sprays during 2021

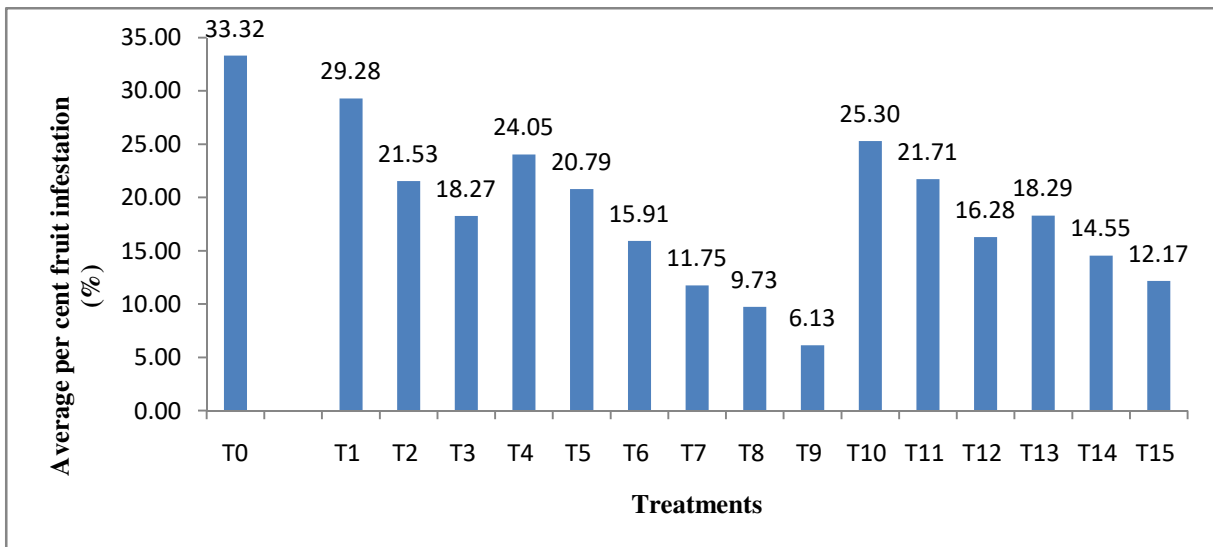


Fig. 4.6 Average per cent fruit infestation by shoot and fruit borer in brinjal after two sprays during 2022

Our results correspond with those of Niranjana et al. (2017), who found that the chlorantraniliprole 18.5 % SC was superior in producing brinjal fruits with the least amount of *L. orbonalis* damage, with shoot infestations of 6.5 and 2.6 per cent and fruit infestations of 15.40 and 9.90 per cent after the first and second sprays. Misra (2008) conducted another study that showed chlorantraniliprole @ 40 and 50 g a.i./ha considerably superior than untreated control in reducing shoot damage by 95.00-97.00 per cent and fruit damage by 87.00-90.00 per cent on a number basis and 88.00-90.00 per cent on a weight basis (10 days after fourth spray). According to Dey et al. (2019) findings, the effects of chlorpyrifos at 2000 ml/ha recorded 9.00, 7.30 and 11.30 per cent and 9.70, 17.00 and 9.70 per cent shoot

infestation and 8.90, 8.40 and 8.90 per cent and 7.90, 9.70 and 7.80 per cent fruit infestation at 4th and 10th days, respectively, after first, second and third spray. Raina et al. (2016) revealed from their study that 6.51 and 6.65 per cent of shoot infestation and 8.29 and 19.94 per cent of fruit damage was recorded after application of fenvalerate 20EC @ 40 g a.i./ ha and chlorpyrifos 20EC @ 200 g a.i. which was in close proximity of our findings.

4.1.3 Phytotoxicity studies

All the treatments under observation does not show any phytotoxic symptoms like yellowing, stunting, necrosis, chlorosis, vein clearing, epinasty and hyponasty when applied on brinjal plants after first and second application of respective pesticides. Our results were similar to that of Dey et al. (2019) who evaluated phytotoxic effect of chlorpyrifos 20EC on brinjal crop and observed that on interval of 1, 3, 7 10 and 15 days (after each spray) no phytotoxicity symptoms i.e. leaf injury, wilting, epinasty and hyponasty, necrosis, etc. were observed in all the treatments including higher dosages of chlorpyrifos 20 % EC. Chlorantraniliprole (Coragen 18.5 SC) when applied @ 100, 125 and 150 ml/ha in the chilli showed no phytotoxic symptoms to the crop (Randhawa et al. 2020).

4.1.4 Effect of pesticides on the population of coccinellids in brinjal

The effect of five pesticides *viz.*, chlorantraniliprole, fenazaquin, spiromesifen, fenvalerate and chlorpyrifos at three different doses i.e. lesser than single dose (x), single dose (X) and double dose (2X) were evaluated on population of coccinellids on brinjal crop in the two consecutive years 2021 and 2022.

4.1.4.1 Effect of pesticides on the population of coccinellids after first spray in brinjal during 2021

The data presented in Table 4.9 revealed that before the first spray of pesticides, number of coccinellid beetle ranged from 0.93-1.40 beetles per five plants. Observation taken at 1, 3, 5, 7 and 10 days interval showed that, among treatments T₇ (chlorantraniliprole @ 30 g a.i./ha) (0.72 beetles/5 plants) showed the highest number of coccinellids population which was statistically equivalent to T₈ (chlorantraniliprole @ 40 g a.i./ha), T₉ (chlorantraniliprole @ 80 g a.i./ha) and T₁₀ (Fenvalerate @ 60 g a.i./ha) and recorded 0.63, 0.58 and 0.63 beetles per five plants, respectively. Likewise, T₁₁ (fenvalerate @ 75 g a.i./ha) recorded 0.50 beetles per five plant and was statistically at par with T₁₂ (fenvalerate @ 150 g a.i./ha) (0.44 beetles/5 plants), T₁ (spiromesifen @ 72 g a.i./ha) (0.44 beetles/5 plants), T₄ (fenazaquin @ 94 g a.i./ha) (0.41 beetles/5 plants), T₁₃ (chlorpyrifos @ 150 g a.i./ha) (0.40 beetles/5 plants), T₂ (spiromesifen @ 96 g a.i./ha) (0.39 beetles/5 plants) and T₅ (fenazaquin @ 125 g a.i./ha) (0.37

beetles/5 plants). Least population was recorded in the plots treated with T₁₅ (chlorpyrifos @ 400 g a.i./ha) (0.21 beetles/5 plants) followed by T₁₄ (chlorpyrifos @ 200 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha) and T₃ (spiromesifen @ 192 g a.i./ha) with population of 0.29, 0.30 and 0.31 beetles per five plants, respectively.

Table 4.9 Effect of pesticides on the population of coccinellids after first spray in brinjal during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	Pre-count (No. of coccinellids/ 5 plants)	No. of coccinellids per five plants**					Mean
				1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	1.33 (1.53)*	1.27 (1.50)	1.33 (1.53)	1.47 (1.57)	1.47 (1.57)	1.40 (1.55)	1.38 ^a (1.54)
T ₁	Spiromesifen (22.9 % SC) (x)	72	1.00 (1.41)	0.53 (1.24)	0.53 (1.24)	0.40 (1.18)	0.27 (1.13)	0.47 (1.21)	0.44 ^c (1.20)
T ₂	Spiromesifen (22.9 % SC) (X)	96	0.93 (1.39)	0.40 (1.18)	0.33 (1.15)	0.33 (1.15)	0.37 (1.17)	0.53 (1.24)	0.39 ^c (1.18)
T ₃	Spiromesifen (22.9 % SC) (2X)	192	1.00 (1.41)	0.40 (1.18)	0.33 (1.15)	0.17 (1.08)	0.30 (1.14)	0.37 (1.17)	0.31 ^d (1.14)
T ₄	Fenazaquin (10 % EC) (x)	94	1.27 (1.51)	0.47 (1.21)	0.40 (1.18)	0.33 (1.15)	0.30 (1.14)	0.53 (1.24)	0.41 ^c (1.18)
T ₅	Fenazaquin (10 % EC) (X)	125	1.40 (1.55)	0.47 (1.21)	0.40 (1.18)	0.17 (1.08)	0.30 (1.14)	0.53 (1.24)	0.37 ^c (1.17)
T ₆	Fenazaquin (10 % EC) (2X)	250	1.13 (1.46)	0.40 (1.18)	0.33 (1.15)	0.30 (1.14)	0.17 (1.08)	0.30 (1.14)	0.30 ^d (1.14)
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	1.27 (1.50)	0.80 (1.34)	0.60 (1.26)	0.60 (1.26)	0.73 (1.31)	0.87 (1.36)	0.72 ^b (1.31)
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	1.13 (1.46)	0.73 (1.32)	0.47 (1.21)	0.47 (1.21)	0.67 (1.29)	0.80 (1.34)	0.63 ^b (1.27)
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	1.33 (1.53)	0.67 (1.29)	0.43 (1.20)	0.47 (1.21)	0.60 (1.26)	0.73 (1.32)	0.58 ^b (1.25)
T ₁₀	Fenvalerate (20 % EC) (x)	60	0.93 (1.39)	0.73 (1.32)	0.53 (1.23)	0.47 (1.21)	0.60 (1.26)	0.80 (1.34)	0.63 ^b (1.27)
T ₁₁	Fenvalerate (20 % EC) (X)	75	1.00 (1.41)	0.60 (1.26)	0.53 (1.24)	0.30 (1.14)	0.47 (1.21)	0.60 (1.26)	0.50 ^c (1.22)
T ₁₂	Fenvalerate (20 % EC) (2X)	150	1.27 (1.50)	0.53 (1.23)	0.53 (1.24)	0.23 (1.11)	0.30 (1.14)	0.60 (1.27)	0.44 ^c (1.20)
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	1.20 (1.48)	0.53 (1.23)	0.30 (1.14)	0.33 (1.15)	0.23 (1.11)	0.60 (1.27)	0.40 ^c (1.18)
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	1.13 (1.46)	0.40 (1.18)	0.17 (1.08)	0.23 (1.11)	0.23 (1.11)	0.40 (1.18)	0.29 ^d (1.13)
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	1.07 (1.43)	0.37 (1.17)	0.13 (1.06)	0.17 (1.08)	0.20 (1.09)	0.20 (1.09)	0.21 ^d (1.10)
	Mean		NS	0.58 (1.25)	0.46 (1.20)	0.40 (1.18)	0.45 (1.20)	0.61 (1.26)	

*Figure in parentheses is square root transformed values ** Mean of 3 replications DAS- Days after spray

CD_{0.05} (Days): NS

NS- Non significant

(Treatments): 0.06

(Days × Treatments): 0.13

After the application of different pesticidal treatments no significant difference was seen on coccinellid population in different days i.e. 1, 3, 5, 7 and 10 days.

4.1.4.2 Effect of pesticides on the population of coccinellids after second spray in brinjal during 2021

After second spray a similar trend was followed with highest population of 0.69 beetles per 5 plants in T₇ (chlorantraniliprole @ 30 g a.i./ha) which was statistically at par with T₁₀ (fenvalerate @ 60 g a.i./ha) and T₈ (chlorantraniliprole @ 40 g a.i./ha) and recorded population of 0.60 and 0.52 beetles per five plants . A range between 0.33-0.47 beetles per five plants were recorded in the plots T₁₁ (fenvalerate @ 75 g a.i./ha), T₉ (chlorantraniliprole @ 80 g a.i./ha), T₁₂ (fenvalerate @ 150 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha), T₁ (spiromesifen @ 72 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), T₁₃ (chlorpyriphos @ 150 g a.i./ha), T₅

Table 4.10 Effect of pesticides on the population of coccinellids after second spray in brinjal during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	No. of coccinellids per five plants**					Mean
			1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	1.47 (1.57)*	1.33 (1.53)	1.50 (1.58)	1.50 (1.58)	1.52 (1.59)	1.46 (1.57) ^a
T ₁	Spiromesifen (22.9 % SC) (x)	72	0.33 (1.15)	0.27 (1.13)	0.40 (1.18)	0.47 (1.21)	0.53 (1.24)	0.40 (1.18) ^c
T ₂	Spiromesifen (22.9 % SC) (X)	96	0.30 (1.14)	0.43 (1.19)	0.40 (1.18)	0.30 (.14)	0.47 (1.21)	0.38 (1.17) ^c
T ₃	Spiromesifen (22.9 % SC) (2X)	192	0.20 (1.09)	0.23 (1.11)	0.33 (1.15)	0.37 (1.17)	0.40 (1.18)	0.31 (1.14) ^d
T ₄	Fenazaquin (10 % EC) (x)	94	0.40 (1.18)	0.27 (1.13)	0.33 (1.15)	0.47 (1.21)	0.53 (1.24)	0.40 (1.18) ^c
T ₅	Fenazaquin (10 % EC) (X)	125	0.20 (1.09)	0.30 (1.14)	0.30 (1.14)	0.37 (1.17)	0.47 (1.21)	0.33 (1.15) ^c
T ₆	Fenazaquin (10 % EC) (2X)	250	0.27 (1.12)	0.23 (1.11)	0.30 (1.14)	0.40 (1.18)	0.47 (1.21)	0.33 (1.15) ^c
T ₇	Chlorantraniliprole (18.5 % SC)(x)	30	0.47 (1.21)	0.60 (1.26)	0.67 (1.29)	0.87 (1.36)	0.87 (1.36)	0.69 (1.29) ^b
T ₈	Chlorantraniliprole (18.5 % SC)(X)	40	0.33 (1.15)	0.47 (1.21)	0.53 (1.24)	0.60 (1.26)	0.67 (1.29)	0.52 (1.23) ^b
T ₉	Chlorantraniliprole (18.5 % SC)(2X)	80	0.33 (1.15)	0.33 (1.15)	0.40 (1.18)	0.53 (1.24)	0.60 (1.26)	0.44 (1.19) ^c
T ₁₀	Fenvalerate (20 % EC) (x)	60	0.53 (1.23)	0.47 (1.21)	0.60 (1.26)	0.67 (1.29)	0.73 (1.32)	0.60 (1.26) ^b
T ₁₁	Fenvalerate (20 % EC) (X)	75	0.37 (1.17)	0.23 (1.11)	0.53 (1.23)	0.53 (1.23)	0.67 (1.29)	0.47 (1.21) ^c
T ₁₂	Fenvalerate (20 % EC) (2X)	150	0.30 (1.14)	0.30 (1.14)	0.43 (1.20)	0.53 (1.24)	0.60 (1.26)	0.43 (1.19) ^c
T ₁₃	Chlorpyriphos (20 % EC) (x)	150	0.23 (1.11)	0.20 (1.09)	0.30 (1.14)	0.53 (1.24)	0.53 (1.24)	0.36 (1.16) ^c
T ₁₄	Chlorpyriphos (20 % EC) (X)	200	0.23 (1.11)	0.23 (1.11)	0.30 (1.14)	0.40 (1.18)	0.47 (1.21)	0.33 (1.15) ^c
T ₁₅	Chlorpyriphos (20 % EC) (2X)	400	0.17 (1.08)	0.13 (1.06)	0.23 (1.11)	0.30 (1.14)	0.30 (1.14)	0.23 (1.11) ^d
	Mean		0.38 (1.17)	0.38 (1.17)	0.47 (1.21)	0.55 (1.24)	0.61 (1.27)	

*Figure in parentheses is square root transformed values ** Mean of 3 replications DAS- Days after spray

CD_{0.05} (Days): NS

(Treatments): 0.06

(Days × Treatments): 0.12

NS- Non significant

(fenazaquin @ 125 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha) and T₁₄ (chlorpyriphos @ 200 g a.i./ha) which were also found to be statistically at par with T₁₁. Minimum number of coccinellids were found in the treatment T₁₅ (chlorpyriphos @ 400 g a.i./ha) and T₃ (spiromesifen @ 192 g a.i./ha) i.e 0.23 and 0.31 beetles per five plants, respectively (Table 4.10).

4.1.4.3 Effect of pesticides on the population of coccinellids after first spray in brinjal during 2022

The data presented in Table 4.11 revealed that the observations made a day before spray recorded population of beetles in a range between 0.80-1.40 beetles per five plants and

Table 4.11 Effect of pesticides on the population of coccinellids after first spray in brinjal during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	Pre-count (No. of coccinellids/ 5 plants)	No. of coccinellids per five plants**					
				1DAS	3DAS	5DAS	7DAS	10 DAS	Mean
T ₀	Untreated control	-	1.13 (1.45)*	1.13 (1.45)	1.20 (1.48)	1.27 (1.50)	1.33 (1.53)	1.33 (1.53)	1.25 _a (1.50)
T ₁	Spiromesifen (22.9 % SC) (x)	72	0.80 (1.34)	0.53 (1.24)	0.33 (1.15)	0.40 (1.18)	0.47 (1.21)	0.53 (1.24)	0.45 _c (1.20)
T ₂	Spiromesifen (22.9 % SC) (X)	96	0.93 (1.39)	0.40 (1.18)	0.33 (1.15)	0.23 (1.11)	0.40 (1.18)	0.47 (1.21)	0.37 _c (1.17)
T ₃	Spiromesifen (22.9 % SC) (2X)	192	1.07 (1.44)	0.40 (1.18)	0.33 (1.15)	0.33 (1.15)	0.23 (1.11)	0.47 (1.21)	0.35 _c (1.16)
T ₄	Fenazaquin (10 % EC) (x)	94	1.20 (1.48)	0.40 (1.18)	0.33 (1.15)	0.27 (1.13)	0.40 (1.18)	0.53 (1.24)	0.39 _c (1.18)
T ₅	Fenazaquin (10 % EC) (X)	125	1.27 (1.50)	0.27 (1.13)	0.20 (1.10)	0.33 (1.15)	0.33 (1.15)	0.40 (1.18)	0.31 _d (1.14)
T ₆	Fenazaquin (10 % EC) (2X)	250	1.13 (1.46)	0.47 (1.21)	0.47 (1.21)	0.33 (1.15)	0.27 (1.13)	0.27 (1.13)	0.36 _c (1.17)
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	1.07 (1.44)	0.67 (1.29)	0.60 (1.26)	0.53 (1.23)	0.67 (1.29)	0.80 (1.34)	0.65 _b (1.28)
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	1.00 (1.41)	0.60 (1.27)	0.53 (1.24)	0.30 (1.14)	0.53 (1.23)	0.67 (1.29)	0.53 _b (1.23)
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	1.13 (1.46)	0.60 (1.26)	0.53 (1.24)	0.53 (1.24)	0.40 (1.18)	0.47 (1.21)	0.51 _b (1.23)
T ₁₀	Fenvalerate (20 % EC) (x)	60	1.33 (1.53)	0.67 (1.29)	0.47 (1.21)	0.40 (1.18)	0.60 (1.26)	0.73 (1.31)	0.57 _b (1.25)
T ₁₁	Fenvalerate (20 % EC) (X)	75	1.27 (1.51)	0.47 (1.21)	0.40 (1.18)	0.33 (1.15)	0.47 (1.21)	0.50 (1.22)	0.43 _c (1.19)
T ₁₂	Fenvalerate (20 % EC) (2X)	150	1.00 (1.41)	0.47 (1.21)	0.40 (1.18)	0.27 (1.13)	0.33 (1.15)	0.40 (1.18)	0.37 _c (1.17)
T ₁₃	Chlorpyriphos (20 % EC) (x)	150	1.27 (1.50)	0.40 (1.18)	0.27 (1.13)	0.40 (1.18)	0.47 (1.21)	0.47 (1.21)	0.40 _c (1.18)
T ₁₄	Chlorpyriphos (20 % EC) (X)	200	1.40 (1.55)	0.33 (1.15)	0.33 (1.15)	0.27 (1.13)	0.40 (1.18)	0.47 (1.21)	0.36 _c (1.16)
T ₁₅	Chlorpyriphos (20 % EC) (2X)	400	1.13 (1.46)	0.47 (1.21)	0.17 (1.08)	0.13 (1.06)	0.23 (1.11)	0.23 (1.11)	0.25 _d (1.11)
	Mean		NS	0.52 (1.23)	0.43 (1.20)	0.40 (1.18)	0.47 (1.21)	0.55 (1.25)	

*Figure in parentheses is square root transformed values ** Mean of 3 replications DAS- Days after spray

CD_{0.05} (Days): NS

NS- Non significant

(Treatments): 0.05

(Days × Treatments): 0.11

they were evenly distributed over the field. Maximum population of coccinellid beetles were recorded in T₇ (chlorantraniliprole @ 30 g a.i./ha) (0.65 beetles/5 plants) which was statistically equivalent to T₁₀ (fenvalerate @ 60 g a.i./ha), T₈ (chlorantraniliprole @ 40 g a.i./ha) and T₉ (chlorantraniliprole @ 80 g a.i./ha) and recorded 0.57, 0.53 and 0.51 beetles per five plants, respectively. The next treatment T₁ (spiromesifen @ 72 g a.i./ha) recorded 0.45 beetles per five plants which was statistically at par with T₁₁ (fenvalerate @ 75 g a.i./ha), T₄ (fenazaquin @ 94 g a.i./ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), T₁₂ (fenvalerate @ 150 g a.i./ha), T₃ (spiromesifen @ 192 g a.i./ha) and T₁₄ (chlorpyrifos @ 200 g a.i./ha) and recorded beetles in the range between 0.36 to 0.43 beetles per five plants. Treatments T₁₅ (chlorpyrifos @ 400 g a.i./ha) and T₅ (fenazaquin @ 125 g a.i./ha) recorded least number of population i.e. 0.25 and 0.31 beetles, respectively.

4.1.4.4 Effect of pesticides on the population of coccinellids after second spray in brinjal during 2022

The data presented in Table 4.12 showed that after second spray during 2022 a similar trend was followed where the highest number of coccinellid beetles were recorded under untreated control (T₀) (1.44 beetles/5 plants) followed by T₇ (chlorantraniliprole @ 30 g a.i./ha) (0.65 beetles/5 plants) which was statistically at par with T₁₀ (fenvalerate @ 60 g a.i./ha), T₈ (chlorantraniliprole @ 40 g a.i./ha) and T₉ (chlorantraniliprole @ 80 g a.i./ha) and recorded 0.65, 0.59 and 0.57 beetles per five plants further followed by T₁₁ (fenvalerate @ 75 g a.i./ha) (0.50 beetles/5 plants) which was statistically equivalent to T₁₂ (fenvalerate @ 150 g a.i./ha), T₁ (spiromesifen @ 72 g a.i./ha), T₂ (spiromesifen @ 96 g a.i./ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha) and T₄ (fenazaquin @ 94 g a.i./ha) and recorded population in the range of 0.38-0.50 beetles per five plants. Minimum number of coccinellids were found in the treatment T₁₅ (chlorpyrifos @ 400 g a.i./ha), T₆ (fenazaquin @ 250 g a.i./ha), T₁₄ (chlorpyrifos @ 200 g a.i./ha), T₃ (spiromesifen @ 192 g a.i./ha) and T₅ (fenazaquin @ 125 g a.i./ha) with 0.27, 0.28, 0.31, 0.35 and 0.35 and beetles per five plants, respectively.

Table 4.12 Effect of pesticides on the population of coccinellids after second spray in brinjal during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	No. of coccinellids per five plants**					Mean
			1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	1.33 (1.53)*	1.40 (1.55)	1.47 (1.57)	1.47 (1.57)	1.53 (1.59)	1.44 ^a (1.56)
T ₁	Spiromesifen (22.9 % SC) (x)	72	0.47 (1.21)	0.23 (1.11)	0.40 (1.18)	0.47 (1.21)	0.57 (1.25)	0.43 ^c (1.20)
T ₂	Spiromesifen (22.9 % SC) (X)	96	0.40 (1.18)	0.27 (1.13)	0.40 (1.18)	0.47 (1.21)	0.47 (1.21)	0.40 ^c (1.18)
T ₃	Spiromesifen (22.9 % SC) (2X)	192	0.40 (1.18)	0.20 (1.09)	0.33 (1.15)	0.40 (1.18)	0.40 (1.18)	0.35 ^d (1.16)
T ₄	Fenazaquin (10 % EC) (x)	94	0.30 (1.14)	0.33 (1.15)	0.40 (1.18)	0.40 (1.18)	0.47 (1.21)	0.38 ^c (1.17)
T ₅	Fenazaquin (10 % EC) (X)	125	0.33 (1.15)	0.23 (1.11)	0.33 (1.15)	0.33 (1.15)	0.53 (1.23)	0.35 ^d (1.16)
T ₆	Fenazaquin (10 % EC) (2X)	250	0.20 (1.10)	0.20 (1.10)	0.23 (1.11)	0.33 (1.15)	0.40 (1.18)	0.28 ^d (1.13)
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	0.60 (1.26)	0.40 (1.18)	0.60 (1.26)	0.73 (1.32)	0.93 (1.39)	0.65 ^b (1.28)
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	0.53 (1.24)	0.47 (1.21)	0.53 (1.24)	0.53 (1.23)	0.87 (1.37)	0.59 ^b (1.26)
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	0.40 (1.18)	0.53 (1.24)	0.53 (1.24)	0.67 (1.29)	0.73 (1.31)	0.57 ^b (1.25)
T ₁₀	Fenvalerate (20 % EC) (x)	60	0.60 (1.26)	0.40 (1.18)	0.60 (1.26)	0.73 (1.32)	0.93 (1.39)	0.65 ^b (1.28)
T ₁₁	Fenvalerate (20 % EC) (X)	75	0.40 (1.18)	0.30 (1.14)	0.47 (1.21)	0.67 (1.29)	0.67 (1.29)	0.50 ^c (1.22)
T ₁₂	Fenvalerate (20 % EC) (2X)	150	0.47 (1.21)	0.30 (1.14)	0.40 (1.18)	0.53 (1.24)	0.67 (1.29)	0.47 ^c (1.21)
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	0.33 (1.15)	0.20 (1.09)	0.53 (1.24)	0.47 (1.21)	0.47 (1.21)	0.40 ^c (1.18)
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	0.33 (1.15)	0.13 (1.06)	0.23 (1.11)	0.33 (1.15)	0.53 (1.24)	0.31 ^d (1.14)
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	0.30 (1.14)	0.13 (1.06)	0.23 (1.11)	0.33 (1.15)	0.43 (1.19)	0.27 ^d (1.13)
	Mean		0.46 (1.21)	0.36 (1.17)	0.48 (1.22)	0.55 (1.24)	0.66 (1.29)	

*Figure in parentheses is square root transformed values ** Mean of 3 replications DAS- Days after spray

CD_{0.05} (Days): NS

NS- Non significant

(Treatments): 0.05

(Days × Treatments): 0.12

4.1.4.5 Mean number of coccinellid population following two applications of pesticides during 2021 and 2022

In both years, the data showed that after control the highest number of coccinellid population was recorded in untreated control followed by T₇ (chlorantraniliprole @ 30 g a.i./ha) which showed the maximum population of beetles in brinjal and minimum in T₁₅ (chlorpyrifos @ 400 g a.i./ha) (Fig. 4.7 and 4.8).

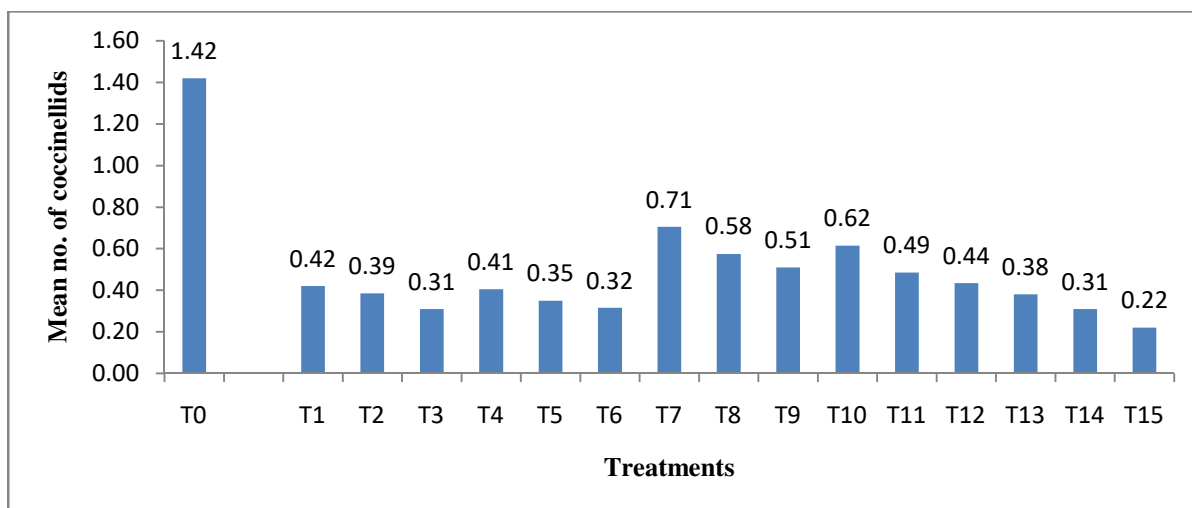


Fig. 4.7 Mean number of coccinellids in brinjal after two sprays during 2021

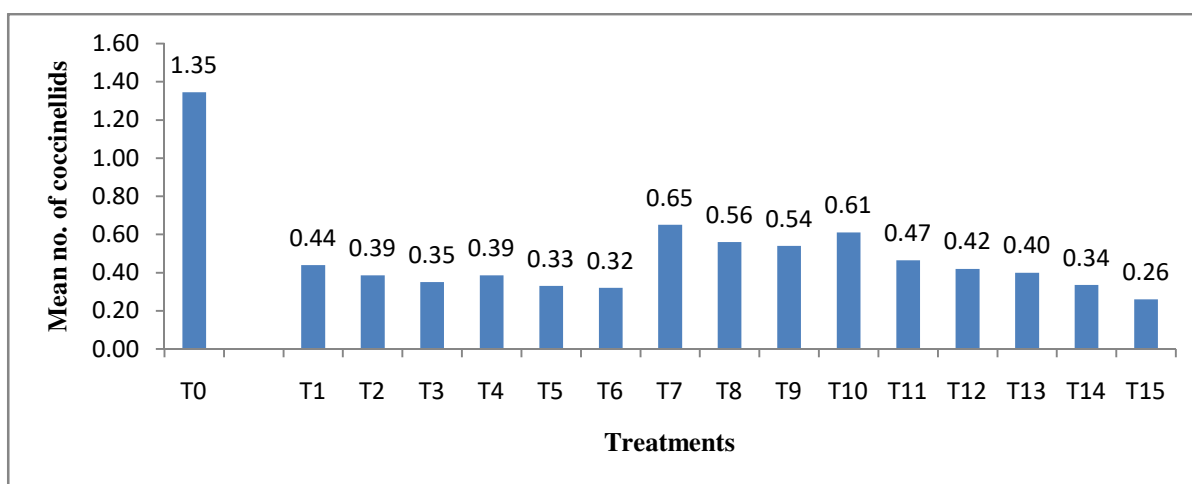


Fig. 4.8 Mean number of coccinellids in brinjal after two sprays during 2022

In present findings, the treatments evaluated against insect pests of brinjal were found comparatively safer to coccinellids in the field. Maximum number of coccinellids were recorded in chlorantraniliprole @ 30 g a.i./ha i.e. 0.71 and 0.65 coccinellids per five plants and lowest number was recorded in the plots treated with chlorpyrifos @ 400 g a.i./ha i.e. 0.22 and 0.27 coccinellids per five plants during 2021 and 2022, respectively. Similar results were noticed by Khinchi and Kumawat (2021) who noticed that after spray of chlorantraniliprole 18.5 % SC @ 100 ml/ha in field of soyabean the population of coccinellids increased by 4.73 to 6.93 coccinellids/plant at 7th and 14th day of 2nd spray after control. On the other side Natikar et al. (2016) found that comparatively lower beetle population was observed in plots treated with chlorpyrifos 20 EC @ 2.00 ml/l (0.19 coccinellids/ plant) in soyabean which was in similarity with our results. In other study conducted by Douressamy et al. (2018) it was noticed that when chlorantraniliprole @ 62 g a.i./ha was sprayed on sugarcane a population of 3.66 coccinellids/hill was recorded, also in chlorpyrifos @ 250 g a.i./ha treated plots

population of 3.22 coccinellids/hill on 14th day of application was recorded. Sudhanan et al. (2017) found that chlorpyrifos 20 EC at 250 g a.i./ha had a pronounced adverse effect on the coccinellid population in sugarcane and had lowest population (2.99 beetles/ten plants) of coccinellids during second field trial in sugarcane.

4.1.5 Pesticides benefit cost ratio (BCR) in brinjal

The benefit cost ratio of different treatments used against insect pests of brinjal *viz.*, jassids and shoot and fruit borer were calculated and are presented in Table 4.13 and Table 4.14, during 2021 and 2022. The summary of all cost and returns have been given in appendices along with the detailed description of the cost of cultivation of the test crops followed as per the package of practices given by the Dr. YSP University of Horticulture and Forestry.

4.1.5.1 Economics of different treatments used against brinjal insect pest during 2021

Benefit cost ratio (B:C) analysis of the different treatments has been presented in the Table 4.13. Treatment fruit yields and costs were derived from individual plots and converted further into data per hectare. The benefit cost ratio was worked out to know the economics of pesticidal treated plots. The results revealed that the maximum net income of Rs. 412491.96/ha was recorded in T₉ (chlorantraniliprole @ 80 g a.i./ha) followed by T₈ (chlorantraniliprole @ 40 g a.i./ha) (Rs. 410125.30/ha), T₆ (fenazaquin @ 250 g a.i./ha) (Rs. 382998.63/ha), T₅ (fenazaquin (@ 125 g a.i./ha) (Rs. 380198.63/ ha), T₃ (spiromesifen (@ 192 g a.i./ha) (Rs. 374038.63/ha), T₁₅ (chlorpyrifos @ 400 g a.i./ha) (Rs. 372438.63/ha), T₁₂ (fenvalerate @ 150 g a.i./ha) (Rs. 369083.63/ha), T₄ (fenazaquin @ 94 g a.i./ha) (Rs. 369032.23/ha), T₁₁ (fenvalerate @ 75 g a.i./ha) (Rs. 359161.13/ha), T₇ (chlorantraniliprole @ 30 g a.i./ha) (Rs. 359153.63/ha), T₂ (spiromesifen @ 96 g a.i./ha) (Rs. 355918.63/ha), T₁₄ (chlorpyrifos @ 200 g a.i./ha) (Rs. 354238.63/ha), T₁ (spiromesifen @ 72 g a.i./ha) (Rs. 351938.63/ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha) (Rs. 344408.63/ha), T₁₀ (fenvalerate @ 60 g a.i./ha) (Rs. 339065.63/ha). The minimum net income was recorded from untreated control (Rs. 315358.63/ ha). The benefit cost ratio of various pesticide treatments was varied from 3.51:1 to 4.22:1. For each rupee invested on jassids and shoot and fruit borer management a profit of Rs. 4.22 was achieved through treatment of chlorantraniliprole (@ 40 g a.i./ha), which was the maximum whereas, the least output of Rs. 3.51 for every rupee spent was achieved with untreated control. Table 4.13 showed that the net income and marginal benefits vary according to cost of pesticide application and their dosage (g a.i./ha).

Table 4.13: Economics of different treatments used against brinjal insect pest during 2021

Treatments	Pesticide	Dosage (g a.i./ha)	Yield (q/ha)	Fixed Cost (Rs.)	Variable Cost (Rs.)	Total Cost (Rs.)	Gross Income (Rs.)	Net Income (Rs.)	B:C
T ₀	Control	-	184.20	60074.55	29806.82	89881.37	405240.00	315358.63	3.51:1
T ₁	Spiromesifen (22.9 % SC) (x)	72	202.60	60074.55	33706.82	93781.37	445720.00	351938.63	3.75:1
T ₂	Spiromesifen (22.9 % SC) (X)	96	205.00	60074.55	35006.82	95081.37	451000.00	355918.63	3.74:1
T ₃	Spiromesifen (22.9 % SC) (2X)	192	215.60	60074.55	40206.82	100281.37	474320.00	374038.63	3.73:1
T ₄	Fenazaquin (10 % EC) (x)	94	211.40	60074.55	35973.22	96047.77	465080.00	369032.23	3.84:1
T ₅	Fenazaquin (10 % EC) (X)	125	217.40	60074.55	38006.82	98081.37	478280.00	380198.63	3.88:1
T ₆	Fenazaquin (10 % EC) (2X)	250	222.40	60074.55	46206.82	106281.37	489280.00	382998.63	3.60:1
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	206.60	60074.55	35291.82	95366.37	454520.00	359153.63	3.77:1
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	230.60	60074.55	37120.15	97194.70	507320.00	410125.30	4.22:1
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	235.00	60074.55	44433.49	104508.04	517000.00	412491.96	3.95:1
T ₁₀	Fenvalerate (20 % EC) (x)	60	195.20	60074.55	30299.82	90374.37	429440.00	339065.63	3.75:1
T ₁₁	Fenvalerate (20 % EC) (X)	75	204.40	60074.55	30444.32	90518.87	449680.00	359161.13	3.97:1
T ₁₂	Fenvalerate (20 % EC) (2X)	150	209.20	60074.55	31081.82	91156.37	460240.00	369083.63	4.05:1
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	197.80	60074.55	30676.82	90751.37	435160.00	344408.63	3.80:1
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	202.40	60074.55	30966.82	91041.37	445280.00	354238.63	3.89:1
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	211.20	60074.55	32126.82	92201.37	464640.00	372438.63	4.04:1

4.1.5.2 Economics of different treatments used against brinjal insect pest during 2022

In second season, the Table 4.14 revealed that the net income was (Rs. 421291.96/ha) maximum in T₉ (chlorantraniliprole @ 80 g a.i./ha) followed by T₈ (chlorantraniliprole @ 40 g a.i./ha) (Rs. 416725.30/ha), T₇ (chlorantraniliprole @ 30 g a.i./ha) (Rs. 369273.63/ha), T₁₂ (fenvalerate @ 150 g a.i./ha) (Rs. 367763.63/ha), T₆ (fenazaquin @ 250 g a.i./ha) (Rs. 367158.63/ha), T₁₅ (chlorpyrifos @ 400 g a.i./ha) (Rs. 357038.63/ha), T₁₁ (fenvalerate @ 75 g a.i./ha) (Rs. 354321.13/ha), T₅ (fenazaquin @ 125 g a.i./ha) (Rs. 352038.63/ha), T₃ (spiromesifen @ 192 g a.i./ha) (Rs. 350718.63/ha), T₁₄ (chlorpyrifos @ 200 g a.i./ha) (Rs. 343238.63/ha), T₂ (spiromesifen @ 96 g a.i./ha) (Rs. 339638.63/ha), T₁₀ (fenvalerate @ 60 g a.i./ha) (Rs. 339505.63/ha), T₄ (fenazaquin @ 94 g a.i./ha) (Rs. 338672.23/ha), T₁ (spiromesifen @ 72 g a.i./ha) (Rs. 331698.63/ha), T₁₃ (chlorpyrifos @ 150 g a.i./ha) (Rs. 320208.63/ha). The minimum net income was recorded from untreated control (Rs. 295118.63/ha). The benefit cost ratio of various pesticide treatments was varied from 3.28:1 to 4.29:1 with highest in chlorantraniliprole (@ 40 g a.i./ha) (4.29:1) and minimum in untreated control (3.28:1) (Table 4.14).

Table 4.14: Economics of different treatments used against brinjal insect pest during 2022

Treatments	Pesticide	Dosage (g a.i./ha)	Yield (q/ha)	Fixed Cost (Rs.)	Variable Cost (Rs.)	Total Cost (Rs.)	Gross Income (Rs.)	Net Income (Rs.)	B:C
T ₀	Control	-	175.00	60074.55	29806.82	89881.40	385000.00	295118.63	3.28:1
T ₁	Spiromesifen (22.9 % SC) (x)	72	193.40	60074.55	33706.82	93781.40	425480.00	331698.63	3.54:1
T ₂	Spiromesifen (22.9 % SC) (X)	96	197.60	60074.55	35006.82	95081.40	434720.00	339638.63	3.57:1
T ₃	Spiromesifen (22.9 % SC) (2X)	192	205.00	60074.55	40206.82	100281.40	451000.00	350718.63	3.50:1
T ₄	Fenazaquin (10 % EC) (x)	94	197.60	60074.55	35973.22	96047.80	434720.00	338672.23	3.53:1
T ₅	Fenazaquin (10 % EC) (X)	125	204.60	60074.55	38006.82	98081.40	450120.00	352038.63	3.59:1
T ₆	Fenazaquin (10 % EC) (2X)	250	215.20	60074.55	46206.82	106281.40	473440.00	367158.63	3.45:1
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	211.20	60074.55	35291.82	95366.40	464640.00	369273.63	3.87:1
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	233.60	60074.55	37120.15	97194.70	513920.00	416725.30	4.29:1
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	239.00	60074.55	44433.49	104508.00	525800.00	421291.96	4.03:1
T ₁₀	Fenvalerate (20 % EC) (x)	60	195.40	60074.55	30299.82	90374.40	429880.00	339505.63	3.76:1
T ₁₁	Fenvalerate (20 % EC) (X)	75	202.20	60074.55	30444.32	90518.90	444840.00	354321.13	3.91:1
T ₁₂	Fenvalerate (20 % EC) (2X)	150	208.60	60074.55	31081.82	91156.40	458920.00	367763.63	4.03:1
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	186.80	60074.55	30676.82	90751.40	410960.00	320208.63	3.53:1
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	197.40	60074.55	30966.82	91041.40	434280.00	343238.63	3.77:1
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	204.20	60074.55	32126.82	92201.40	449240.00	357038.63	3.87:1

4.2 Bioefficacy studies on chilli

The bioefficacy of five pesticides *viz.*, cyantraniliprole, imidacloprid, spirotetramat, flubendiamide and fenazaquin at three different doses i.e. lesser than recommended dose (x), recommended dose (X) and double the recommended dose (2X) were evaluated against thrips (*Scirtothrips dorsalis*) on chilli crop in the two consecutive years 2021 and 2022.

4.2.1 Bioefficacy of pesticides against thrips in chilli

4.2.1.1 Per cent reduction of thrips after first spray application of pesticides on chilli during 2021

The data depicted in Table 4.15 revealed that all the pesticides under study were significantly superior over untreated control in reducing the thrips population at 1, 3, 5, 7 and 10 days after spray (DAS). Observations recorded at one day before spray application revealed that population of thrips varied from 5.01 to 6.41 thrips per plant.

The plots treated with treatment T₃ (cyantraniliprole @ 120 g a.i./ha) provided maximum overall reduction 81.90 per cent of thrips population. After 5 days of spray treatment, T₃ (cyantraniliprole @ 120 g a.i./ha) provided highest i.e. 86.53 per cent reduction. The next best treatment was T₂ (cyantraniliprole @ 60 g a.i./ha) with 77.15 per cent reduction which was statistically at par with treatment T₆ (imidacloprid @ 50 a.i./ha) with reduction of 75.91 per cent. Treatment T₅ (imidacloprid @ 25 g a.i./ha) proved to be the next best treatment with the reduction of 73.14 per cent. The plot with treatment T₉ (spirotetramat @ 120 g a.i./ha) was the next best treatment with 68.54 per cent reduction which was statistically at par with

T₁₅ (fenazaquin @ 250 g a.i./ha) which further with a reduction of 66.11 per cent was statistically at par with T₈ (spirotetramat @ 60 g a.i./ha) (64.36 %) which further was at par with T₁ (cyantraniliprole @ 45 g a.i./ha) (63.38 %). The next effective treatments were T₁₄ (fenazaquin @ 125 g a.i./ha) and T₄ (imidacloprid @ 19 a.i./ha) with a reduction of 60.42 and 60.05 per cent, respectively followed by T₇ (spirotetramat @ 45 g a.i./ha) (54.67 %) and T₁₃ (fenazaquin @ 94 g a.i./ha) (52.09 %). Least effective treatments were T₁₀ (flubendamide @ 38 g a.i./ha), T₁₁ (flubendamide @ 50 g a.i./ha) and T₁₂ (flubendamide @ 100 g a.i./ha) with 31.94, 32.35 and 37.07 per cent reduction, respectively.

Table 4.15 Bioefficacy of pesticides against thrips after first spray on chilli during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	Pre-count (No. of thrips/plant)	Per cent reduction of thrips per plant***					
				1DAS	3DAS	5DAS	7DAS	10 DAS	Mean
T ₀	Untreated control	-	5.03 (2.45)**	-	-	-	-	-	
T ₁	Cyantraniliprole (10.26 %OD) (x)	45	5.01 (2.45)	57.76 (49.46)*	65.23 (53.85)	68.20 (55.66)	65.43 (54.00)	60.28 (50.95)	63.38 (52.78) ^{f,g}
T ₂	Cyantraniliprole (10.26 %OD) (X)	60	5.19 (2.49)	74.07 (59.41)	80.06 (63.47)	82.66 (65.39)	77.03 (61.37)	71.91 (57.99)	77.15 (61.53) ^b
T ₃	Cyantraniliprole (10.26 %OD) (2X)	120	5.42 (2.53)	85.05 (67.26)	82.75 (65.44)	86.53 (68.45)	79.07 (62.77)	76.11 (60.74)	81.90 (64.93) ^a
T ₄	Imidacloprid (17.8 % SL) (x)	19	5.22 (2.49)	56.19 (48.55)	66.64 (54.70)	62.23 (52.06)	60.69 (51.15)	54.49 (47.57)	60.05 (50.81) ^h
T ₅	Imidacloprid (17.8 % SL) (X)	25	6.02 (2.65)	76.40 (60.94)	73.98 (59.31)	74.41 (59.64)	71.31 (57.59)	69.62 (56.53)	73.14 (58.80) ^c
T ₆	Imidacloprid (17.8 % SL) (2X)	50	6.41 (2.72)	78.48 (62.34)	81.83 (64.76)	73.91 (59.26)	73.37 (58.92)	71.98 (58.02)	75.91 (60.66) ^b
T ₇	Spirotetramat (15.31 % OD) (x)	45	6.21 (2.68)	48.68 (44.23)	57.80 (49.47)	62.61 (52.29)	54.21 (47.40)	50.03 (45.00)	54.67 (47.68) ⁱ
T ₈	Spirotetramat (15.31 % OD) (X)	60	5.68 (2.58)	64.84 (53.64)	60.88 (51.28)	69.32 (56.35)	67.93 (55.50)	58.83 (50.10)	64.36 (53.37) ^e
T ₉	Spirotetramat (15.31 % OD) (2X)	120	6.25 (2.69)	63.78 (53.01)	68.59 (55.89)	76.09 (60.74)	68.75 (56.14)	65.48 (54.07)	68.54 (55.94) ^d
T ₁₀	Flubendiamide (20 % WG) (x)	38	5.32 (2.51)	36.28 (37.02)	33.92 (35.60)	32.23 (34.57)	29.67 (32.96)	27.60 (31.67)	31.94 (34.36) ^k
T ₁₁	Flubendiamide (20 % WG) (X)	50	5.23 (2.49)	39.00 (38.62)	34.73 (36.09)	31.54 (34.14)	29.40 (32.81)	27.06 (31.30)	32.35 (34.59) ^k
T ₁₂	Flubendiamide (20 % WG) (2X)	100	5.20 (2.49)	41.64 (40.17)	43.38 (41.15)	35.41 (36.50)	34.02 (35.66)	30.88 (33.71)	37.07 (37.44) ^j
T ₁₃	Fenazaquin (10 % EC) (x)	94	5.93 (2.63)	45.71 (42.52)	56.66 (48.81)	54.87 (47.78)	53.61 (47.05)	49.56 (44.73)	52.09 (46.18) ⁱ
T ₁₄	Fenazaquin (10 % EC) (X)	125	5.61 (2.57)	63.78 (53.13)	63.60 (52.88)	65.58 (54.08)	57.91 (49.54)	51.24 (45.69)	60.42 (51.07) ^{g,h}
T ₁₅	Fenazaquin (10 % EC) (2X)	250	5.47 (2.54)	64.40 (53.35)	68.00 (55.55)	71.52 (57.73)	64.78 (53.60)	61.83 (51.84)	66.11 (54.41) ^{d,e,f}
	Mean		NS	59.74 (50.91) ^b	62.54 (52.55) ^a	63.14 (52.98) ^a	59.15 (50.43) ^b	55.13 (47.99) ^c	

*Figure in parentheses is arc sine transformed values, **Figure in parentheses is square root transformed values

***Mean of 3 replications DAS- Days after spray NS- Non significant

CD_{0.05} (Days): 0.95

(Treatments): 1.70

(Days × Treatments): 3.68

The trend of pesticide bioefficacy described that per cent reduction of thrips increased till 5th day of spray in the treatments T₁ (cyantraniliprole @ 45 g a.i./ha), T₂ (cyantraniliprole

@ 60 g a.i./ha), T₇ (spirotetramat @ 45 g a.i./ha), T₉ (spirotetramat @ 120 g a.i./ha) and T₁₅ (fenazaquin @ 250 g a.i./ha). However, the trend of per cent reduction increased upto 3 days after spray in case of treatment T₄ (imidacloprid @ 19 a.i./ha), T₆ (imidacloprid @ 50 a.i./ha) and T₁₃ (fenazaquin @ 94 g a.i./ha). A different trend was noticed in the treatments T₃ (cyantraniliprole @ 120 g a.i./ha), T₈ (spirotetramat @ 60 g a.i./ha), T₅ (imidacloprid @ 25 g a.i./ha) and T₁₄ (fenazaquin @ 125 g a.i./ha) where first there was increase in per cent reduction at 1DAS and then slight decrease at 3DAS and then increase in 5DAS, although there was decrease after the 5th day of spray. The reason behind this changing trend can be the change in the climatic conditions during the observations. Overall decreasing trend in per cent reduction was noticed in the least effective treatments i.e. T₁₀ (flubendamide @ 38 g a.i./ha), T₁₁ (flubendamide @ 50 g a.i./ha) and T₁₂ (flubendamide @ 100 g a.i./ha).

4.2.1.2 Per cent reduction of thrips after second spray application of pesticides on chilli during 2021

The data in Table 4.16 revealed that after one day of second spray, the plots treated with cyantraniliprole at recommended (cyantraniliprole @ 60 g a.i./ha) and double the recommended dose (cyantraniliprole @ 120 g a.i./ha) were found to be the most effective with 82.12 and 84.23 per cent reduction and were statistically at par with each other. The second best treatment was T₆ (imidacloprid @ 50 a.i./ha) with the per cent reduction of 78.01 per cent. Treatment T₅ (imidacloprid @ 25 g a.i./ha) was the next best treatment with 74.74 per cent reduction which was statistically at par with treatment T₁ (cyantraniliprole @ 45 g a.i./ha) with 72.57 per cent reduction in the population of thrips. The next best treatment in the series was T₉ (spirotetramat @ 120 g a.i./ha) which provided 69.93 per cent reduction and was at par with T₁₅ (fenazaquin @ 250 g a.i./ha) (68.12 %) and T₈ (spirotetramat @ 60 g a.i./ha) (67.64 %) also, treatment T₈ (spirotetramat @ 60 g a.i./ha) was statistically at par with T₁₄ (fenazaquin @ 125 g a.i./ha) and T₄ (imidacloprid @ 19 a.i./ha) providing 65.20 and 65.02 per cent reduction, respectively. The plot treated with treatment T₁₀ (flubendamide @ 38 g a.i./ha) provided highest population of thrips with least per cent reduction (34.54 %). The other treatments i.e. T₇ (spirotetramat @ 45 g a.i./ha), T₁₃ (fenazaquin @ 94 g a.i./ha), T₁₂ (flubendamide @ 100 g a.i./ha), T₁₁ (flubendamide @ 50 g a.i./ha), and T₁₀ (flubendamide @ 38 g a.i./ha), provided 56.07, 53.85, 41.49, 37.55 and 34.54 per cent reduction, respectively.

Table 4.16 Bioefficacy of pesticides against thrips after second spray on chilli during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	Per cent reduction of thrips per plant**					Mean
			1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	-	-	-	-	-	-
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	62.46 (52.23)*	79.00 (62.93)	75.93 (60.66)	75.07 (61.14)	68.88 (56.09)	72.57 (58.61) ^c
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	75.07 (60.19)	84.31 (66.97)	86.04 (68.05)	87.32 (69.28)	77.85 (61.91)	82.12 (65.28) ^a
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	86.56 (68.65)	79.86 (63.32)	90.58 (72.12)	88.23 (70.00)	75.90 (60.64)	84.23 (66.95) ^a
T ₄	Imidacloprid (17.8 % SL) (x)	19	58.34 (49.80)	68.83 (56.05)	71.91 (57.99)	65.94 (54.32)	60.06 (50.80)	65.02 (53.79) ^f
T ₅	Imidacloprid (17.8 % SL) (X)	25	76.56 (61.110)	85.05 (67.28)	79.48 (63.06)	72.18 (58.14)	60.43 (51.01)	74.74 (60.12) ^c
T ₆	Imidacloprid (17.8 % SL) (2X)	50	80.57 (63.83)	87.00 (69.01)	87.60 (69.40)	69.51 (56.49)	65.36 (53.93)	78.01 (62.53) ^b
T ₇	Spirotetramat (15.31 % OD) (x)	45	52.29 (46.29)	59.07 (50.21)	63.73 (52.97)	55.42 (48.11)	49.82 (44.88)	56.07 (48.49) ^g
T ₈	Spirotetramat (15.31 % OD) (X)	60	58.16 (49.69)	70.96 (57.39)	70.33 (57.02)	75.89 (58.61)	65.85 (54.23)	67.64 (55.39) ^{d,e,f}
T ₉	Spirotetramat (15.31 % OD) (2X)	120	64.97 (53.71)	73.26 (58.92)	73.46 (58.99)	70.32 (57.04)	67.67 (55.35)	69.93 (56.80) ^d
T ₁₀	Flubendiamide (20 % WG) (x)	38	40.33 (39.41)	36.17 (36.94)	34.71 (36.08)	31.93 (34.36)	29.55 (32.90)	34.54 (35.94) ^j
T ₁₁	Flubendiamide (20 % WG) (X)	50	42.85 (40.87)	38.88 (38.56)	36.78 (37.32)	36.15 (36.93)	33.10 (35.10)	37.55 (37.75) ⁱ
T ₁₂	Flubendiamide (20 % WG) (2X)	100	44.25 (41.68)	43.90 (41.48)	48.24 (43.97)	38.07 (38.07)	32.98 (35.04)	41.49 (40.05) ^h
T ₁₃	Fenazaquin (10 % EC) (x)	94	47.39 (43.49)	57.48 (49.28)	59.65 (50.55)	54.27 (47.44)	50.47 (45.25)	53.85 (47.20) ^g
T ₁₄	Fenazaquin (10 % EC) (X)	125	64.74 (53.57)	68.92 (56.11)	72.26 (58.21)	62.86 (52.43)	57.24 (49.14)	65.20 (53.89) ^{e,f}
T ₁₅	Fenazaquin (10 % EC) (2X)	250	65.81 (54.31)	71.21 (57.55)	76.07 (60.70)	66.68 (54.72)	60.82 (51.24)	68.12 (55.70) ^d
	Mean		60.92 (51.65) ^d	66.41 (55.09) ^b	68.68 (56.63) ^a	63.44 (53.27) ^c	57.44 (49.40) ^e	

*Figure in parentheses is arc sine transformed values, **Mean of 3 replications DAS- Days after spray

CD_{0.05} (Days): 1.02

(Treatments): 1.74

(Days × Treatments): 3.91

The mean per cent reduction of almost each pesticide was maximum at 5th day followed by 3rd day whereas, minimum reduction was found on 7th day after spray.

4.2.1.3 Per cent reduction of thrips after first spray application of pesticides on chilli during 2022

The data presented in Table 4.17 revealed that there was significant reduction in the population levels of chilli thrips at 1, 3, 5, 7 and 10 days after spray (DAS) in all the treatments. Observations recorded at one day before spray revealed that population of chilli thrips was uniformly distributed in the field ranging from 5.40 to 6.67 thrips per plant.

After first spray in second year again the treatment T₃ (cyantraniliprole @ 120 g a.i./ha) proved to be the most effective with maximum per cent reduction of 83.89 per cent in

thrips population (Table 4.17). The plots with treatment T₂ (cyantraniliprole @ 60 g a.i./ha) was the second best treatment with 81.89 per cent reduction in thrips population and the maximum per cent reduction in both the treatments was on 7th (T₃) (cyantraniliprole @ 120 g a.i./ha) and 5th (T₂) (cyantraniliprole @ 60 g a.i./ha) day, respectively. The next best treatment was T₆ (imidacloprid @ 50 a.i./ha) with 78.12 per cent reduction which was statistically at par with treatment T₅ (imidacloprid @ 25 g a.i./ha) (76.29 %). The next best treatment in the series

Table 4.17 Bioefficacy of pesticides against thrips after first spray on chilli during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	Pre-count (No. of thrips/plant)	Per cent reduction of thrips per plant***					
				1DAS	3DAS	5DAS	7DAS	10 DAS	Mean
T ₀	Untreated control	-	6.30 (2.7)**	-	-	-	-	-	
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	6.67 (2.77)	61.26 (51.53)*	69.20 (56.27)	73.77 (59.18)	69.46 (56.43)	64.78 (53.60)	67.69 (55.40) d,c
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	5.62 (2.57)	72.50 (58.39)	86.47 (68.40)	87.89 (69.62)	87.19 (69.04)	75.40 (60.26)	81.89 (65.14) b
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	5.93 (2.63)	75.07 (60.05)	85.28 (67.43)	88.12 (69.81)	90.37 (71.92)	80.60 (63.85)	83.89 (66.61) a
T ₄	Imidacloprid (17.8 % SL) (x)	19	6.31 (2.70)	70.85 (57.32)	67.94 (55.51)	64.49 (53.41)	61.94 (51.89)	59.81 (50.64)	65.01 (53.76) g
T ₅	Imidacloprid (17.8 % SL) (X)	25	5.57 (2.56)	80.84 (64.04)	78.74 (62.53)	75.47 (60.34)	75.19 (60.17)	71.22 (57.60)	76.29 (60.94) c
T ₆	Imidacloprid (17.8 % SL) (2X)	50	5.87 (2.62)	83.20 (65.81)	80.07 (63.49)	78.94 (62.68)	76.24 (60.81)	72.13 (58.12)	78.12 (62.18) c
T ₇	Spirotetramat (15.31 % OD) (x)	45	6.30 (2.70)	51.79 (46.01)	58.77 (50.44)	66.19 (54.44)	61.81 (51.82)	56.70 (48.84)	59.05 (50.23) h
T ₈	Spirotetramat (15.31 % OD) (X)	60	6.67 (2.77)	55.36 (48.06)	66.29 (54.50)	75.02 (60.02)	69.26 (56.33)	59.73 (50.60)	65.13 (53.90) f,g
T ₉	Spirotetramat (15.31 % OD) (2X)	120	6.41 (2.72)	59.72 (50.60)	70.51 (57.09)	79.09 (62.82)	68.95 (56.12)	62.97 (52.51)	68.25 (55.82) d
T ₁₀	Flubendiamide (20 % WG) (x)	38	5.70 (2.59)	43.61 (41.31)	37.00 (37.44)	33.34 (35.25)	32.36 (34.66)	27.84 (31.83)	34.83 (36.10) k
T ₁₁	Flubendiamide (20 % WG) (X)	50	5.96 (2.64)	45.48 (42.38)	42.08 (40.42)	37.74 (37.88)	34.15 (35.74)	24.58 (29.65)	36.81 (37.21) k
T ₁₂	Flubendiamide (20 % WG) (2X)	100	5.93 (2.63)	48.89 (44.34)	44.65 (41.91)	40.83 (39.70)	38.29 (38.21)	37.04 (37.47)	41.94 (40.33) j
T ₁₃	Fenazaquin (10 % EC) (x)	94	5.93 (2.63)	46.01 (42.69)	57.47 (49.28)	64.47 (53.40)	58.92 (50.14)	52.41 (46.37)	55.86 (48.37) i
T ₁₄	Fenazaquin (10 % EC) (X)	125	5.40 (2.53)	50.78 (45.43)	61.61 (51.70)	69.30 (56.40)	66.08 (54.39)	56.56 (48.77)	60.87 (51.34) h
T ₁₅	Fenazaquin (10 % EC) (2X)	250	6.13 (2.67)	54.08 (47.32)	71.07 (57.46)	75.35 (60.23)	65.84 (54.22)	62.54 (52.25)	65.78 (54.30) e,f,g
	Mean		NS	59.96 (51.02) ^d	65.14 (54.23) ^b	67.33 (55.68) ^a	63.74 (53.46) ^c	57.62 (49.49) ^d	

*Figure in parentheses is arc sine transformed values, **Figure in parentheses is square root transformed values

***Mean of 3 replications DAS- Days after spray NS- Non significant

CD_{0.05} (Days): 0.76

(Treatments): 1.33

(Days × Treatments): 2.97

was T₉ (spirotetramat @ 120 g a.i./ha) with 68.25 per cent reduction and T₁ (cyantraniliprole @ 45 g a.i./ha) with 67.69 per cent reduction, being statistically at par with T₁₅ (fenazaquin @ 250 g a.i./ha) (65.78 %), further T₁₅ was at par with T₈ (spirotetramat @ 60 g a.i./ha) and T₄ (imidacloprid @ 19 a.i./ha) with the per cent reduction of 65.13 and 65.01 per cent, respectively. The next best treatment in the series is T₁₄ (fenazaquin @ 125 g a.i./ha) with 60.87 per cent reduction and was at par with T₇ (spirotetramat @ 45 g a.i./ha). The least effective treatments were T₁₀ (flubendamide @ 38 g a.i./ha), T₁₁ (flubendamide @ 50 g a.i./ha), T₁₂ (flubendamide @ 100 g a.i./ha) and T₁₃ (fenazaquin @ 94 g a.i./ha) with 34.83, 36.81, 41.94 and 55.86 per cent reduction, respectively. The effectiveness of pesticides increased till 5th day after spray in all the treatments except treatment T₃ (cyantraniliprole @ 120 g a.i./ha) where population of thrips decreased till 7th day after spray. In other treatments i.e. T₄ (imidacloprid @ 19 a.i./ha), T₅ (imidacloprid @ 25 g a.i./ha), T₆ (imidacloprid @ 50 a.i./ha), T₁₀ (flubendamide @ 38 g a.i./ha), T₁₁ (flubendamide @ 50 g a.i./ha) and T₁₂ (flubendamide @ 100 g a.i./ha) there was an increasing trend in reduction of thrips population.

4.2.1.4 Per cent reduction of thrips after second spray application of pesticides on chilli during 2022

After second spray of selective pesticides again the plots treated with T₃ (cyantraniliprole @ 120 g a.i./ha) provided best results with 86.65 per cent overall reduction followed by treatment T₂ (cyantraniliprole @ 60 g a.i./ha) with 83.43 per cent reduction. Treatments T₆ (imidacloprid @ 50 a.i./ha) (79.43 %) and T₅ (imidacloprid @ 25 g a.i./ha) (77.75 %) and T₉ (spirotetramat @ 120 g a.i./ha) (74.89 %) and T₁ (cyantraniliprole @ 45 g a.i./ha) (72.95 %) were the next best treatments in reducing the population of thrips which were statistically at par with each other. Treatments T₈ (spirotetramat @ 60 g a.i./ha) (69.72 %), T₄ (imidacloprid @ 19 g a.i./ha) (68.80 %) and T₁₅ (fenazaquin @ 250 g a.i./ha) (68.60 %) were found to be statistically at par with each other. The next best treatments in the series were treatment T₁₄ (fenazaquin @ 125 g a.i./ha) and T₇ (spirotetramat @ 45 g a.i./ha) which provided 64.42 and 61.64 per cent reduction in the population of thrips. Other treatments i.e. T₁₁ (flubendamide @ 50 g a.i./ha), T₁₂ (flubendamide @ 100 g a.i./ha) and T₁₃ (fenazaquin @ 94 g a.i./ha) showed per cent reduction of 44.41, 47.00 and 58.28 per cent, respectively. The plots treated with treatment T₁₀ (flubendamide @ 38 g a.i./ha) recorded highest population of thrips with least per cent reduction (36.77 %) (Table 4.18)

Table 4.18 Bioefficacy of pesticides against thrips on chilli after second spray during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	Per cent reduction of thrips per plant**					Mean
			1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	-	-	-	-	-	-
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	66.65 (54.72)*	72.87 (58.64)	76.63 (61.09)	78.09 (62.22)	70.53 (57.12)	72.95 (58.76) ^d
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	73.27 (58.86)	89.35 (70.97)	92.63 (74.29)	83.57 (66.09)	78.32 (62.24)	83.43 (66.49) ^b
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	74.29 (59.56)	89.65 (71.23)	92.53 (74.11)	92.93 (74.56)	83.87 (66.53)	86.65 (69.20) ^a
T ₄	Imidacloprid (17.8 % SL) (x)	19	73.17 (58.79)	71.49 (57.71)	68.88 (56.08)	65.58 (54.07)	64.88 (53.64)	68.80 (56.06) ^c
T ₅	Imidacloprid (17.8 % SL) (X)	25	84.06 (66.45)	79.67 (63.19)	76.37 (60.90)	74.88 (59.94)	73.79 (59.21)	77.75 (61.94) ^c
T ₆	Imidacloprid (17.8 % SL) (2X)	50	87.80 (69.60)	82.71 (65.51)	77.52 (61.68)	76.10 (60.78)	73.00 (58.70)	79.43 (63.25) ^c
T ₇	Spirotetramat (15.31 % OD) (x)	45	53.10 (46.77)	63.02 (52.54)	71.29 (57.68)	63.30 (52.74)	57.47 (49.31)	61.64 (51.81) ^f
T ₈	Spirotetramat (15.31 % OD) (X)	60	56.14 (48.51)	71.94 (58.00)	78.83 (62.60)	74.33 (59.57)	67.37 (55.15)	69.72 (56.77) ^e
T ₉	Spirotetramat (15.31 % OD) (2X)	120	65.89 (54.25)	74.72 (59.80)	80.63 (63.92)	79.72 (63.22)	73.48 (59.00)	74.89 (60.04) ^d
T ₁₀	Flubendiamide (20 % WG) (x)	38	46.61 (43.04)	38.58 (38.36)	35.45 (36.51)	32.93 (35.00)	30.27 (33.31)	36.77 (37.24) ⁱ
T ₁₁	Flubendiamide (20 % WG) (X)	50	49.34 (44.60)	49.29 (44.58)	44.82 (42.00)	40.84 (39.68)	37.76 (37.88)	44.41 (41.75) ^b
T ₁₂	Flubendiamide (20 % WG) (2X)	100	55.47 (48.13)	53.19 (46.82)	47.01 (43.26)	41.57 (40.13)	37.74 (37.88)	47.00 (43.24) ^h
T ₁₃	Fenazaquin (10 % EC) (x)	94	48.37 (44.05)	62.87 (52.45)	66.87 (54.84)	59.60 (50.52)	53.69 (47.10)	58.28 (49.79) ^g
T ₁₄	Fenazaquin (10 % EC) (X)	125	58.57 (49.92)	72.95 (58.64)	69.05 (56.18)	64.94 (53.67)	56.61 (48.80)	64.42 (53.44) ^f
T ₁₅	Fenazaquin (10 % EC) (2X)	250	61.35 (51.57)	76.67 (61.12)	75.76 (60.50)	66.99 (54.97)	62.25 (52.12)	68.60 (56.05) ^c
	Mean		63.61 (53.25) ^c	69.93 (57.30) ^a	70.28 (57.71) ^a	66.36 (55.14) ^b	61.40 (51.87) ^d	

*Figure in parentheses is arc sine transformed values, **Mean of 3 replications DAS- Days after spray

CD_{0.05} (Days): 0.97

(Treatments): 1.68

(Days × Treatments): 3.77

4.1.2.5 Average per cent reduction of thrips following two applications of pesticides during 2021 and 2022

With every spray over the course of the two years, every insecticide presented the same pattern. It was found that the applied treatments were superior over the control in each spray. According to the findings of all pesticide applications, treatment T₃ (cyantraniliprole @ 120 g a.i/ha) was the most effective, whereas treatment T₁₀ (flubendiamide @ 38 g a.i/ha) recorded less effectiveness than all other treatments (Fig. 4.9 and 4.10).

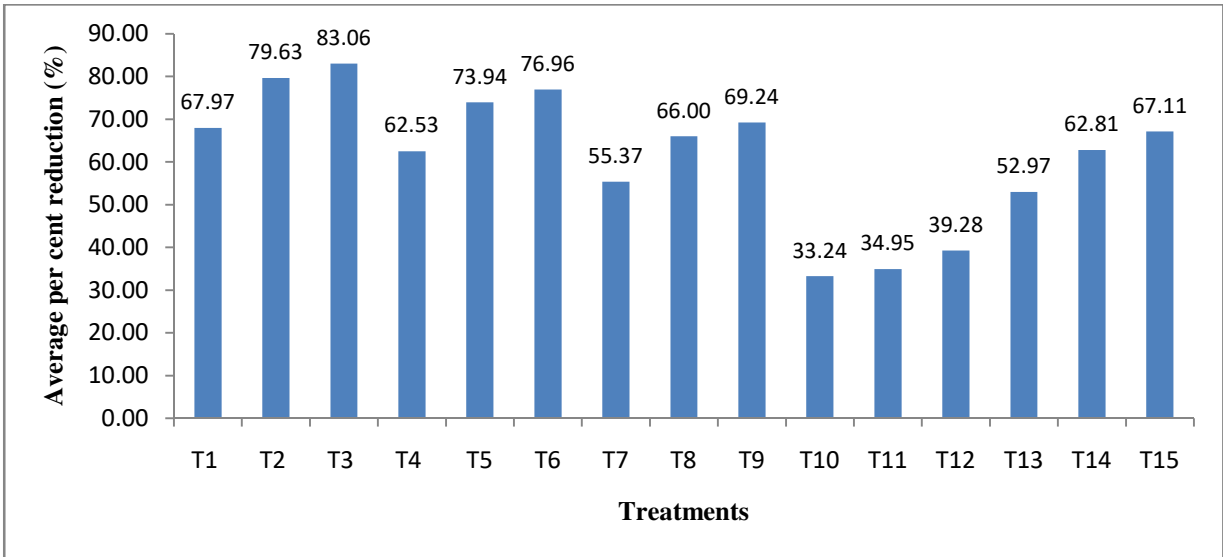


Fig. 4.9 Average per cent reduction of thrips (*S. dorsalis*) in chilli after two sprays during 2021

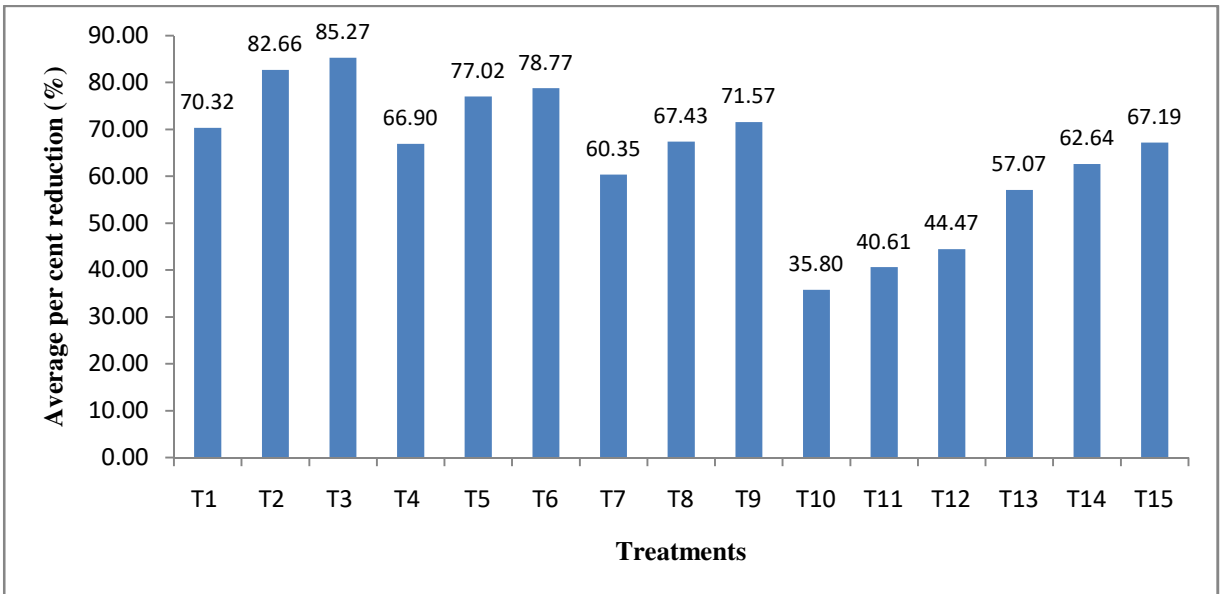


Fig. 4.10 Average per cent reduction of thrips (*S. dorsalis*) in chilli after two sprays during 2022

The current studies were carried out in order to assess the bioefficacy of several pesticides against thrips in chilli. The findings of the current study demonstrated that plots treated with cyantraniliprole at a double dose (@ 120 g a.i./ha) caused a mean reduction in thrips population of 83.06 and 85.27 per cent in 2021 and 2022, respectively. The results of Akshima (2019) after the first, second and third spray treatments of cyantraniliprole at a rate of 60 g a.i./ha on chilli were similar to our results and concluded that the mean percentage of thrips was reduced by 82.64, 84.61 and 86.72 percent, respectively on chilli. Karthik et al. (2017), who discovered that cyantraniliprole @ 90 g a.i /ha was more effective against thrips (*Scirtothrips dorsalis*) in cotton, resulting in 93.42 and 97.49 per cent control after first and

second spray, respectively, corroborates with the present studies. Similarly, the findings of Lodaya et al. (2017) stated that the pooled data of two years on the bioefficacy of cyantraniliprole demonstrated its superiority in suppressing thrips population over other treatments as cyantraniliprole @ 90 g a.i./ha recorded the lowest number of thrips population (0.69 thrips/ 3 leaves). The plots treated with imidacloprid at a rate of 50 g a.i./ha had the next-best results, with mean thrips population reductions of 76.96 and 78.77 per cent in 2021 and 2022, respectively (Fig 4.9 and 4.10). According to Priyadarshini et al. (2019), imidacloprid @ 50 g a.i./ha demonstrated 84.15, 86.04, and 86.46 percent reduction of chilli thrips after the first, second, and third sprays, respectively.

The lowest per cent mean reduction of thrips in chilli was in the plots treated with flubendiamide @ 38 g a.i./ha with the mean per cent reduction of 33.24 and 35.80 per cent during 2021 and 2022, respectively. The present findings are in agreement with the findings of Vanisree et al. (2017) who reported 42.12 per cent reduction in thrips population after 14 days of flubendiamide spray application at 0.012 per cent concentration in chilli. Sangamithra et al. (2018) found 71.71 per cent reduction in thrips population after application of higher dose of flubendiamide @ 90 g a.i./ha in brinjal.

4.2.2 Phytotoxicity studies

When applied to chilli plants after the first and second applications of the corresponding pesticides, none of the treatments under observation exhibit any phytotoxic signs including yellowing, stunting, necrosis, chlorosis, vein clearing, epinasty, or hyponasty.

Our results were similar to that conducted by Karthik et al. (2015) who found that no phytotoxic symptoms appeared on okra leaves, flowers or fruits following the foliar application of imidacloprid 70 WG at 49 g a.i./ha at 1, 3, 7 and 10 days after spray. Another study was conducted by Sangamithra et al. (2018) who found that the hills sprayed with imidacloprid 17.1 % SL @ 60, 120 and 240 g a.i./ha in rice did not show any phytotoxic symptoms like leaf tip injury, wilting, vein clearing, necrosis, epinasty, hyponasty at 1, 3, 7, 10, 14 and 21 days after spray. All the doses of cyantraniliprole 10 OD (75, 150 and 300 g a.i./ha) as foliar application in different seasons did not cause any noticeable phytotoxic symptoms at 1, 3, 5, 7, 10 and 15 days after application in potato (Vinothkumar 2020). Balikai and Mallapur (2017) reported that gherkin plants sprayed with flubendiamide @ 60, 120, and 180 g a.i./ha did not show any phytotoxic symptoms at 1, 3, 7, 10 and 15 days.

4.2.3 Effect of pesticides on the population of coccinellids in chilli

4.2.3.1 Effect of different pesticides on coccinellid population in chilli after first spray during 2021

The data recorded on population of predators was analyzed statistically and data was recorded from treatments plots at 1, 3, 5, 7 and 10 days after each spray. Before spray the data was collected and a range of 0.80-1.13 beetles per five plants were recorded. From the Table 4.19 it was found that control plot (T₀- 1.20 beetles/5 plants) recorded higher population of coccinellid beetles.

Table 4.19 Effect of different pesticides on coccinellid population in chilli after first spray during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	Pre-count (No. of coccinellids/ 5 plants)	No. of coccinellids per five plants**					
				1DAS	3DAS	5DAS	7DAS	10 DAS	Mean
T ₀	Untreated control	-	1.07 (1.44)	1.13 (1.46)*	1.13 (1.46)	1.20 (1.48)	1.27 (1.51)	1.27 (1.51)	1.20 (1.51) ^a
T ₁	Cyantraniliprole (10.26 % OD)(x)	45	1.00 (1.41)	0.80 (1.34)	0.60 (1.26)	0.53 (1.24)	0.67 (1.29)	0.87 (1.36)	0.69 (1.30) ^b
T ₂	Cyantraniliprole (10.26 % OD)(X)	60	0.80 (1.34)	0.53 (1.24)	0.53 (1.24)	0.47 (1.21)	0.67 (1.29)	0.80 (1.34)	0.60 (1.26) ^c
T ₃	Cyantraniliprole (10.26 % OD)(2X)	120	1.13 (1.46)	0.60 (1.26)	0.47 (1.21)	0.40 (1.18)	0.53 (1.24)	0.67 (1.29)	0.53 (1.24) ^c
T ₄	Imidacloprid (17.8 % SL) (x)	19	1.07 (1.44)	0.53 (1.24)	0.47 (1.21)	0.33 (1.15)	0.33 (1.15)	0.47 (1.21)	0.43 (1.19) ^d
T ₅	Imidacloprid (17.8 % SL) (X)	25	0.93 (1.39)	0.67 (1.29)	0.40 (1.18)	0.27 (1.13)	0.27 (1.13)	0.20 (1.09)	0.36 (1.16) ^d
T ₆	Imidacloprid (17.8 % SL) (2X)	50	0.80 (1.34)	0.40 (1.18)	0.33 (1.15)	0.33 (1.15)	0.27 (1.13)	0.17 (1.08)	0.30 (1.14) ^d
T ₇	Spirotetramat (15.31 % OD) (x)	45	1.13 (1.46)	0.93 (1.39)	0.80 (1.34)	0.60 (1.26)	0.47 (1.21)	0.53 (1.24)	0.67 (1.28) ^b
T ₈	Spirotetramat (15.31 % OD) (X)	60	1.07 (1.44)	0.87 (1.36)	0.67 (1.29)	0.47 (1.21)	0.47 (1.21)	0.27 (1.13)	0.56 (1.24) ^c
T ₉	Spirotetramat (15.31 % OD) (2X)	120	1.13 (1.46)	0.80 (1.34)	0.53 (1.24)	0.40 (1.18)	0.33 (1.15)	0.33 (1.15)	0.48 (1.21) ^c
T ₁₀	Flubendiamide (20 % WG) (x)	38	1.00 (1.41)	0.93 (1.39)	0.87 (1.36)	0.67 (1.28)	0.73 (1.32)	0.80 (1.34)	0.80 (1.34) ^b
T ₁₁	Flubendiamide (20 % WG) (X)	50	0.93 (1.39)	0.80 (1.34)	0.67 (1.29)	0.67 (1.29)	0.60 (1.26)	0.73 (1.32)	0.69 (1.30) ^b
T ₁₂	Flubendiamide (20 % WG) (2X)	100	0.80 (1.34)	0.60 (1.26)	0.47 (1.21)	0.47 (1.21)	0.60 (1.26)	0.60 (1.26)	0.55 (1.24) ^c
T ₁₃	Fenazaquin (10 % EC) (x)	94	1.00 (1.41)	0.60 (1.27)	0.53 (1.24)	0.53 (1.24)	0.33 (1.15)	0.33 (1.15)	0.46 (1.21) ^c
T ₁₄	Fenazaquin (10 % EC) (X)	125	0.80 (1.34)	0.53 (1.24)	0.33 (1.15)	0.27 (1.13)	0.33 (1.15)	0.40 (1.18)	0.37 (1.17) ^d
T ₁₅	Fenazaquin (10 % EC) (2X)	250	0.80 (1.34)	0.40 (1.18)	0.47 (1.21)	0.33 (1.15)	0.33 (1.15)	0.27 (1.13)	0.36 (1.18) ^d
	Mean		NS	0.70 (1.30)	0.58 (1.26)	0.50 (1.22)	0.51 (1.23)	0.54 (1.24)	

*Figure in parentheses is square root transformed values

CD_{0.05} (Days): NS

(Treatments):0.06

(Days × Treatments): 0.12

**Mean of 3 replications

NS- Non significant

DAS- Days after spray

4.2.3.2 Effect of different pesticides on coccinellid population in chilli after second spray during 2021

During 2021, a similar trend was recorded after second spray where highest population was recorded in plots treated with treatment T₁₀ (flubendiamide @ 38 g a.i./ha) (0.65 beetles/5 plants) and was statistically equivalent to T₁ (cyantraniliprole @ 45 g a.i./ha), T₁₁ (flubendiamide @ 50 g a.i./ha), T₇ (spirotetramat @ 45 g a.i./ha), T₂ (cyantraniliprole @ 60 g a.i./ha), T₁₂ (flubendiamide @ 100 g a.i./ha), T₈ (spirotetramat @ 60 g a.i./ha) and T₃ (cyantraniliprole @ 120 g a.i./ha) recorded 0.59, 0.59, 0.59, 0.57, 0.57, 0.53 and 0.51 beetles per five plants .

Table 4.20 Effect of different pesticides on coccinellid population in chilli after second spray during 2021

Treatments	Pesticides	Dosage (g a.i./ha)	No. of coccinellids per five plants**					Mean
			1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	1.20 (1.48)*	1.27 (1.51)	1.33 (1.53)	1.33 (1.53)	1.40 (1.55)	1.31 (1.52) ^a
T ₁	Cyantraniliprole (10.26 %OD)(x)	45	0.47 (1.21)	0.53 (1.24)	0.60 (1.26)	0.67 (1.29)	0.67 (1.29)	0.59 (1.26) ^b
T ₂	Cyantraniliprole (10.26 %OD)(X)	60	0.53 (1.24)	0.47 (1.21)	0.47 (1.21)	0.67 (1.29)	0.73 (1.32)	0.57 (1.25) ^b
T ₃	Cyantraniliprole (10.26 %OD)(2X)	120	0.33 (1.15)	0.47 (1.21)	0.53 (1.24)	0.53 (1.24)	0.67 (1.29)	0.51 (1.23) ^b
T ₄	Imidacloprid (17.8 % SL) (x)	19	0.23 (1.11)	0.17 (1.08)	0.27 (1.13)	0.40 (1.18)	0.40 (1.18)	0.29 (1.13) ^d
T ₅	Imidacloprid (17.8 % SL) (X)	50	0.27 (1.13)	0.17 (1.08)	0.17 (1.08)	0.23 (1.11)	0.33 (1.15)	0.23 (1.11) ^d
T ₆	Imidacloprid (17.8 % SL) (2X)	25	0.33 (1.15)	0.27 (1.13)	0.13 (1.06)	0.13 (1.06)	0.30 (1.14)	0.23 (1.11) ^d
T ₇	Spirotetramat (15.31 % OD) (x)	45	0.33 (1.15)	0.47 (1.21)	0.53 (1.24)	0.67 (1.29)	0.93 (1.39)	0.59 (1.26) ^b
T ₈	Spirotetramat (15.31 % OD) (X)	60	0.40 (1.18)	0.40 (1.18)	0.60 (1.26)	0.60 (1.26)	0.67 (1.29)	0.53 (1.24) ^b
T ₉	Spirotetramat (15.31 % OD) (2X)	120	0.47 (1.21)	0.37 (1.17)	0.47 (1.21)	0.47 (1.21)	0.67 (1.29)	0.49 (1.22) ^c
T ₁₀	Flubendiamide (20 % WG) (x)	38	0.47 (1.21)	0.40 (1.18)	0.60 (1.26)	0.87 (1.36)	0.93 (1.39)	0.65 (1.28) ^b
T ₁₁	Flubendiamide (20 % WG) (X)	50	0.67 (1.29)	0.47 (1.21)	0.33 (1.15)	0.53 (1.24)	0.93 (1.39)	0.59 (1.26) ^b
T ₁₂	Flubendiamide (20 % WG) (2X)	100	0.53 (1.24)	0.33 (1.15)	0.53 (1.24)	0.67 (1.29)	0.80 (1.34)	0.57 (1.25) ^b
T ₁₃	Fenazaquin (10 % EC) (x)	94	0.47 (1.21)	0.40 (1.18)	0.33 (1.15)	0.27 (1.13)	0.47 (1.21)	0.39 (1.18) ^c
T ₁₄	Fenazaquin (10 % EC) (X)	125	0.47 (1.21)	0.27 (1.13)	0.27 (1.13)	0.33 (1.15)	0.53 (1.24)	0.37 (1.17) ^c
T ₁₅	Fenazaquin (10 % EC) (2X)	250	0.33 (1.15)	0.33 (1.15)	0.27 (1.13)	0.40 (1.18)	0.40 (1.18)	0.35 (1.16) ^d
	Mean		0.47 (1.21)	0.42 (1.19)	0.46 (1.21)	0.55 (1.24)	0.68 (1.30)	

*Figure in parentheses is square root transformed values

**Mean of 3 replications

DAS- Days after spray

CD_{0.05} (Days): NS

NS- Non significant

(Treatments): 0.05

(Days × Treatments): 0.10

Treatment T₉ (spirotetramat @ 120 g a.i./ha) showed 0.49 beetles per five plants which was further at par with T₁₃ (fenazaquin @ 94 g a.i./ha) (0.39 beetles/5 plants) and T₁₄ (fenazaquin @ 125 g a.i./ha) (0.37 beetles/ 5 plants). Minimum number of coccinellids was found in the treatments T₆ (imidacloprid @ 50 g a.i./ha), T₅ (imidacloprid @ 25 g a.i./ha), T₄ (imidacloprid @ 19 g a.i./ha) and T₁₅ (fenazaquin @ 250 g a.i./ha) with a range between 0.23-0.35 beetles per five plants (Table 4.20).

4.2.3.3 Effect of different pesticides on coccinellid population in chilli after first spray during 2022

The data presented in Table 4.21 revealed that before spray the population of coccinellids ranged from 0.33-0.80 beetles per five plants and further data was recorded at 1, 3, 5, 7 and 10 days after each spray.

Table 4.21 Effect of different pesticides on coccinellid population in chilli after first spray during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	Pre-count (No. of coccinellids/5 plants)	No. of coccinellids per five plants**					Mean
				1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control	-	0.73 (1.31)	0.73 (1.31)*	0.80 (1.34)	0.87 (1.37)	0.93 (1.39)	0.93 (1.39)	0.85 (1.36) ^a
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	0.67 (1.29)	0.60 (1.26)	0.47 (1.21)	0.33 (1.15)	0.60 (1.26)	0.87 (1.37)	0.57 (1.25) ^b
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	0.80 (1.34)	0.73 (1.32)	0.47 (1.21)	0.40 (1.18)	0.27 (1.13)	0.53 (1.24)	0.48 (1.21) ^c
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	0.60 (1.26)	0.53 (1.24)	0.47 (1.21)	0.47 (1.21)	0.40 (1.18)	0.53 (1.24)	0.48 (1.22) ^c
T ₄	Imidacloprid (17.8 % SL) (x)	19	0.53 (1.24)	0.47 (1.21)	0.27 (1.13)	0.40 (1.18)	0.47 (1.21)	0.47 (1.21)	0.42 (1.16) ^d
T ₅	Imidacloprid (17.8 % SL) (X)	25	0.60 (1.26)	0.40 (1.18)	0.33 (1.15)	0.23 (1.11)	0.20 (1.09)	0.37 (1.17)	0.31 (1.14) ^d
T ₆	Imidacloprid (17.8 % SL) (2X)	50	0.47 (1.21)	0.27 (1.13)	0.33 (1.15)	0.33 (1.15)	0.23 (1.11)	0.30 (1.14)	0.29 (1.14) ^d
T ₇	Spirotetramat (15.31 % OD) (x)	45	0.67 (1.29)	0.53 (1.24)	0.33 (1.15)	0.60 (1.26)	0.67 (1.28)	0.73 (1.31)	0.57 (1.23) ^c
T ₈	Spirotetramat (15.31 % OD) (X)	60	0.53 (1.24)	0.47 (1.21)	0.40 (1.18)	0.33 (1.15)	0.47 (1.21)	0.47 (1.21)	0.43 (1.21) ^c
T ₉	Spirotetramat (15.31 % OD) (2X)	120	0.73 (1.31)	0.47 (1.21)	0.33 (1.15)	0.40 (1.18)	0.40 (1.18)	0.53 (1.24)	0.43 (1.19) ^c
T ₁₀	Flubendiamide (20 % WG) (x)	38	0.67 (1.29)	0.53 (1.24)	0.67 (1.29)	0.73 (1.32)	0.53 (1.24)	0.80 (1.34)	0.65 (1.28) ^b
T ₁₁	Flubendiamide (20 % WG) (X)	50	0.73 (1.31)	0.60 (1.26)	0.60 (1.26)	0.53 (1.24)	0.67 (1.28)	0.73 (1.31)	0.63 (1.27) ^b
T ₁₂	Flubendiamide (20 % WG) (2X)	100	0.47 (1.21)	0.33 (1.15)	0.47 (1.21)	0.53 (1.24)	0.60 (1.26)	0.60 (1.26)	0.51 (1.23) ^c
T ₁₃	Fenazaquin (10 % EC) (x)	94	0.33 (1.15)	0.29 (1.14)	0.27 (1.13)	0.40 (1.18)	0.53 (1.24)	0.60 (1.26)	0.42 (1.20) ^c
T ₁₄	Fenazaquin (10 % EC) (X)	125	0.60 (1.26)	0.37 (1.17)	0.37 (1.17)	0.20 (1.09)	0.47 (1.21)	0.53 (1.24)	0.39 (1.19) ^c
T ₁₅	Fenazaquin (10 % EC) (2X)	250	0.67 (1.29)	0.33 (1.15)	0.30 (1.14)	0.30 (1.14)	0.33 (1.15)	0.47 (1.21)	0.35 (1.16) ^d
	Mean		NS	0.48 (1.22)	0.43 (1.20)	0.44 (1.20)	0.49 (1.22)	0.59 (1.26)	

*Figure in parentheses is square root transformed values **Mean of 3 replications DAS- Days after spray
CD_{0.05} (Days): NS
(Treatments): 0.05
(Days × Treatments): 0.11
 NS- Non significant

Maximum number of population of coccinellids among all treatments were recorded from T₁₀ (flubendiamide @ 38 g a.i./ha) (0.65 beetles/5 plants) which was statistically equivalent to T₁₁ (flubendiamide @ 50 g a.i./ha) (0.63 beetles/5 plants) and T₁ (cyantraniliprole @ 45 g a.i./ha) (0.57 beetles/ 5 plants) followed by T₇ (spirotetramat @ 45 g a.i./ha) (0.57 beetles/5 plants) which was statistically at par with T₁₂ (flubendiamide @ 100 g a.i./ha), T₃ (cyantraniliprole @ 120 g a.i./ha), T₂ (cyantraniliprole @ 60 g a.i./ha), T₈ (spirotetramat @ 60 g a.i./ha), T₁₃ (fenazaquin @ 94 g a.i./ha), T₉ (spirotetramat @ 120 g a.i./ha) and T₁₄ (fenazaquin @125 g a.i./ha) and recorded a range of 0.39-0.51 beetles per five plants. Least number of population of beetles were recorded from treatments T₆ (imidacloprid @ 50 g a.i./ha), T₅ (imidacloprid @ 25 g a.i./ha), T₁₅ (fenazaquin @ 250 g a.i./ha) and T₄ (imidacloprid @ 19 g a.i./ha) recorded 0.29, 0.31, 0.35 and 0.42 beetles per five plants, respectively.

4.2.3.4 Effect of different pesticides on coccinellid population in chilli after second spray during 2022

After 10th day of second spray during 2022, maximum number of coccinellid beetles were recorded in T₁₀ (flubendiamide @ 38 g a.i./ha) (0.57 beetles/5 plants) and was statistically equivalent to T₁ (cyantraniliprole @ 45 g a.i./ha), T₇ (spirotetramat @ 45 g a.i./ha), T₁₁ (flubendiamide @ 50 g a.i./ha), T₂ (cyantraniliprole @ 60 g a.i./ha), T₈ (spirotetramat @ 60 g a.i./ha), T₁₂ (flubendiamide @ 100 g a.i./ha), T₃ (cyantraniliprole @ 120 g a.i./ha) and T₉ (spirotetramat @ 120 g a.i./ha) and recorded 0.55, 0.53, 0.50, 0.47, 0.44, 0.43, 0.41 and 0.41 beetles per five plants, respectively. Treatment T₁₃ (fenazaquin @ 94 g a.i./ha) (0.38 beetles/ 5 plants) was statistically at par with, T₁₄ (fenazaquin @125 g a.i./ha) (0.32 beetles/ 5 plants), T₄ (imidacloprid @ 19 g a.i./ha) (0.31 beetles/ 5 plants), T₅ (imidacloprid @ 25 g a.i./ha) (0.30 beetles/5 plants). Minimum number of coccinellids was found in the treatments T₆ (imidacloprid @ 50 g a.i./ha) and T₁₅ (fenazaquin @ 250 g a.i./ha) and with 0.22 and 0.25 beetles per five plants (Table 4.22).

Table 4.22 Effect of different pesticides on coccinellid population in chilli after second spray during 2022

Treatments	Pesticides	Dosage (g a.i./ha)	No. of coccinellids per five plants**					Mean
			1DAS	3DAS	5DAS	7DAS	10 DAS	
T ₀	Untreated control		0.87 (1.37)*	0.87 (1.37)	0.93 (1.39)	1.00 (1.41)	1.00 (1.41)	0.93 (1.39) ^a
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	0.60 (1.27)	0.53 (1.24)	0.47 (1.21)	0.53 (1.24)	0.60 (1.26)	0.55 (1.24) ^b
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	0.53 (1.24)	0.47 (1.21)	0.37 (1.17)	0.43 (1.19)	0.53 (1.24)	0.47 (1.21) ^b
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	0.33 (1.15)	0.40 (1.18)	0.40 (1.18)	0.47 (1.21)	0.47 (1.21)	0.41 (1.19) ^b
T ₄	Imidacloprid (17.8 % SL) (x)	19	0.27 (1.21)	0.23 (1.11)	0.30 (1.14)	0.33 (1.15)	0.40 (1.18)	0.31 (1.14) ^c
T ₅	Imidacloprid (17.8 % SL) (X)	25	0.23 (1.15)	0.27 (1.13)	0.23 (1.11)	0.30 (1.14)	0.47 (1.21)	0.30 (1.13) ^c
T ₆	Imidacloprid (17.8 % SL) (2X)	50	0.23 (1.15)	0.17 (1.08)	0.13 (1.06)	0.23 (1.11)	0.33 (1.15)	0.22 (1.11) ^d
T ₇	Spirotetramat (15.31 % OD) (x)	45	0.67 (1.29)	0.40 (1.18)	0.33 (1.15)	0.53 (1.24)	0.73 (1.32)	0.53 (1.24) ^b
T ₈	Spirotetramat (15.31 % OD) (X)	60	0.40 (1.18)	0.40 (1.18)	0.27 (1.13)	0.53 (1.24)	0.60 (1.26)	0.44 (1.20) ^b
T ₉	Spirotetramat (15.31 % OD) (2X)	120	0.33 (1.15)	0.27 (1.13)	0.40 (1.18)	0.47 (1.21)	0.60 (1.27)	0.41 (1.19) ^b
T ₁₀	Flubendiamide (20 % WG) (x)	38	0.53 (1.24)	0.47 (1.21)	0.53 (1.24)	0.67 (1.29)	0.67 (1.29)	0.57 (1.25) ^b
T ₁₁	Flubendiamide (20 % WG) (X)	50	0.47 (1.21)	0.43 (1.19)	0.47 (1.21)	0.53 (1.24)	0.60 (1.26)	0.50 (1.22) ^b
T ₁₂	Flubendiamide (20 % WG) (2X)	100	0.33 (1.15)	0.47 (1.21)	0.50 (1.22)	0.47 (1.21)	0.40 (1.18)	0.43 (1.20) ^b
T ₁₃	Fenazaquin (10 % EC) (x)	94	0.30 (1.14)	0.27 (1.13)	0.33 (1.15)	0.47 (1.21)	0.53 (1.24)	0.38 (1.17) ^c
T ₁₄	Fenazaquin (10 % EC) (X)	125	0.30 (1.14)	0.37 (1.16)	0.30 (1.14)	0.23 (1.11)	0.40 (1.18)	0.32 (1.14) ^c
T ₁₅	Fenazaquin (10 % EC) (2X)	250	0.23 (1.11)	0.20 (1.09)	0.23 (1.11)	0.27 (1.13)	0.33 (1.15)	0.25 (1.12) ^d
	Mean		0.41 (1.19)	0.39 (1.18)	0.39 (1.18)	0.47 (1.21)	0.54 (1.24)	

*Figure in parentheses is square root transformed values **Mean of 3 replications DAS- Days after spray
 CD_{0.05} (Days): NS NS- Non significant
 (Treatments): 0.06
 (Days × Treatments): 0.12

4.2.3.5 Mean number of coccinellid population following two applications of pesticides during 2021 and 2022 in chilli

In both years, the data showed that after control the highest number of coccinellid population was recorded in treatment T₁₀ (flubendiamide @ 38 g a.i./ha) in chilli and the least number of coccinellid was recorded in treatment T₆ (imidacloprid @ 50 g a.i./ha) (Fig. 4.11 and 4.12)

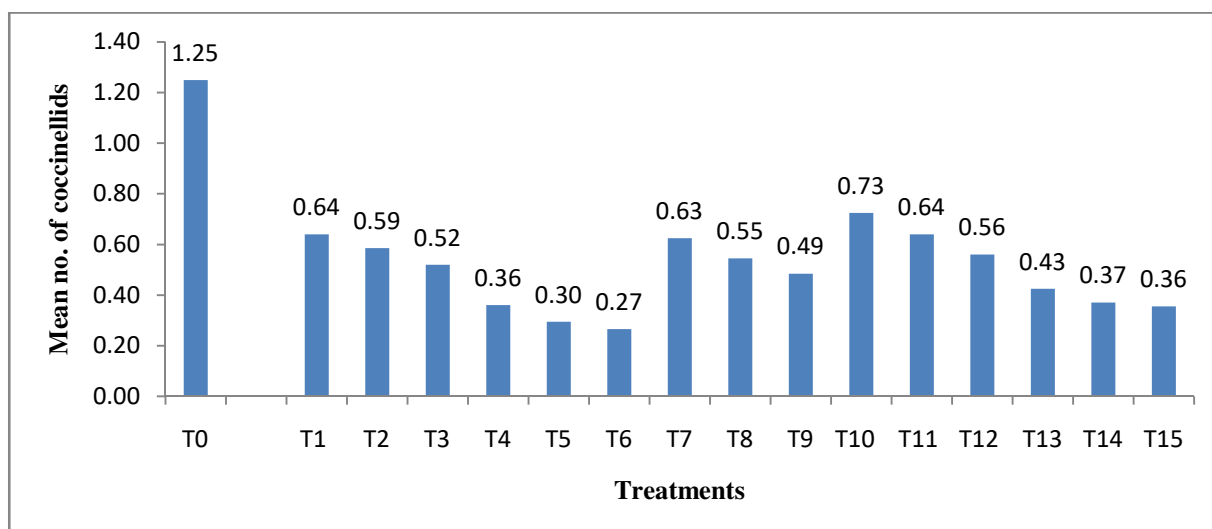


Fig. 4.11 Mean number of coccinellids in chilli after two sprays during 2021

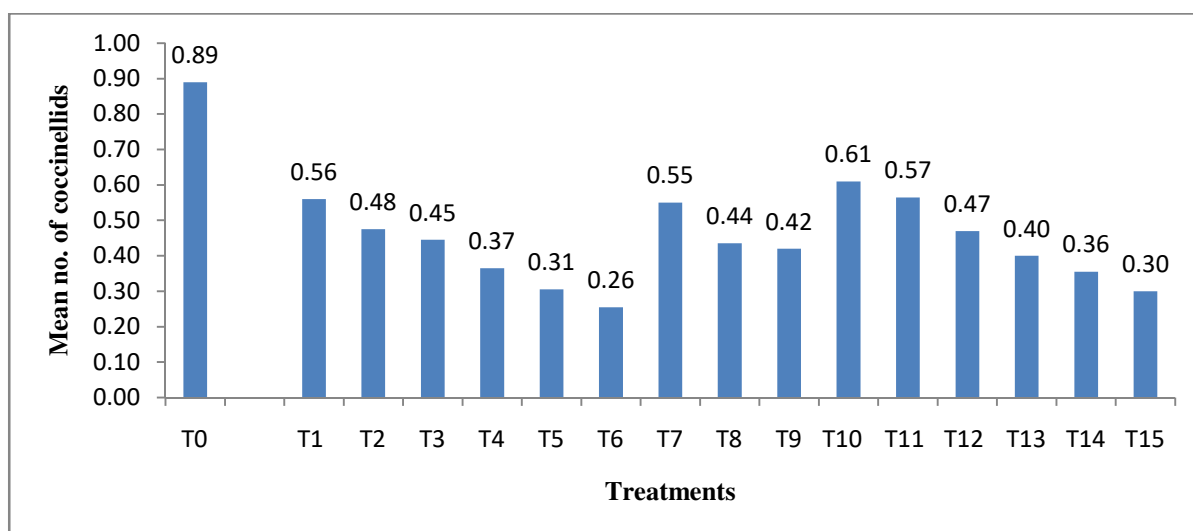


Fig. 4.12 Mean number of coccinellids in chilli after two sprays during 2022

From the present investigation it was found that the untreated control recorded the highest population of coccinellids in the field in both the seasons followed by flubendiamide @ 38 g a.i./ha where population of 0.73 and 0.61 coccinellids/5 plants was recorded during 2021 and 2022, respectively. Similar to our study Sudhanan et al. (2017) also reported that after the untreated control (5.7 beetles/ten plants), the highest population of coccinellids was found in lower dose of flubendiamide 20 WG (40 g a.i./ha) of 4.3 beetles/ten plants followed by flubendiamide 20 WG at 50 g a.i./ha (4.0 beetles/ ten plants) in sugarcane. Another study conducted by Narayan et al. (2019a) also revealed that control plot recorded higher population of ladybird beetles with 2.65 beetles per plant followed by cyantraniliprole 10 % OD (0.0143 %) (1.34 beetles/plant) and flubendiamide 39.36 % SC (0.0098 %) with 1.08 beetles per plant. Maximum reduction of coccinellid population was recorded when imidacloprid 17.8 % SL was

applied @ 175 ml/ha (0 and 0.33 beetles/plant) followed by 150 ml/ha (0.11 and 0.50 beetles/plant) at 3 and 7 days after spray, respectively in tomato field (Kar 2017).

4.2.4 Pesticide benefit cost ratio (BCR) in chilli

The benefit cost ratio of different treatments used against thrips in chilli is presented in Table 4.23 and Table 4.24, during 2021 and 2022. The summary of all cost and returns have been given in appendices along with the detailed description of the cost of cultivation of the test crops followed as per the package of practices given by the Dr. YSP University of Horticulture and Forestry.

4.2.4.1 Economics of different treatments used against chilli thrips during 2021

The benefit cost ratio was calculated for different treatments used against chilli thrips are presented in Table 4.23. The BCR was worked out on the basis of marketable yield of chilli fruits obtained from each treatment. In the experiment maximum net return of Rs. 439830.95/ha was obtained from T₃ (cyantraniliprole @ 120 g a.i./ha) followed by T₂ (cyantraniliprole @ 60 g a.i./ha), T₁₅ (fenazaquin @ 250 g a.i./ha), T₁₄ (fenazaquin @ 125 g a.i./ha), T₁₃ (fenazaquin @ 94 g a.i./ha), T₁ (cyantraniliprole @ 45 g a.i./ha), T₉ (spirotetramat @ 120 g a.i./ha), T₆ (imidacloprid @ 50 g a.i./ha), T₈ (spirotetramat @ 60 g a.i./ha), T₁₂ (flubendiamide @ 100 g a.i./ha), T₅ (imidacloprid @ 25 g a.i./ha), T₁₁ (flubendiamide @ 50 g a.i./ha), T₇ (spirotetramat @ 45 g a.i./ha), T₄ (imidacloprid @ 19 g a.i./ha), T₁₀ (flubendiamide @ 38 g a.i./ha) with net monetary returns of Rs.430942.95/ha, Rs. 408454.95/ha, Rs.389354.95/ha, Rs.364088.55/ha, Rs.363620.95/ha, Rs.361194.95/ha, Rs.355654.95/ha, Rs.347174.95/ha, Rs.344474.95/ha, Rs.341954.95/ha, Rs.338814.95/ha, Rs.309544.95/ha, Rs.303002.95 and Rs.301341.67/ha, respectively. Lowest net return of Rs. 273654.95/ha was observed in the untreated control. The highest benefit cost ratio of 2.98:1 was recorded from the T₂ (cyantraniliprole @ 60 g a.i./ha). The treatments with next best benefit cost ratio were T₁₄ (fenazaquin @ 125 g a.i./ha), T₃ (cyantraniliprole @ 120 g a.i./ha), T₁₅ (fenazaquin @ 250 g a.i./ha), T₆ imidacloprid (@ 50 g a.i./ha), T₁₃ (fenazaquin @ 94 g a.i./ha), T₉ (spirotetramat @ 120 g a.i./ha), T₅ (imidacloprid @ 25 g a.i./ha), T₈ (spirotetramat @ 60 g a.i./ha), T₁ (cyantraniliprole @ 45 g a.i./ha), T₁₁ (flubendiamide @ 50 g a.i./ha), T₁₂ (flubendiamide @ 100 g a.i./ha), T₇ (spirotetramat @ 45 g a.i./ha), T₄ (imidacloprid @ 19 g a.i./ha), T₁₀ (flubendiamide @ 38 g a.i./ha), showing the ratio of 2.80:1, 2.78:1, 2.77:1, 2.68:1, 2.66:1, 2.62:1, 2.59:1, 2.58:1, 2.58:1, 2.51:1, 2.47:1, 2.32:1, 2.30:1 and 2.25:1, respectively. The lowest benefit cost ratio of 2.09:1 was calculated in untreated control.

Table 4.23: Economics of different treatments used against chilli thrips during 2021

Treatments	Pesticide	Dosage (g a.i./ha)	Yield (q/ha)	Fixed Cost (Rs.)	Variable Cost (Rs.)	Total Cost (Rs.)	Gross Income (Rs.)	Net Income (Rs.)	B:C
T ₀	Control		115.60	65474.55	65470.50	130945.05	404600.00	273654.95	2.09:1
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	144.20	65474.55	75604.50	141079.05	504700.00	363620.95	2.58:1
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	164.40	65474.55	78982.50	144457.05	575400.00	430942.95	2.98:1
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	170.80	65474.55	92494.50	157969.05	597800.00	439830.95	2.78:1
T ₄	Imidacloprid (17.8 % SL) (x)	19	124.20	65474.55	66222.50	131697.05	434700.00	303002.95	2.30:1
T ₅	Imidacloprid (17.8 % SL) (X)	25	135.40	65474.55	66470.50	131945.05	473900.00	341954.95	2.59:1
T ₆	Imidacloprid (17.8 % SL) (2X)	50	139.60	65474.55	67470.50	132945.05	488600.00	355654.95	2.68:1
T ₇	Spirotetramat (15.31 % OD) (x)	45	126.60	65474.55	68080.50	133555.05	443100.00	309544.95	2.32:1
T ₈	Spirotetramat (15.31 % OD) (X)	60	137.60	65474.55	68950.50	134425.05	481600.00	347174.95	2.58:1
T ₉	Spirotetramat (15.31 % OD) (2X)	120	142.60	65474.55	72430.50	137905.05	499100.00	361194.95	2.62:1
T ₁₀	Flubendiamide (20 % WG) (x)	38	124.40	65474.55	68583.78	134058.33	435400.00	301341.67	2.25:1
T ₁₁	Flubendiamide (20 % WG) (X)	50	135.40	65474.55	69610.50	135085.05	473900.00	338814.95	2.51:1
T ₁₂	Flubendiamide (20 % WG) (2X)	100	138.20	65474.55	73750.50	139225.05	483700.00	344474.95	2.47:1
T ₁₃	Fenazaquin (10 % EC) (x)	94	143.20	65474.55	71636.90	137111.45	501200.00	364088.55	2.66:1
T ₁₄	Fenazaquin (10 % EC) (X)	125	151.00	65474.55	73670.50	139145.05	528500.00	389354.95	2.80:1
T ₁₅	Fenazaquin (10 % EC) (2X)	250	158.80	65474.55	81870.50	147345.05	555800.00	408454.95	2.77:1

4.3.2.2 Economics of different treatments used against chilli thrips during 2022

In 2022, it was concluded that the maximum net return of Rs.454530.95/ha was obtained from T₃ (cyantraniliprole @ 120 g a.i./ha) which was followed by T₂ (cyantraniliprole @ 60 g a.i./ha), T₁₂ (flubendiamide @ 100 g a.i./ha), T₁ (cyantraniliprole @ 45 g a.i./ha), T₉ (spirotetramat @ 120 g a.i./ha), T₁₅ (fenazaquin @ 250 g a.i./ha), T₆ (imidacloprid @ 50 g a.i./ha), T₁₄ (fenazaquin @ 125 g a.i./ha), T₈ (spirotetramat @ 60 g a.i./ha), T₅ (imidacloprid @ 25 g a.i./ha), T₁₁ (flubendiamide @ 50 g a.i./ha), T₁₃ (fenazaquin @ 94 g a.i./ha), T₄ (imidacloprid @ 19 g a.i./ha), T₇ (spirotetramat @ 45 g a.i./ha), T₁₀ (flubendiamide @ 38 g a.i./ha) with net monetary returns of Rs.449142.95/ha, Rs.392774.95/ha, Rs.387420.95/ha, Rs.376594.95/ha, Rs.372754.95/ha, Rs.371754.95/ha, Rs.365554.95/ha, Rs.363974.95/ha, Rs.357354.95/ha, Rs.348614.95/ha, Rs.336788.55/ha, Rs.327502.95/ha, Rs.326344.95/ha and Rs.318141.67/ha, respectively. Lowest net return of Rs. 298154.95/ha was observed in the untreated control. The highest cost benefit ratio of 3.11:1 was recorded from the treatment T₂ (cyantraniliprole @ 60 g a.i./ha).

Table 4.24: Economics of different treatments used against chilli thrips during 2022

Treatments	Pesticide	Dosage (g a.i./ha)	Yield (q/ha)	Fixed Cost (Rs.)	Variable Cost (Rs.)	Total Cost (Rs.)	Gross Income (Rs.)	Net Income (Rs.)	B:C
T ₀	Control	-	122.60	65474.55	65470.50	130945.10	429100.00	298154.95	2.28:1
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	151.00	65474.55	75604.50	141079.10	528500.00	387420.95	2.75:1
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	169.60	65474.55	78982.50	144457.10	593600.00	449142.95	3.11:1
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	175.00	65474.55	92494.50	157969.10	612500.00	454530.95	2.88:1
T ₄	Imidacloprid (17.8 % SL) (x)	19	131.20	65474.55	66222.50	131697.10	459200.00	327502.95	2.49:1
T ₅	Imidacloprid (17.8 % SL) (X)	25	139.80	65474.55	66470.50	131945.10	489300.00	357354.95	2.71:1
T ₆	Imidacloprid (17.8 % SL) (2X)	50	144.20	65474.55	67470.50	132945.10	504700.00	371754.95	2.80:1
T ₇	Spirotetramat (15.31 % OD) (x)	45	131.40	65474.55	68080.50	133555.10	459900.00	326344.95	2.44:1
T ₈	Spirotetramat (15.31 % OD) (X)	60	142.40	65474.55	68950.50	134425.10	498400.00	363974.95	2.71:1
T ₉	Spirotetramat (15.31 % OD) (2X)	120	147.00	65474.55	72430.50	137905.10	514500.00	376594.95	2.73:1
T ₁₀	Flubendiamide (20 % WG) (x)	38	129.20	65474.55	68583.78	134058.30	452200.00	318141.67	2.37:1
T ₁₁	Flubendiamide (20 % WG) (X)	50	138.20	65474.55	69610.50	135085.10	483700.00	348614.95	2.58:1
T ₁₂	Flubendiamide (20 % WG) (2X)	100	152.00	65474.55	73750.50	139225.10	532000.00	392774.95	2.82:1
T ₁₃	Fenazaquin (10 % EC) (x)	94	135.40	65474.55	71636.90	137111.50	473900.00	336788.55	2.46:1
T ₁₄	Fenazaquin (10 % EC) (X)	125	144.20	65474.55	73670.50	139145.10	504700.00	365554.95	2.63:1
T ₁₅	Fenazaquin (10 % EC) (2X)	250	148.60	65474.55	81870.50	147345.10	520100.00	372754.95	2.53:1

The treatments with next best benefit cost ratio were T₃ (cyantraniliprole @ 120 g a.i./ha), T₁₂ (flubendiamide @ 100 g a.i./ha), T₆ (imidacloprid (@ 50 g a.i./ha), T₁ (cyantraniliprole @ 45 g a.i./ha), T₉ (spirotetramat @ 120 g a.i./ha), T₈ (spirotetramat @ 60 g a.i./ha), T₅ (imidacloprid @ 25 g a.i./ha), T₁₄ (fenazaquin @ 125 g a.i./ha), T₁₁ (flubendiamide @ 50 g a.i./ha), T₁₅ (fenazaquin @ 250 g a.i./ha), T₄ (imidacloprid @ 19 g a.i./ha), T₁₃ (fenazaquin @ 94 g a.i./ha), T₇ (spirotetramat @ 45 g a.i./ha), T₁₀ (flubendiamide @ 38 g a.i./ha) and recorded as 2.88:1, 2.82:1, 2.80:1, 2.75:1, 2.73:1, 2.71:1, 2.71:1, 2.63:1, 2.58:1, 2.53:1, 2.49:1, 2.46:1, 2.44:1 and 2.37:1, respectively. The lowest benefit cost ratio of 2.28:1 was calculated with untreated control (Table 4.24).

4.3 Validation of the analytical method (QuEChERS) for determination of pesticides in brinjal and chilli

The process of proving that analytical techniques are appropriate for their intended purpose is known as method validation. In more detail, analytical method validation involves generating verified data that the recommended approach will reliably produce correct test

findings that assess a product against its set specifications and quality attributes. The approach should be suitable for routine tasks in the Quality Control environment and be validatable, transferrable, durable, reliable, accurate and exact (Chowdary et al. 2020). The steps that must be taken to validate the analytical techniques are described in the parameters listed below.

4.3.1 System precision

The primary step of method validation is system precision. One concentration (0.1 mg/kg) of each pesticide *viz.*, spiromesifen, fenazaquin, fenvalerate, chlorpyrifos, chlorantraniliprole, cyantraniliprole, spirotetramat, imidacloprid and flubendiamide was used in the study with five replications.

The data given in Table 4.25 shows the average retention time (RT) and peak areas for various pesticides tested in the experiment, namely chlorantraniliprole, spiromesifen, fenazaquin, fenvalerate I, fenvalerate II and chlorpyrifos in GC-MS/MS and cyantraniliprole, spirotetramat, imidacloprid and flubendiamide in LC-MS/MS. The calculated average retention times for chlorantraniliprole, spiromesifen, fenazaquin, fenvalerate I, fenvalerate II, chlorpyrifos, cyantraniliprole, spirotetramat, imidacloprid and flubendiamide were in range of 8.799-8.882 minutes, 28.579-28.588 minutes, 29.982-29.985 minutes, 36.762-36.772 minutes, 37.298-37.309 minutes, 19.537-19.540 minutes, 8.479-8.481 minutes, 9.120-9.130 minutes, 3.599-3.601 minutes, 9.720-9.730 minutes, respectively. The per cent relative standard deviation (RSD) of retention time ranged for different pesticides from 0.005-0.880 per cent. As per the SANTE guidelines (SANTE 2021) the acceptance criteria for retention time is ≤ 0.1 minute and for per cent relative standard deviation ≤ 20 per cent (Table 4.25). The chromatographic response of different pesticides at 0.1 mg/kg fortification level is given in Fig. 4.13 and 4.14.

According to Singh et al. (2012), the retention period for chlorantraniliprole in vegetables at 0.1 mg/kg was 9.82 minutes. According to Chowdhury et al. (2013), who validated 19 pesticides in various plants for GC-MS analysis, the retention periods of acephate and chlorpyrifos were 10.64 and 13.33 minutes, respectively. Using UHPLC analysis, Monica et al. (2021) determined the retention times of chlorantraniliprole and cyantraniliprole in potato to be 4.9 minutes and 6.9 minutes, respectively. Shrivastava et al. (2021) utilized the HPLC-UV to analyse nine pesticides in okra and found that imidacloprid had a retention

period of 12.30 minutes. The retention time for spirotetramat during HPTLC analysis was 8.51 minutes, according to the study conducted by Singh et al. (2013).

For chlorantraniliprole, spiromesifen, fenazaquin, fenvalerate I, fenvalerate II and chlorpyrifos, cyantraniliprole, spirotetramat, imidacloprid, flubendiamide the mean area of peaks estimated for pesticides dissolved in solvent was 6126.64, 17453.60, 160570.20, 6808.60, 2666.68, 29804.00, 9770.88, 114637.44, 12970.24 and 26343.00 with per cent relative standard deviation (RSD) in the range of 1.07-4.58 per cent. The variations in the retention times of pesticides are mainly due to employment of different methods standardised by various workers.

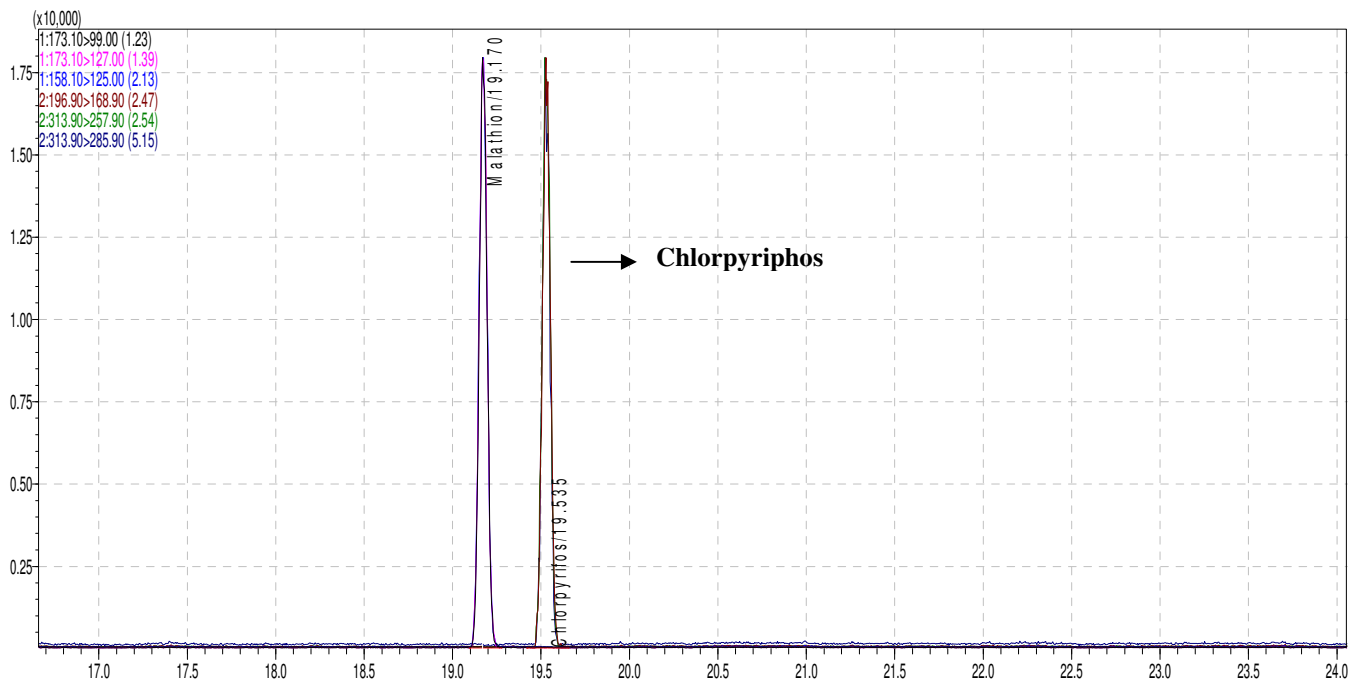
Table 4.25 Retention time and area of pesticides at 0.1 mg/kg concentration

Pesticides	Retention Time (minutes)		Area	
	RT Range	%RSD	Mean	%RSD
Spiromesifen	28.579-28.588	0.013	17453.60	2.16
Fenazaquin	29.982-29.985	0.005	160570.20	4.39
Chlorantraniliprole	8.799-8.882	0.411	6126.64	1.07
Chlorpyrifos	19.537-19.540	0.880	29804.00	1.32
Fenvalrate-I	36.762-36.772	0.012	6808.60	1.38
Fenvalrate-II	37.298-37.309	0.011	2666.68	2.68
Cyantraniliprole	8.479-8.481	0.008	9770.88	1.29
Flubendamide	9.720-9.730	0.046	26343.00	4.58
Spirotetramat	9.120-9.130	0.048	114637.44	3.76
Imidacloprid	3.599-3.601	0.025	12970.24	1.03
Acceptance Criteria for % RSD		<20 %		
Acceptance Criteria for RT		≤0.1 min.		

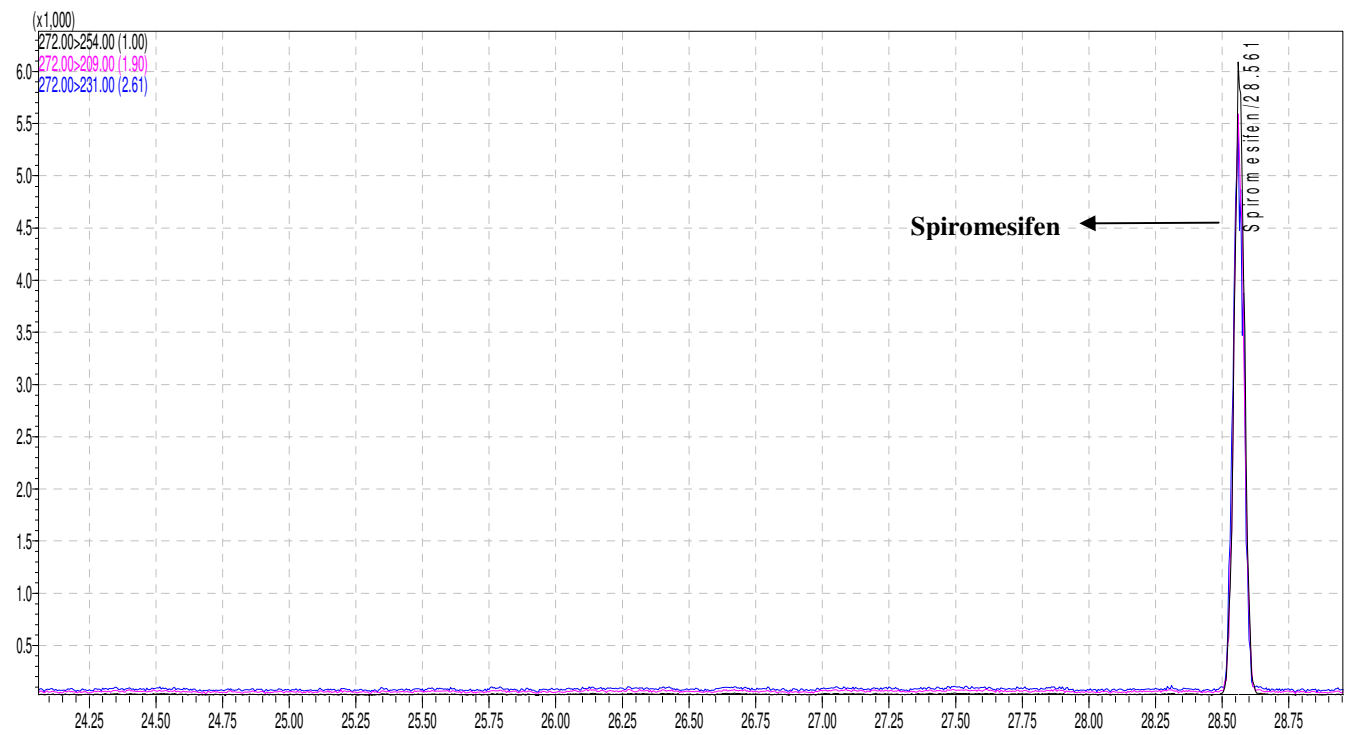
4.3.2 Matrix match effect

By injecting a standard of the pesticides, the impact of matrices for brinjal and chilli in LC-MS/MS and GC-MS/MS was examined. The information in Table 4.26 showed that there was no visible peak in the chromatograms of untreated brinjal and chilli samples injected at the particular retention period of the corresponding pesticides under examination. In order to monitor the matrix effect, the areas of the corresponding peaks of each pesticide were used to compare the effect of the matrix (brinjal and chilli) to that of the solvent and further statistically determined by student's t-test which further resulted in non-significant effect of each pesticide.

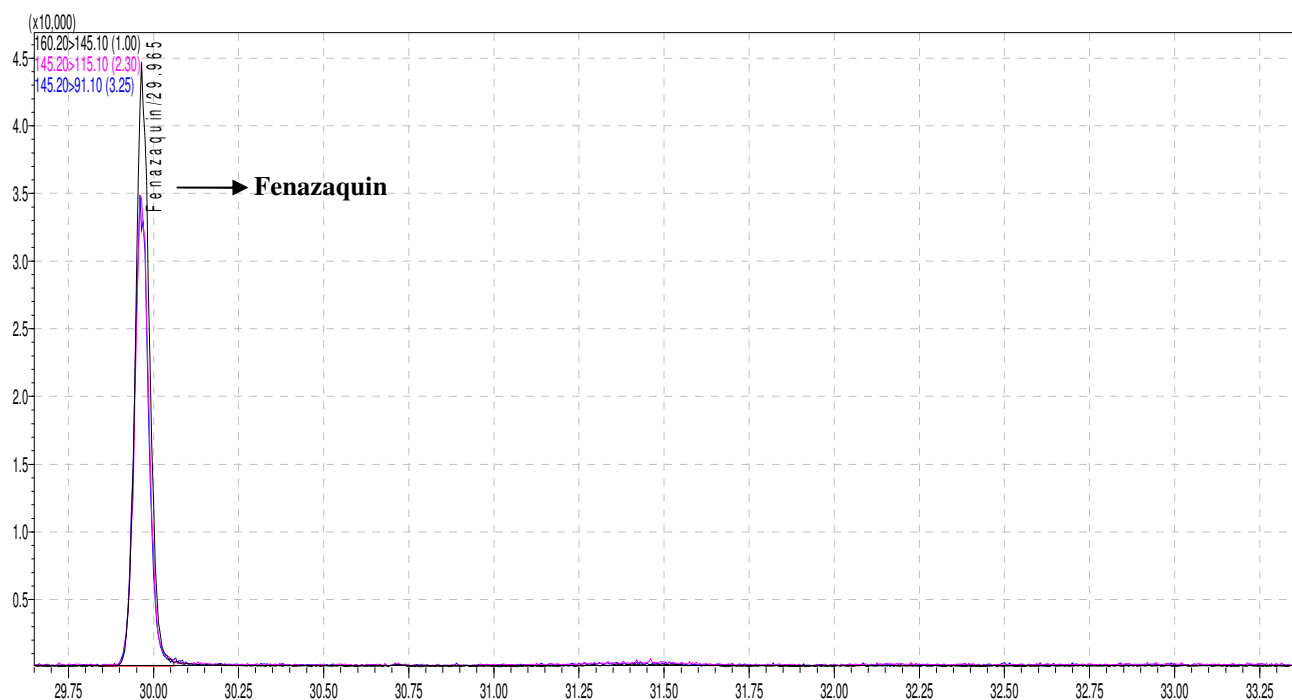
Our findings got similarity with the work conducted by Singh (2021) who reported that fenazaquin and imidacloprid had no matrix effects on tomato and capsicum. By comparing the effects of two sample matrices (Golden Delicious and Starking Delicious apples) on pesticides,



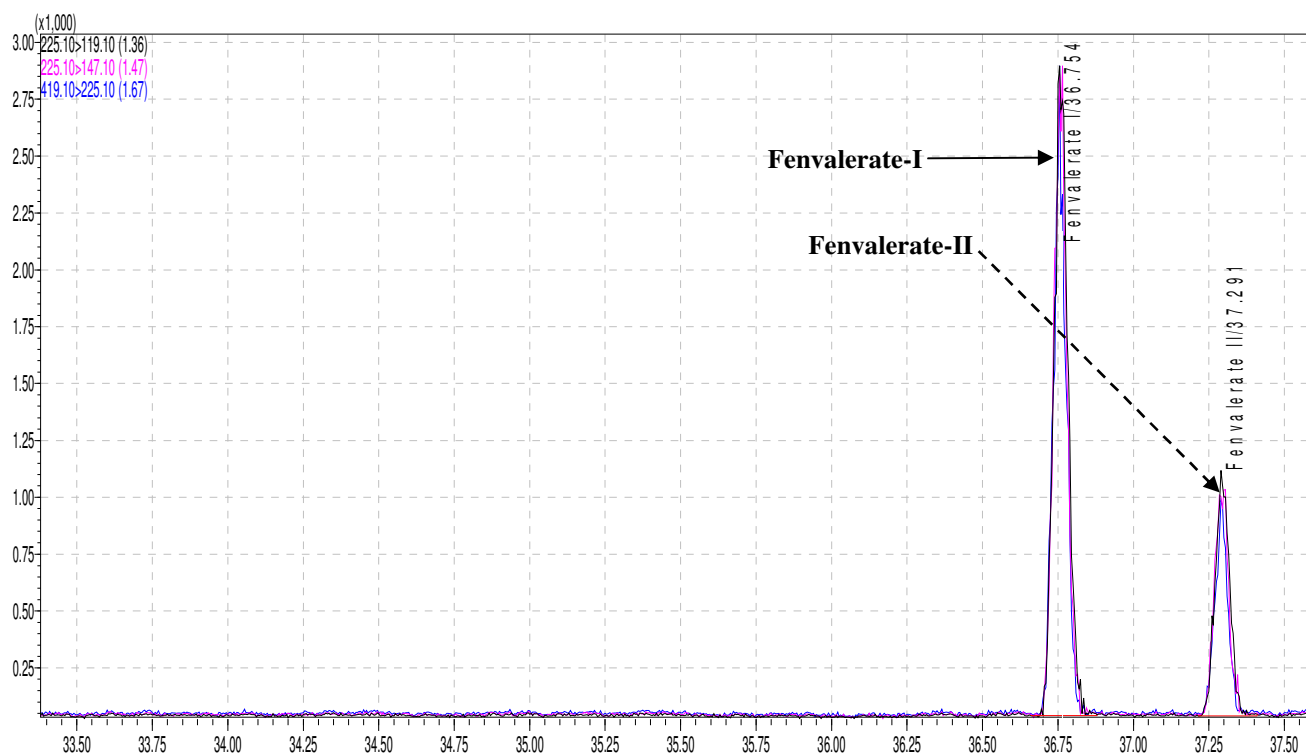
(a)



(b)

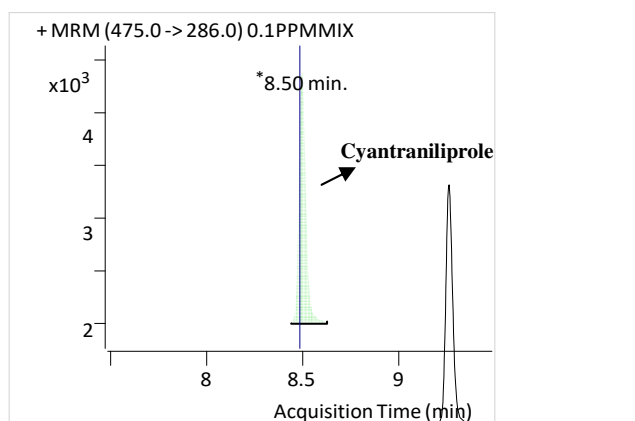


(c)

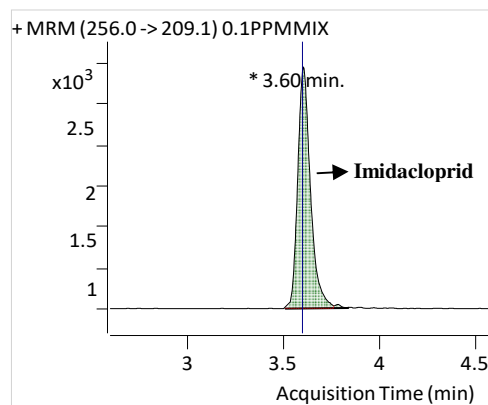


(d)

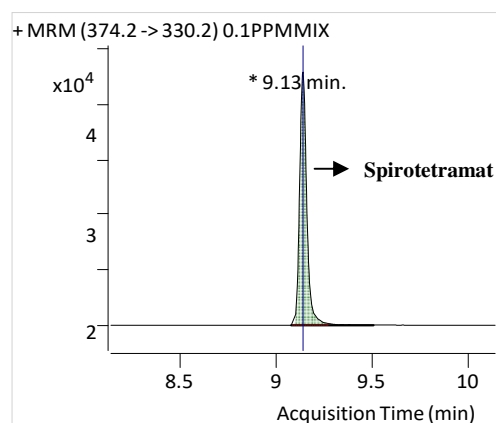
Fig. 4.13 Chromatograms of pesticides at 0.1 mg/kg fortification level: a) chlorpyrifos b) spiromesifen c) fenazaquin d) fenvalerate (GC-MS/MS)



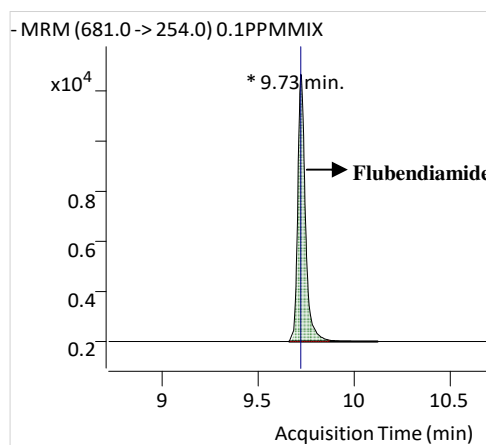
(a)



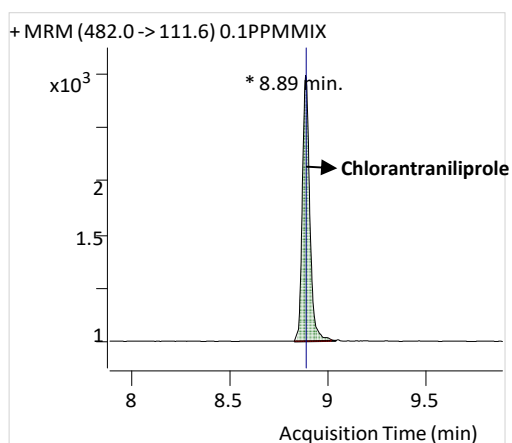
(b)



(c)



(d)



(e)

Fig. 4.14 Chromatograms of pesticides at 0.1 mg/kg fortification level: a) cyantraniliprole b) imidacloprid c) spirotetramat d) flubendiamide e) chlorantraniliprole (LC-MS/MS)

Tiryaki (2016) discovered that the effects of the matrices were significant for dimethoate, indoxacarb and imidacloprid but not for chlorpyrifos. For 19 pesticides, Dashtbozorgi et al. (2013) found no statistically significant differences between cucumber and tomato matrices. Non-significant impact of chlorpyrifos on brinjal was also noted by Brar (2018).

Table 4.26 Effect of brinjal and chilli matrix on the response of different pesticides

Crop	Pesticides	Matrix effect (ME %)	Student T _{cal.}	Significant/Non Significant
Brinjal	Spiromesifen	0.8	0.542	Non Significant
	Fenazaquin	1.0	0.276	Non Significant
	Chlorantranilprole	1.6	0.958	Non Significant
	Chlorpyrifos	1.0	0.831	Non Significant
	Fenvalrate-I Fenvalrate-II	1.0 0.4	0.537 0.306	Non Significant
Chilli	Fenazaquin	1.6	0.830	Non Significant
	Cyantranilprole	0.8	0.411	Non Significant
	Flubendamide	2.8	0.975	Non Significant
	Spirotetramat	1.0	0.547	Non Significant
	Imidacloprid	2.0	0.997	Non Significant
T _{tabulated, 4 at 0.05} =2.77				

4.3.3 Specificity and Precision

The ability to detect the analyte of interest precisely and particularly in the presence of other components, including as contaminants, degradation products and matrix components, which may be anticipated to be present in the sample matrix, is known as specificity. The absence of spiking materials (impurities and/or excipients) must be shown to have no impact on the analytical procedure. Specificity and precision of the procedure were tested by injecting five replications of each pesticide at a concentration of 0.005-0.500 mg/kg (spiromesifen, fenazaquin and chlorpyrifos) in brinjal matrix with a mean area in the range of 1132.10-86710.78, 9532.11-820248.58, 1620.38-150914.62 with the relative standard deviations (RSD) ranged from 1.19-6.47, 0.41-6.48 per cent and 1.03-8.01 per cent except chlorantranilprole and fenvalerate I and fenvalerate II which was carried out at a concentration ranged between 0.005- 0.200 mg/kg and 0.01- 0.500 mg/kg with a mean area of 401.28-12600.19 and 451.96-36878.37 and 298.32-13258.30 and relative standard deviations (RSD) ranged from 1.16-5.84 and 0.52-3.71 and 1.14-3.86 per cent, respectively (Table 4.27 and Table 4.28). Similarly in case of chilli, five replications of each pesticide at a concentration of 0.005-0.200 mg/kg (cyantranilprole, flubendiamide, spirotetramat and imidacloprid) with a mean area in the range of 547.66-20022.77, 1278.56-54133.92, 6074.53-235840.30, 574.19-27122.48 with the relative standard deviations (RSD) ranged from 1.46-6.38, 1.22-7.61, 0.75-8.98, 0.79-5.36 per

cent except fenazaquin which was carried out at a concentration of 0.005-0.500 mg/kg with a mean area of 9868.05-821687.50 and relative standard deviations (RSD) ranged from 1.07-5.04 per cent, respectively (Table 4.29 and Table 4.30) As per the SANTE guidelines (SANTE 2021) the acceptance criteria for per cent relative standard deviation is less than 20 per cent.

Table 4.27 Specificity and precision of analytical method in GC-MS/MS after spiking pesticides in brinjal matrix at different levels

Fortification level (mg/kg)	Spiromesifen		Fenazaquin		Chlorpyrifos		Fenvalrate-I		Fenvalrate-II	
	Mean Area*	% RSD	Mean Area*	% RSD	Mean Area*	% RSD	Mean Area*	% RSD	Mean Area*	% RSD
0.005	1132.10	5.05	9532.11	5.46	1620.38	5.42	-	-	-	-
0.010	2317.24	6.47	19030.10	6.48	3307.45	8.01	451.96	2.48	298.32	3.86
0.020	-	-	-	-	-	-	983.40	2.98	593.81	2.24
0.050	9292.42	3.83	85035.71	1.31	15637.66	4.27	3460.98	3.71	1400.86	2.03
0.100	17593.23	2.47	160570.20	2.07	30102.04	2.32	6849.45	2.06	2677.35	1.14
0.250	43734.08	1.19	411200.59	0.95	76201.67	1.03	18328.26	0.52	6520.67	1.14
0.500	86710.78	3.32	820248.58	0.41	150914.62	2.98	36878.37	2.43	13258.30	2.22

*Mean of 5 replications RSD- Relative Standard Deviation

Table 4.28 Specificity and precision of analytical method in LC-MS/MS after spiking chlorantraniliprole in brinjal matrix at different levels

Fortification level (mg/kg)	Chlorantraniliprole	
	Mean Area*	% RSD
0.005	401.28	4.52
0.01	743.17	5.84
0.025	1720.49	1.16
0.05	3209.29	1.77
0.1	6224.67	3.52
0.2	12600.19	1.95

*Mean of 5 replications RSD- Relative Standard Deviation

Table 4.29 Specificity and precision of analytical method in LC-MS/MS after spiking pesticides in chilli matrix at different levels

Fortification level (mg/kg)	Cyantraniliprole		Flubendamide		Spirotetramat		Imidacloprid	
	Mean Area*	% RSD	Mean Area*	% RSD	Mean Area*	% RSD	Mean Area*	% RSD
0.005	547.66	6.38	1278.56	5.50	6074.53	4.66	574.19	5.36
0.01	1020.67	4.45	2802.84	4.39	11428.86	8.98	1225.80	3.93
0.025	2389.92	1.46	6921.18	1.22	28408.98	0.75	3173.31	0.79
0.05	5187.57	3.18	14276.86	7.61	60682.55	8.38	6838.44	3.57
0.1	9849.05	4.11	27080.60	4.37	115783.82	1.57	13177.76	3.38
0.2	20022.77	2.28	54133.92	1.65	235840.30	2.56	27122.48	0.96

*Mean of 5 replications RSD- Relative Standard Deviation

Table 4.30 Specificity and precision of analytical method in GC-MS/MS after spiking fenazaquin in chilli matrix at different levels

Fortification level (mg/kg)	Fenazaquin	
	Mean Area*	%RSD
0.005	9868.05	2.79
0.01	19448.40	5.04
0.050	85361.73	1.07
0.100	183188.52	3.02
0.250	404199.42	2.93
0.500	821687.50	1.38

*Mean of 5 replications RSD- Relative Standard Deviation

4.3.4 Linearity

Linearity is the ability of the method to elicit test results that are directly or by a well-defined mathematical transformation, proportional to analyte concentration within a given range (Anonymous 2009). The linear response obtained when all the pesticides at five different concentrations were plotted. The linearity was calculated at five different concentrations *viz.*, 0.005, 0.01, 0.050, 0.100, 0.250, 0.500 ppm (spiromesifen, chlorpyrifos, fenazaquin, fenvalerate I and fenvalerate II) and 0.005, 0.01, 0.025, 0.05, 0.1 and 0.2 ppm (chlorantraniliprole, cyantraniliprole, flubendiamide, spirotetramat, imidacloprid) with deviation of back-calculated concentration from true concentration as criterion ≤ 20 per cent (SANTE 2021).

The deviation of back calculated concentration from true concentration for spiromesifen, fenvalerate-I, fenvalerate- II, chlorpyrifos and fenazaquin were in the range of -1.60 to 3.20 per cent, -3.64 to 3.00 per cent, 0.28 to 6.40 per cent, -2.40 to 5.40 per cent and -3.36 to 0.80 per cent, respectively (Table 4.31). On the other side, deviation of back calculated concentration from true concentration for cyantraniliprole, imidacloprid, spirotetramat flubendiamide and chlorantraniliprole were in the range of 0.20 to 4.00 per cent, -8.40 to 3.16 per cent, -1.60 to 4.80 per cent, 0.50 to 7.75 per cent and 0.76 to 5.60 per cent, respectively (Table 4.32) (Fig. 4.15 – 4.24).

Table 4.31 Linearity of different pesticides using back calculated concentration (GC-MS/MS)

Conc.	Spiromesifen		Fenvalerate-I		Fenvalerate-II		Chlorpyrifos		Fenazaquin	
	Observed value	Back calculated value	Observed value	Back calculated value	Observed value	Back calculated value	Observed value	Back calculated value	Observed value	Back calculated value
0.005	0.0052	3.20	0.0049	-2.80	0.0053	6.40	0.0050	0.40	0.0050	0.80
0.01	0.0099	-1.40	0.0103	3.00	0.0105	4.60	0.0105	5.40	0.0101	0.60
0.05	0.0492	-1.60	0.0482	-3.64	0.0514	2.88	0.0492	-1.60	0.0483	-3.36
0.10	0.1008	0.80	0.1006	0.60	0.1004	0.40	0.1010	1.00	0.1006	0.60
0.25	0.2548	1.92	0.2490	-0.40	0.2512	0.48	0.2508	0.32	0.2510	0.40
0.5	0.5040	0.80	0.5028	0.56	0.5014	0.28	0.4880	-2.40	0.5006	0.12

Table 4.32 Linearity of different pesticides using back calculated concentration (LC-MS/MS)

Conc.	Cyantraniliprole		Imidacloprid		Spirotetramat		Flubendiamide		Chlorantraniliprole	
	Observed value	Back calculated value	Observed value	Back calculated value	Observed value	Back calculated value	Observed value	Back calculated value	Observed value	Back calculated value
0.005	0.0052	4.00	0.0046	-8.40	0.0049	-1.60	0.0054	7.75	0.0053	5.60
0.01	0.0104	3.60	0.0099	-1.40	0.0103	2.60	0.01012	1.19	0.0104	3.80
0.025	0.0253	1.28	0.0252	0.80	0.0249	-0.40	0.02548	1.88	0.0255	1.92
0.05	0.0503	0.56	0.0516	3.16	0.0524	4.80	0.0514	2.72	0.0504	0.76
0.10	0.1008	0.80	0.1010	1.00	0.0990	-1.00	0.1028	2.72	0.1016	1.60
0.20	0.2004	0.20	0.2012	0.60	0.2004	0.20	0.201	0.50	0.202	1.00

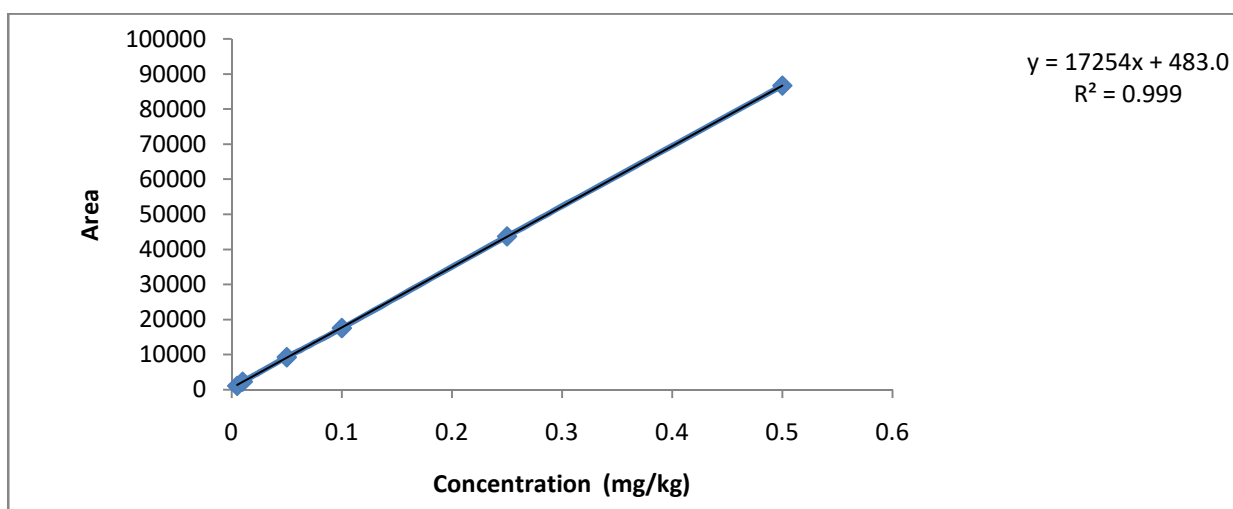


Fig. 4.15 Linearity of spiromesifen

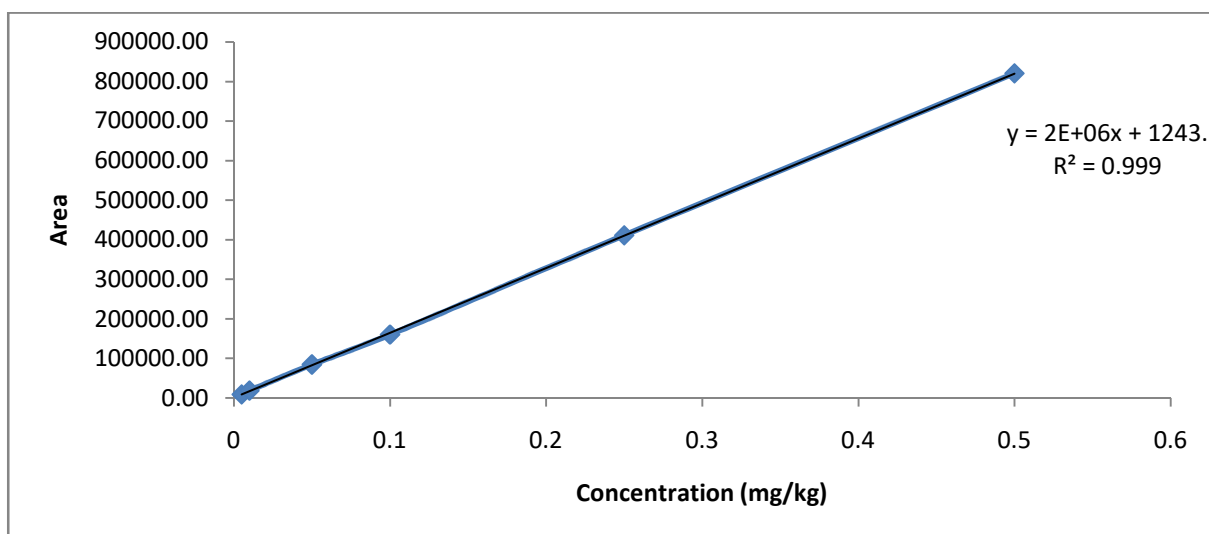


Fig. 4.16 Linearity of fenazaquin

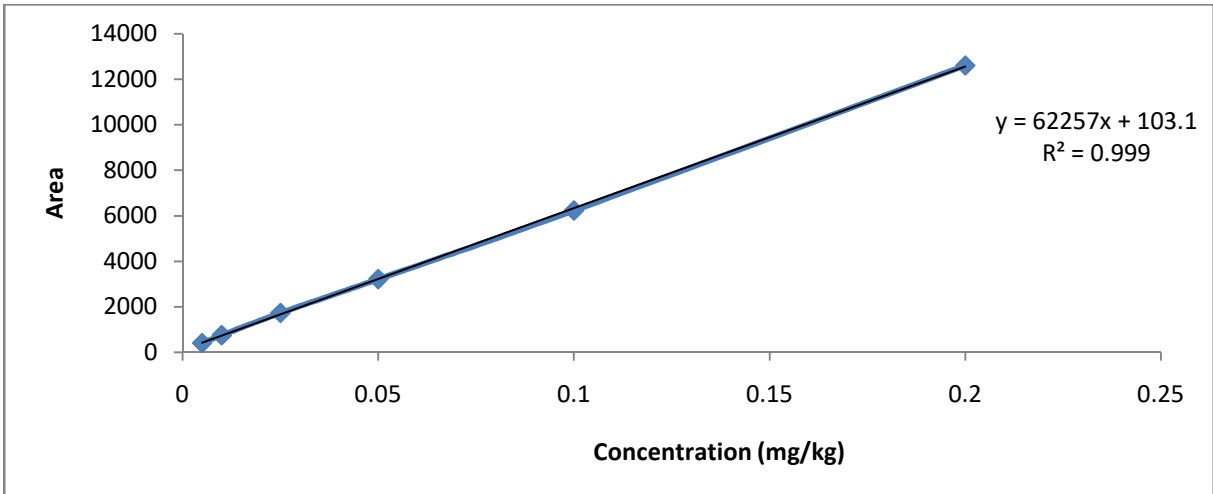


Fig. 4.17 Linearity chlorantraniliprole

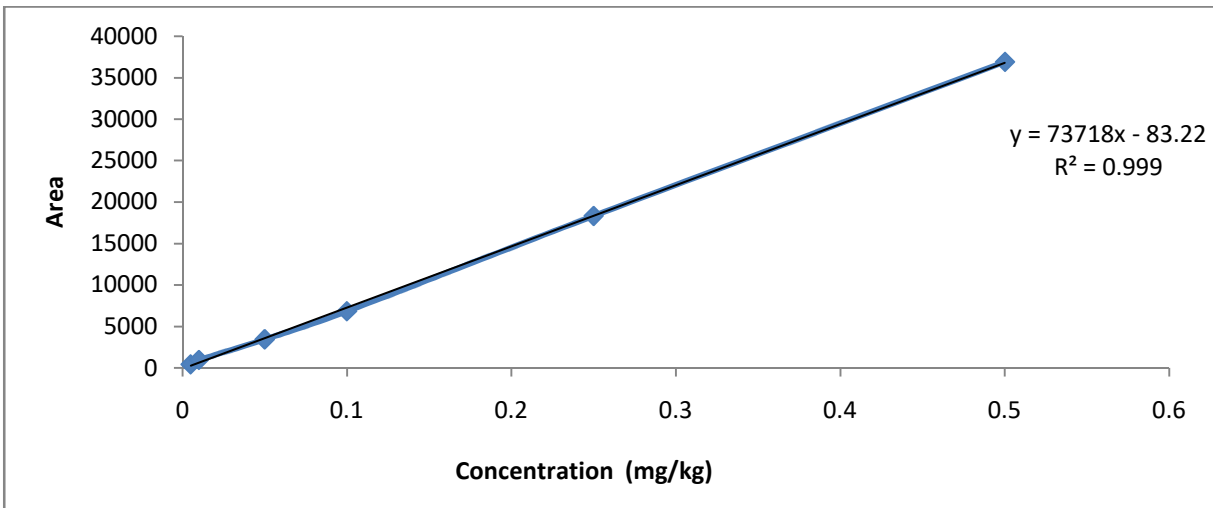


Fig. 4.18 Linearity of fenvalerate-I

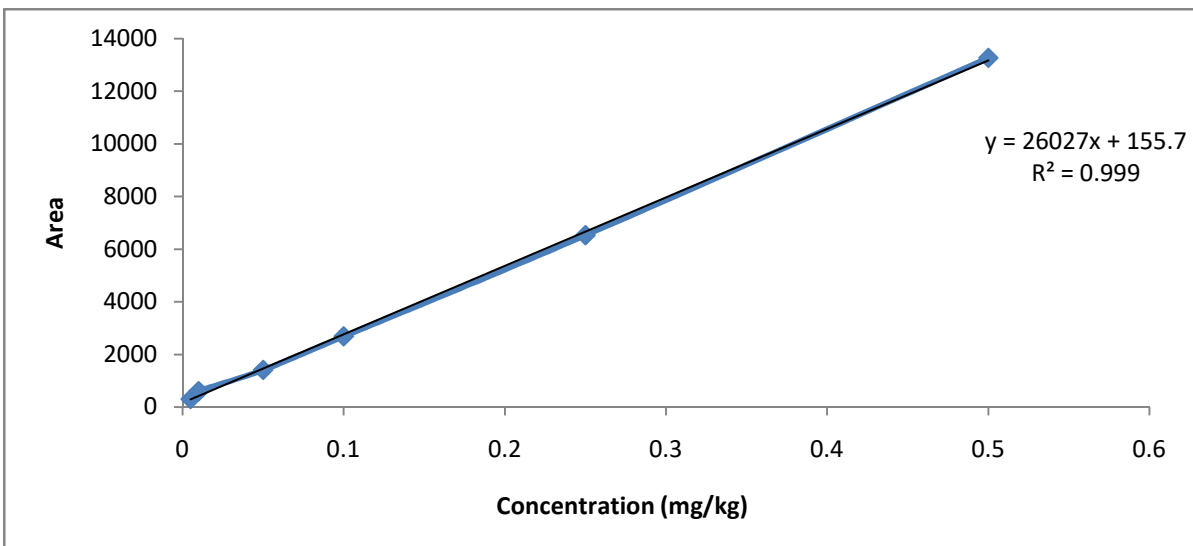


Fig. 4.19 Linearity of fenvalerate-II

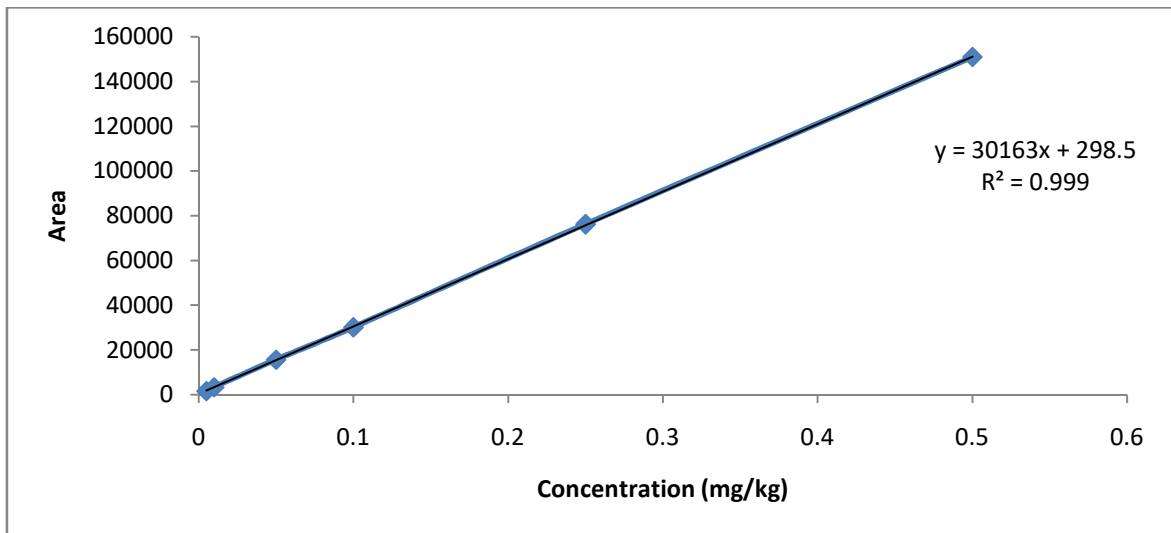


Fig. 4.20 Linearity of chlorpyrifos

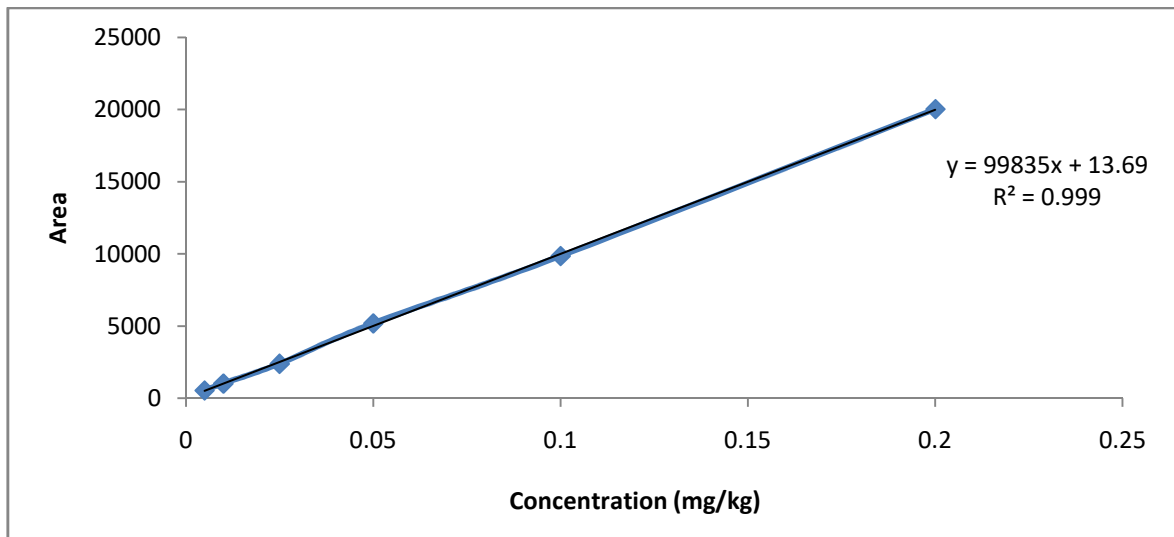


Fig. 4.21 Linearity of cyantraniliprole

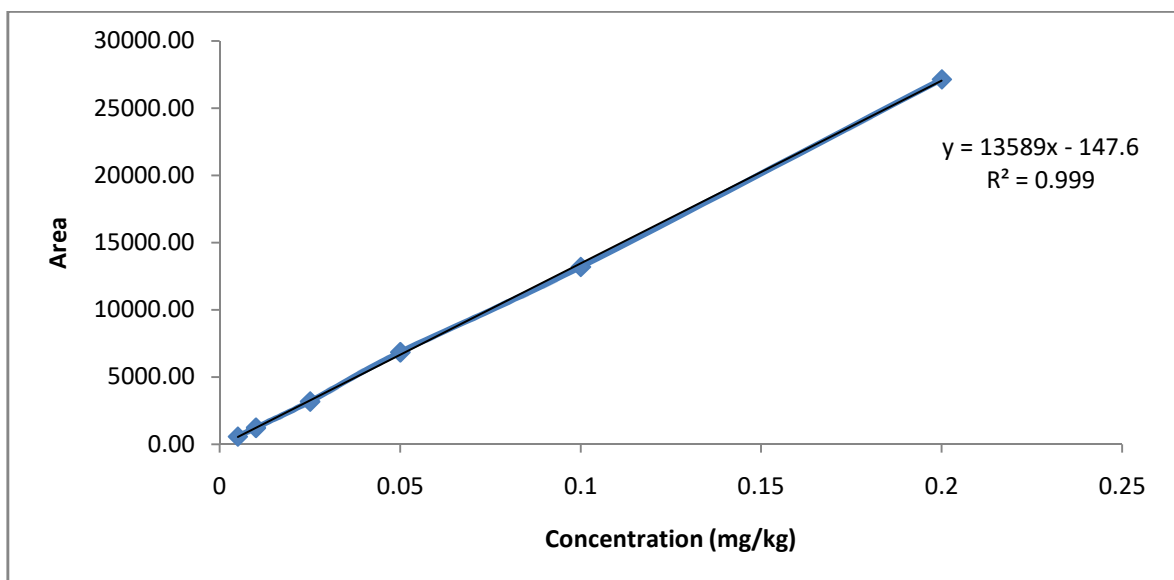


Fig. 4.22 Linearity of imidacloprid

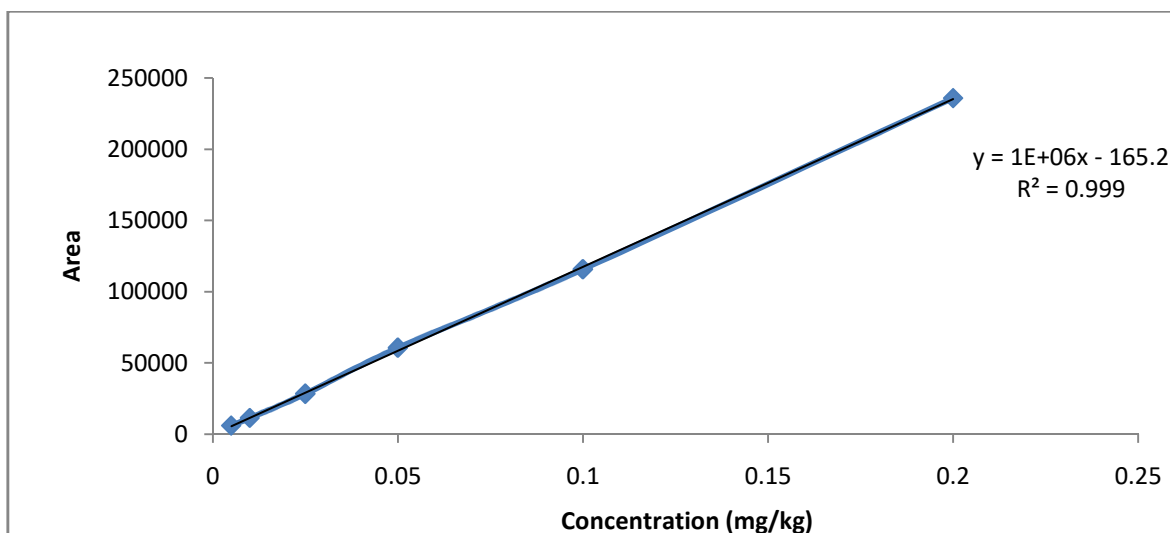


Fig. 4.23 Linearity of spirotetramat

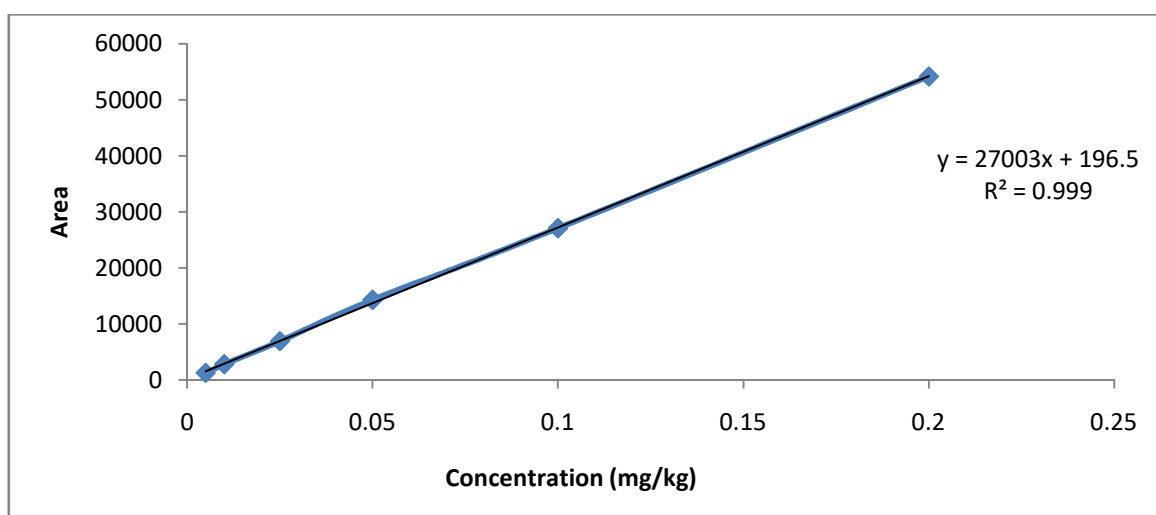


Fig. 4.24 Linearity of flubendiamide

In support of our findings, Tiryaki (2016) also discovered linearity for imidacloprid at fortification levels ranging from 5-200 ng/mL for Golden and Starking delicious with r values >0.99. However, Singh et al. (2012) carried out an experiment in which they found that the correlation coefficient for chlorantraniliprole at the concentrations of 0.10, 0.25, 0.50, 1.00, 1.50 and 2.00 g/mL on various vegetables was equivalent to 0.996 (R^2). The correlation coefficient (R^2) achieved was 0.992 and the linearity of the calibration curves for spiromesifen in brinjal was established in the range of 0.05 to 0.8 $\mu\text{g/g}$ (Vinothkumar et al. 2018). A good linearity of cyantraniliprole in packchoi was achieved from 0.005 to 1 mg/kg with a correlation coefficient 0.992 (R^2) (Sun et al. 2012).

4.3.5 Determination of limit of detection (LOD) and limit of quantification (LOQ)

The Limit of Detection is defined as the lowest concentration of an analyte in a sample that can be detected, not quantified. The Limit of Quantification is the lowest concentration of an analyte in a sample that can be determined with acceptable precision and accuracy under the stated operational conditions of the analytical procedures (Anonymous 2009).

The LOD and LOQ was found to be 0.005 mg/kg and 0.01 mg/kg, respectively for different pesticides (spiromesifen, chlorpyrifos, fenazaquin, chlorantraniliprole) in brinjal matrix and (cyantraniliprole, flubendiamide, spirotetramat, imidacloprid and fenazaquin) in chilli matrix except for fenvalerate in brinjal where LOD and LOQ was found to be 0.01 mg/kg and 0.02 mg/kg, respectively (Table 4.33).

Table 4.33 Limit of Detection (LOD), Limit of Quantification (LOQ) and Correlation coefficient (R²) of pesticides

Crop	Pesticides	LOD (mg/kg)	LOQ (mg/kg)	Correlation coefficient (R ²)	FSSAI MRL (mg/kg)
Brinjal	Spiromesifen	0.005	0.01	0.999	0.5
	Fenazaquin	0.005	0.01	0.999	0.01
	Chlorantraniliprole	0.005	0.01	0.999	0.6
	Chlorpyrifos	0.005	0.01	0.999	0.2
	Fenvalrate-I Fenvalrate-II	0.01 0.01	0.02 0.02	0.999 0.999	2 2
Chilli	Fenazaquin	0.005	0.01	0.999	0.5
	Cyantraniliprole	0.005	0.01	0.999	0.5
	Flubendiamide	0.005	0.01	0.999	0.02
	Spirotetramat	0.005	0.01	0.999	2
	Imidacloprid	0.005	0.01	0.999	0.3

The LOD and LOQ values for chlorantraniliprole for brinjal, cabbage, capsicum, cauliflower, okra and tomato were 0.03 mg/kg and 0.1 mg/kg, respectively, according to Singh et al. (2012) when compared to our values of 0.005 mg/kg (LOD) and 0.01 mg/kg (LOQ). The limit of quantification for spiromesifen in brinjal samples, according to Vinothkumar et al. (2018), was 0.05 µg/g, whereas the limit of detection was found to be 0.015 µg/g. Chlorpyrifos had a limit of detection of 0.01 mg/kg and a limit of quantification of 0.05 mg/kg, according to Brar (2018).

4.3.6 Accuracy

By spiking the pesticides at LOQ, 5X LOQ and 10X LOQ, the accuracy were determined. The percentages of spiromesifen, fenazaquin, chlorantraniliprole, chlorpyrifos

and fenvalerate recovered at LOQ were 96.20, 91.80, 102.60, 99.00 and 99.90 per cent, respectively, from the brinjal matrix (Table 4.34).

Table 4.34 Accuracy of analytical method after fortification of brinjal and chilli matrix at different levels of insecticides

Crop	Pesticide	Level	Fortification level (mg/kg)	Accuracy	
				% Recovery	% RSD
Brinjal	Spiromesifen	LOQ	0.01	96.20	7.51
		5XLOQ	0.05	98.68	4.28
		10XLOQ	0.1	93.60	9.39
	Fenazaquin	LOQ	0.01	91.80	9.29
		5XLOQ	0.05	96.44	3.14
		10XLOQ	0.1	95.20	6.70
	Chlorantraniliprole	LOQ	0.01	102.60	7.87
		5X LOQ	0.05	99.28	3.12
		10X LOQ	0.1	96.40	9.35
	Chlorpyrifos	LOQ	0.01	99.00	8.86
		5X LOQ	0.05	98.48	4.13
		10X LOQ	0.1	94.60	9.05
Fenvalerate	LOQ	0.02	99.90	3.31	
	5XLOQ	0.1	101.60	3.59	
	10X LOQ	0.2	100.10	2.48	
Chilli	Fenazaquin	LOQ	0.01	96.80	7.43
		5X LOQ	0.05	98.88	4.23
		10X LOQ	0.1	95.00	6.57
	Cyantraniliprole	LOQ	0.01	93.80	7.05
		5X LOQ	0.05	96.08	4.22
		10X LOQ	0.1	95.40	6.14
	Flubendamide	LOQ	0.01	104.80	7.50
		5X LOQ	0.05	100.44	5.43
		10X LOQ	0.1	97.40	7.84
	Spirotetramat	LOQ	0.01	89.40	6.05
		5X LOQ	0.05	100.60	4.10
		10X LOQ	0.1	94.40	9.61
Imidacloprid	LOQ	0.01	92.80	8.53	
	5X LOQ	0.05	99.44	3.67	
	10X LOQ	0.1	105.80	5.80	

At 5X LOQ, spiromesifen, fenazaquin, chlorantraniliprole, chlorpyrifos and fenvalerate, respectively, showed per cent recoveries of 98.68, 96.44, 99.28, 98.48 and 101.60 per cent. Similar recoveries were found for spiromesifen (93.60 %), fenazaquin (95.20 %), chlorantraniliprole (96.40 %), chlorpyrifos (94.60 %) and fenvalerate (100.10 %) at 10X LOQ. The average recovery of fenazaquin, cyantraniliprole, flubendiamide, spirotetramat and imidacloprid in chilli matrix were 96.80, 93.80, 104.80, 89.40 and 92.80 per cent at LOQ (limit of quantitation), respectively. At 5 times LOQ, the per cent recovery of fenazaquin, cyantraniliprole, flubendiamide, spirotetramat and imidacloprid were 98.88, 96.08, 100.44, 100.60 and 99.44 per cent, respectively. The recovery values were 95.00, 95.40, 97.40, 94.40

and 105.80 per cent at 10X LOQ for fenazaquin, cyantraniliprole, flubendiamide, spirotetramat and imidacloprid in chilli matrix, respectively (Table 4.34).

As per the guidelines of SANCO, the acceptance criteria of per cent recovery varies from 70 to 120 per cent with <20 % relative standard deviation (RSD) (SANTE 2021). Tiriyaki (2016) obtained 95.12 and 93.11 per cent recovery from matrix of golden and starking delicious variety of apple under accuracy for imidacloprid which are somewhat similar to present findings from which 97.53 per cent recovery was obtained from 5X LOQ. The average recoveries to check the accuracy of spiromesifen in cabbage, tomato at spiking level (0.01-0.5 mg/kg) were recorded in range 85.44-100.21 per cent and 72.56-92.78 per cent, respectively (Lekha et al. 2016). Average recoveries to check accuracy of spiromesifen in okra, chilli, capsicum and brinjal was conducted by Dubey et al. (2021) who revealed that at spiking level ranged from 0.025-1.00 mg/kg recoveries between 92.00–100.72, 87.20–100.28, 87.60–99.76 and 89.60–99.76 per cent were obtained, respectively.

4.3.7 Precision of the method

The precision of the analytical method was established through repeatability, reproducibility and ruggedness study. At LOQ, 5X LOQ and 10X LOQ fruits of brinjal and chilli were fortified for all test pesticides (Table 4.35).

The repeatability for spiromesifen, fenazaquin, chlorantraniliprole, chlorpyrifos and fenvalerate in the brinjal matrix at LOQ, 5X LOQ and 10X LOQ in the range of 93.80- 98.20, 91.80-96.44, 93.00-96.36, 91.60-102.80 and 93.20-96.00 per cent with a per cent RSD in a range of 4.20-8.27, 3.14-9.29, 4.21-7.01, 4.54-7.06 and 3.29-6.98 per cent, respectively. In a similar manner, the per cent recovery at LOQ, 5X LOQ and 10X LOQ for fenazaquin, cyantraniliprole, flubendiamide, spirotetramat and imidacloprid was in the range of 94.60-99.00, 88.80-98.16, 94.20-99.40, 98.00-105.00 and 89.60-98.96 per cent with the per cent RSD in range of 4.75-9.05, 3.16-7.41, 4.12-9.68, 3.36-6.81 and 4.29-6.64 per cent, respectively.

The recovery tests of spiromesifen, fenazaquin, chlorantraniliprole, chlorpyrifos and fenvalerate from brinjal sample were used to examine the reproducibility. These investigations produced results in the range of 94.60-100.32, 94.20-95.72, 98.80- 101.40, 89.00- 98.48 and 91.70- 102.60 per cent with per cent RSD in the range of 3.83-7.42, 6.79-8.88, 5.03-8.84, 2.71-9.52 and 3.19-4.39 per cent at LOQ, 5X LOQ and 10X LOQ, respectively. At LOQ, 5X LOQ

and 10X LOQ the per cent recovery of fenazaquin, cyantraniliprole, flubendiamide, spirotetramat and imidacloprid were in the range of 90.40-101.60, 89.20-100.00, 88.00-98.64, 99.60-102.16 and 86.40-97.84 per cent with the per cent RSD ranging from 3.89-7.63, 2.94-9.17, 4.97-8.69, 3.67-9.83 and 2.26-6.75 per cent, respectively in the chilli matrix (Table 4.35).

Table 4.35 Repeatability, reproducibility and ruggedness of analytical method

Pesticides	Level	Repeatability		Reproducibility		Ruggedness	
		% Recovery	% RSD	% Recovery	% RSD	% Recovery	% RSD
Brinjal							
Spiromesifen	LOQ	98.20	6.88	94.60	6.96	96.40	5.22
	5X LOQ	97.16	4.20	100.32	3.83	99.04	3.50
	10X LOQ	93.80	8.27	97.80	7.42	94.80	9.45
Fenazaquin	LOQ	91.80	9.29	94.20	8.86	97.40	8.10
	5X LOQ	96.44	3.14	95.72	6.79	100.80	4.11
	10X LOQ	95.20	6.70	94.40	8.88	99.20	9.17
Chlorantraniliprole	LOQ	93.00	7.01	98.80	8.84	101.80	5.69
	5X LOQ	96.36	4.21	99.52	5.03	97.32	4.73
	10X LOQ	93.60	5.73	101.40	6.99	89.80	8.99
Chlorpyrifos	LOQ	96.80	7.06	90.20	9.52	97.00	6.31
	5X LOQ	102.80	5.43	98.48	2.71	102.92	4.52
	10X LOQ	91.60	4.54	89.00	7.62	98.60	7.33
Fenvalrate	LOQ	93.20	4.25	95.60	3.23	91.30	7.15
	5X LOQ	96.00	6.98	102.60	4.39	93.40	7.92
	10X LOQ	95.30	3.29	91.70	3.19	94.70	5.39
Chilli							
Fenazaquin	LOQ	99.00	8.86	101.60	7.63	87.20	9.20
	5X LOQ	97.56	4.75	96.88	3.89	105.20	5.80
	10X LOQ	94.60	9.05	90.40	7.36	98.00	6.65
Cyantraniliprole	LOQ	88.80	5.93	100.00	9.17	91.20	7.77
	5X LOQ	98.16	3.16	99.60	2.94	99.80	5.25
	10X LOQ	97.60	7.41	89.20	7.90	97.20	8.02
Flubendamide	LOQ	96.60	8.04	88.00	8.69	93.60	6.07
	5X LOQ	99.40	4.12	98.64	4.97	101.12	3.37
	10X LOQ	94.20	9.68	89.40	7.73	91.00	7.37
Spirotetramat	LOQ	98.00	6.81	99.60	9.83	92.40	5.33
	5X LOQ	98.76	3.36	102.16	3.67	101.04	4.38
	10X LOQ	105.00	5.99	100.20	6.05	94.60	7.15
Imidacloprid	LOQ	97.00	6.64	86.40	2.26	99.40	6.91
	5X LOQ	98.96	4.51	97.84	4.14	99.64	2.92
	10X LOQ	89.60	4.29	92.80	6.75	92.20	4.16

For spiromesifen, fenazaquin, chlorantraniliprole, chlorpyrifos and fenvalerate in the brinjal matrix, the per cent recovery for ruggedness was in the range of 94.80-99.04, 97.40-100.80, 89.80-101.80, 97.00-102.92 and 91.30-94.70 per cent with the per cent RSD in the range of 3.50-9.45, 4.11-9.17, 4.73-8.99, 4.52-7.33 and 5.39-7.92 per cent at LOQ, 5X LOQ and 10X LOQ, respectively (Table 4.35). In chilli matrix, per cent recoveries of fenazaquin, cyantraniliprole, flubendiamide, spirotetramat and imidacloprid were in the range of 87.20-105.20, 91.20-99.80, 91.00-101.12, 92.40-101.04 and 92.20-99.64 per cent with per cent RSD in the range of 5.80-9.20, 5.25-8.02, 3.37-7.37, 4.38-7.15 and 2.92-6.91 per cent, respectively. According to SANTE recommendations, the per cent recovery for the objectives of

repeatability, reproducibility and ruggedness should be within the acceptable range (70.00-120.00 %) (Table 4.35) with a per cent RSD of less than 20 % (SANTE 2021).

4.3.8 Measurement uncertainty

The identification of uncertainty allows laboratories to carry out or evaluate the precision of results. The determination of measurement uncertainty was calculated by using the EURACHEM guide criteria (EURACHEM 2012). Based on the precision, the standard used at the fortification level, the peak area of the samples, the preparation of the standard using the purity of the standard, the make-up of the volume, pipetting, etc. and the solvent used during the entire extraction and cleanup procedure in the technique, including the weight of the sample and final volume, the estimation of uncertainty is calculated.

Table 4.36 Pesticides measurement uncertainty with the adopted analytical procedure

Crop	Pesticides	Uncertainty (mg/kg)
Brinjal	Spiromesifen	± 0.00164
	Fenazaquin	± 0.00161
	Chlorantraniliprole	± 0.00165
	Chlorpyrifos	± 0.00175
	Fenvalerate-I	± 0.00319
	Fenvalerate-II	± 0.00331
Chilli	Fenazaquin	± 0.00158
	Cyantraniliprole	± 0.00161
	Flubendiamide	± 0.00157
	Spirotetramat	± 0.00174
	Imidacloprid	± 0.00157

The estimation of uncertainty is worked out based on the precision, standard used at fortification level, peak area of samples, including preparation of standard using purity of standard, make-up of volume, pipetting etc. and the solvent used during complete extraction and cleanup procedure in the technique including weight of sample and final volume. In the matrix of brinjal, the uncertainty was ±0.00164, ±0.00161, ±0.00165, ±0.00175, ±0.00319 and ±0.00331 mg/kg for spiromesifen, fenazaquin, chlorantraniliprole, chlorpyrifos, fenvalerate-I and fenvalerate-II, respectively. The measurement uncertainty was ±0.00158, ±0.00161, ±0.00157, ±0.00174, ±0.00157 mg/kg for fenazaquin, cyantraniliprole, flubendamide, spirotetramat, imidacloprid in the matrix of chilli, respectively (Table 4.36).

4.4 Persistence study of pesticides in/on brinjal

4.4.1 Recovery studies in/on brinjal fruits and soil

The recovery studies of chlorantraniliprole, spiromesifen, fenazaquin, fenvalerate and chlorpyrifos were estimated by spiking the brinjal fruit and soil at five different fortification levels *viz.* 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg for spiromesifen, fenazaquin, chlorpyrifos and

fenvalerate in GC-MS/MS and 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg for chlorantraniliprole in LC-MS/MS.

4.4.1.1 Recovery of spiromesifen from fortified brinjal fruits and field soil

The desired recoveries for the pesticide persistence and dissipation experiments should be between 70.00 and 120.00 per cent and the relative standard deviation should be equal to or less than 20 % (SANTE 2021). The average spiromesifen recovery from brinjal fruits fortified at different levels was 102.00, 100.36, 92.86, 98.94 and 98.63 per cent, respectively with a relative standard deviation ranged from 1.28-5.45 per cent, but its average recovery from fortified soil ranged from 96.72 to 99.42 per cent with a relative deviation from 0.90-6.63 per cent, as indicated in Table 4.37 and 4.38. Our results were in proximity to Singh et al. (2021) who concluded that at fortification levels of 0.01, 0.025 and 0.050 mg/kg respectively, the recovery of spiromesifen was between 92.35 and 103.95 per cent in brinjal fruit and 75.86 and 97.15 per cent in soil, while the RSD were between 9.42 and 18.44 per cent in brinjal fruit and soil, respectively. Average recoveries to check accuracy of spiromesifen in okra, chilli, capsicum and brinjal was conducted by Dubey et al. (2021) who revealed that at spiking level ranged from 0.025-1.00 mg/kg recoveries between 92.00–100.72, 87.20–100.28, 87.60–99.76 and 89.60–99.76 per cent were obtained, respectively. At different levels of fortification, i.e., 0.01, 0.1 and 0.5 ppm, Varghese et al. (2011) reported 85.00, 94.00 and 87.00 per cent recovery for spiromesifen from chilli fruits, respectively. When spiked at different fortification levels, i.e., 0.01, 0.05, 0.10 and 0.50 mg/kg, the recovery per cent of spiromesifen was extended between 85.44 and 100.21 per cent and 72.56 to 92.78 per cent and 88.04 to 103.37 per cent, respectively, in cabbage and tomato fruits and field soil (Lekha et al. 2016).

Table 4.37 Recovery of spiromesifen from fortified brinjal fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0104	0.0102	0.0108	0.0097	0.0099	0.0102	102.00	4.22
0.05	0.0498	0.0492	0.0516	0.05	0.0503	0.0502	100.36	1.77
0.1	0.0986	0.0882	0.0869	0.0949	0.0957	0.0929	92.86	5.45
0.25	0.2516	0.2349	0.2511	0.2475	0.2517	0.2474	98.94	2.90
0.5	0.4992	0.4877	0.4959	0.4852	0.4978	0.4932	98.63	1.28

Table 4.38 Recovery of spiromesifen from fortified brinjal field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0098	0.0094	0.0102	0.0097	0.0104	0.0099	99.00	4.04
0.05	0.0496	0.0513	0.0499	0.0508	0.0433	0.0490	97.96	6.63
0.1	0.0999	0.0892	0.0999	0.0989	0.0957	0.0967	96.72	4.70
0.25	0.2498	0.2483	0.2508	0.2489	0.2449	0.2485	99.42	0.90
0.5	0.5088	0.4997	0.4979	0.4799	0.4689	0.4910	98.21	3.30

4.4.1.2 Recovery of fenazaquin from fortified brinjal fruits and field soil

The data in Table 4.39 depicts that the average recovery of fenazaquin from brinjal fruits ranged from 94.61 to 102.16 per cent at various levels of fortification, such as 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg, with per cent recovery values of 99.00, 98.32, 100.28, 102.16 and 94.61 per cent with a relative standard deviation ranged between 1.20 and 6.47 per cent, respectively. The recovery of fenazaquin from brinjal field soil was reported to be 92.20, 98.64, 97.38, 99.14 and 97.23 per cent, respectively, at five different fortification levels, namely 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg (Table 4.40). The average soil recovery was between 92.20 and 99.14 per cent with a relative standard deviation ranged between 0.70 and 4.45 per cent, respectively.

Singh (2021) also conducted a study on fenazaquin in capsicum fruits and soil and recorded average recoveries in a range of 96.80-101.60 and 90.40-97.20 per cent at various fortification levels *viz.*, 0.05, 0.10, 0.25, 0.50 and 1.00 ppm, respectively which were in similarity with our results. At five levels of fortification, Kaur et al. (2022a) observed 85.00-95.33 and 88.33-96.33 per cent recovery of fenazaquin from fortified okra fruits and soil at fortification levels ranging from 0.01-0.50 mg/kg. Duhan et al. (2010) measured 94.80 and 100.70 per cent of fenazaquin recovery from fortified okra fruit samples at concentration level of 0.1 and 0.2 mg/kg, respectively. Average recoveries of fenazaquin from apple fruit samples at fortification levels of 0.01, 0.1 and 0.2 µg/g varied from 80.00 to 94.50 per cent with a per cent RSD in the range of 0.98 to 1.90 per cent (Yaqoob et al. 2021).

Table 4.39 Recovery of fenazaquin from fortified brinjal fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0104	0.0092	0.0104	0.0092	0.0103	0.0099	99.00	6.47
0.05	0.0474	0.0487	0.0511	0.0507	0.0479	0.0492	98.32	3.38
0.1	0.0957	0.1002	0.0983	0.0973	0.1099	0.1003	100.28	5.60
0.25	0.2513	0.2542	0.2555	0.2563	0.2597	0.2554	102.16	1.20
0.5	0.4818	0.4599	0.4654	0.5015	0.4567	0.4731	94.61	3.93

Table 4.40 Recovery of fenazaquin from fortified brinjal field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0094	0.0092	0.0088	0.0092	0.0095	0.0092	92.20	2.91
0.05	0.0508	0.0493	0.0501	0.0476	0.0488	0.0493	98.64	2.49
0.1	0.1008	0.0988	0.0899	0.0997	0.0977	0.0974	97.38	4.45
0.25	0.2465	0.2478	0.2508	0.2467	0.2475	0.2479	99.14	0.70
0.5	0.4988	0.5001	0.4787	0.4998	0.4533	0.4861	97.23	4.21

4.4.1.3 Recovery of chlorantraniliprole from fortified brinjal fruits and field soil

The average recovery of chlorantraniliprole from brinjal fruits ranged from 94.40 to 103.70 per cent at various levels of fortification, such as 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg, with per cent recovery values of 94.40, 97.68, 100.96, 103.70 and 98.88 per cent with a relative standard deviation ranged between 1.95 and 3.31 per cent, respectively (Table 4.41). The recovery of chlorantraniliprole from brinjal field soil was reported to be 99.20, 100.40, 100.36, 98.40 and 97.61 per cent, respectively, at five different fortification levels, namely 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg with a relative standard deviation ranged between 2.10 and 6.15 per cent, respectively (Table 4.42).

Average recoveries of chlorantraniliprole in brinjal and okra were in range of 84.20–91.60 per cent and 81.80–94.90 per cent at fortification level of 0.01, 0.05, 0.10 and 0.50 mg/kg, respectively (Vijayasree et al. 2015) which was in close proximity with our results. Untreated okra fruits and soil were spiked at concentrations of 0.03, 0.25 and 0.50 mg/kg and the average recoveries for okra fruits were in range of 92.40-110.00 per cent and soil in range of 86.7-97.2 per cent with per cent relative standard deviations (RSD) which varied from 1.04 to 3.67 per cent for soil samples and 2.51 to 3.44 per cent for okra, respectively (Singla et al. 2020). Kansara et al. (2021) observed 87.58 to 100.35 per cent and 83.81 to 88.10 per cent recovery with per cent RSD ranged from 4.14 to 8.93 per cent and 3.48 to 11.58 per cent from fortified chlorantraniliprole in pigeonpea and soil, respectively, at fortification levels between 0.005 and 0.05 mg/kg.

Table 4.41 Recovery of chlorantraniliprole from fortified brinjal fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0096	0.0094	0.0092	0.0092	0.0098	0.0094	94.40	2.76
0.025	0.0249	0.0243	0.0249	0.0238	0.0242	0.0244	97.68	1.95
0.05	0.0492	0.0524	0.0511	0.0496	0.0501	0.0505	100.96	2.55
0.1	0.1002	0.1059	0.1085	0.1013	0.1026	0.1037	103.70	3.31
0.2	0.2007	0.2012	0.1988	0.1992	0.1889	0.1978	98.88	2.56

Table 4.42 Recovery of chlorantraniliprole from fortified brinjal field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0098	0.0096	0.0092	0.0102	0.0108	0.0099	99.20	6.15
0.025	0.0259	0.0251	0.0235	0.0258	0.0252	0.0251	100.40	3.83
0.05	0.0499	0.0513	0.0487	0.0499	0.0511	0.0502	100.36	2.10
0.1	0.0922	0.1009	0.1005	0.0987	0.0997	0.0984	98.40	3.62
0.2	0.1998	0.1885	0.1998	0.1994	0.1886	0.1952	97.61	3.12

4.4.1.4 Recovery of fenvalerate from fortified brinjal fruits and field soil

At different levels of fortification *viz.*, 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg, the recovery of fenvalerate ranged between 94.40 and 101.64 per cent, with per cent recovery values of 94.40, 96.20, 101.64, 100.58 and 100.48 per cent, respectively, as shown in Table 4.43. At five different fortification levels, namely 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg, the recovery of fenvalerate from brinjal field soil was found to be 100.60, 100.68, 94.90, 99.35 and 97.82 per cent, respectively. The range of the average recovery from soil was discovered to be between 94.90 and 100.68 per cent. Recovery relative standard deviation ranged from 1.90 to 5.28 per cent, whereas in case of field soil it ranged from 1.15 to 6.73 per cent (Table 4.44). In similarity to our results, Mukherjee and Gopal (1992) recovered 83.00 per cent of fenvalerate from fortified brinjal samples at concentration levels of 0.5 and 1 µg/g. Lozowieka et al. (2012) conducted an experiment on broccoli and revealed that the average recoveries of fenvalerate at different fortification levels of 0.02, 0.20 and 1.00 mg/kg were 107.87, 92.95 and 92.47 per cent with relative standard deviations of 0.72, 2.04 and 2.65 per cent. According to Bansal (2022), fenvalerate was recovered from broccoli matrix and soil at fortification levels ranging from 0.01 to 1.0 mg/kg was 96.00 to 103.00 and 98.00 to 100.30 per cent, respectively.

Table 4.43 Recovery of fenvalerate from fortified brinjal fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0094	0.0088	0.0098	0.0098	0.0094	0.0094	94.40	4.34
0.05	0.0476	0.0469	0.0499	0.0482	0.0479	0.0481	96.20	2.32
0.1	0.0986	0.1112	0.0989	0.0996	0.0999	0.1016	101.64	5.28
0.25	0.2412	0.2519	0.2511	0.2614	0.2517	0.2515	100.58	2.84
0.5	0.4985	0.4899	0.4995	0.5122	0.5119	0.5024	100.48	1.90

Table 4.44 Recovery of fenvalerate from fortified brinjal field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0104	0.0092	0.0108	0.0095	0.0104	0.0101	100.60	6.73
0.05	0.0507	0.0499	0.0511	0.0492	0.0508	0.0503	100.68	1.54
0.1	0.0996	0.0897	0.0886	0.0987	0.0979	0.0949	94.90	5.58
0.25	0.2492	0.2499	0.2501	0.2494	0.2433	0.2484	99.35	1.15
0.5	0.5011	0.4987	0.4877	0.5002	0.4577	0.4891	97.82	3.75

4.4.1.5 Recovery of chlorpyrifos from fortified brinjal fruits and field soil

At different levels of fortification, such as 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg, the data on the average recovery of chlorpyrifos from brinjal fruits ranged from 95.04 to 100.33 per cent, with per cent recovery values of 96.00, 96.64, 95.04, 100.33 and 97.94, respectively (Table 4.45). At five different fortification levels, namely 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg, the recovery of chlorpyrifos from brinjal field soil was reported to be 106.00, 100.96, 101.00, 99.38 and 98.00 per cent, respectively (Table 4.46). The average range of soil recovery was 98.00–106.00 per cent. Brinjal fruit relative standard deviation values ranged from 0.65 to 6.34 per cent and soil relative standard deviation values ranged from 1.00 to 4.47 per cent. The outcomes are comparable with Brar (2018) who obtained per cent recoveries for samples of brinjal at different concentrations (0.05, 0.10, 0.25, 0.5 and 1.00 mg/kg) as 96.00, 101.00, 104.80, 101.00 and 105.30 per cent, respectively. Average recoveries from fortified green beans ranged between 95.20-97.00 per cent at spiking levels ranged between 0.05 to 0.5 mg/kg (Katna et al. 2018). At two fortification levels (0.010 and 0.025 mg/kg), the per cent recoveries in the chilli were 90.50 and 92.10 per cent, while in the soil, they were 92.70 and 93.95 per cent, respectively (Kumari and Chauhan 2015).

Table 4.45 Recovery of chlorpyrifos from fortified brinjal fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0097	0.0092	0.0105	0.0097	0.0089	0.0096	96.00	6.34
0.05	0.0492	0.0479	0.0488	0.0475	0.0482	0.0483	96.64	1.41
0.1	0.0886	0.0982	0.0899	0.1006	0.0979	0.0950	95.04	5.69
0.25	0.2508	0.2499	0.2515	0.2488	0.2531	0.2508	100.33	0.65
0.5	0.4898	0.4763	0.5137	0.4899	0.4787	0.4897	97.94	3.02

Table 4.46 Recovery of chlorpyrifos from fortified brinjal field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0112	0.0108	0.0105	0.0099	0.0106	0.0106	106.00	4.47
0.05	0.0508	0.0511	0.0498	0.0496	0.0511	0.0505	100.96	1.44
0.1	0.1088	0.1003	0.0989	0.0993	0.0977	0.1010	101.00	4.41
0.25	0.2456	0.2469	0.2507	0.2514	0.2477	0.2485	99.38	1.00
0.5	0.5004	0.4899	0.4698	0.5021	0.4877	0.4900	98.00	2.64

4.4.2 Initial deposits and persistence of test pesticides in/on brinjal fruits

4.4.2.1 Initial deposits and persistence of spiromesifen in/on brinjal fruits

Application of the spiromesifen on brinjal at single dose (96 g a.i./ha) and at twice the single dose (192 g a.i./ha) resulted in average initial deposits of spiromesifen in brinjal fruits of 0.672 mg/kg and 1.133 mg/kg respectively. The initial spiromesifen deposits at standard dose (96 g a.i./ha) were 1.68 times lower than those produced from double dose (192 g a.i./ha). At single dose the initial residues dissipated from 45.49 to 93.30 per cent in 1 to 7 days whereas, in double dose initial residues dissipated from 36.53 to 97.68 per cent in 1 to 10 days (Tables 4.47 and 4.48, Fig 4.25).

Our findings were quite similar to those of Vinothkumar et al. (2018), who showed that spiromesifen mean initial deposits on brinjal fruits were 0.715 and 1.123 $\mu\text{g/g}$ at application rates of 96 g a.i./ha and 192 g a.i./ha, respectively. At the X (96 g a.i./ha) dose, the spiromesifen residue dissipated from 48.15 to 92.69 per cent and at 2X (192 g a.i./ha) residues dissipated from 51.16 to 92.02 per cent in 5 days after spray. Both the doses were below the detectable limit (LOQ) on 7th day of spray. The spiromesifen residues in the brinjal at treatment rates of 96 and 192 g a.i./ha were 0.091 and 0.192 mg/kg, respectively (Singh et al. 2021). Similar study of spiromesifen on brinjal was also conducted by Dubey et al. (2021) who revealed that at application rate of 144 g a.i./ha, average residues of spiromesifen in brinjal fruits were 0.738 mg/kg which reduced to 0.041 mg/kg with a per cent dissipation of 94.44 per cent in 7 days. At application rates of 150 and 300 g a.i./ha, respectively, Sharma et al. (2014b) noted that the initial spiromesifen deposits on tomato crops ranged from 0.17 to 0.50 mg/kg which reached LOQ of 0.05 mg/kg in 10 days.

Table 4.47 Persistence of spiromesifen (@ 96 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean \pm SD	
0	0.641	0.664	0.711	0.672 \pm 0.036	-
1	0.357	0.374	0.368	0.366 \pm 0.009	45.49
3	0.171	0.159	0.155	0.162 \pm 0.008	75.94
5	0.072	0.074	0.086	0.077 \pm 0.008	88.49
7	0.054	0.032	0.049	0.045 \pm 0.012	93.30
10	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

Table 4.48 Persistence of spiromesifen (@ 192 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	1.123	1.143	1.134	1.133±0.010	-
1	0.716	0.724	0.718	0.719±0.004	36.53
3	0.387	0.392	0.388	0.389±0.003	65.68
5	0.162	0.151	0.156	0.156±0.006	86.21
7	0.065	0.052	0.069	0.062±0.009	94.53
10	0.033	0.021	0.025	0.026±0.006	97.68
15	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

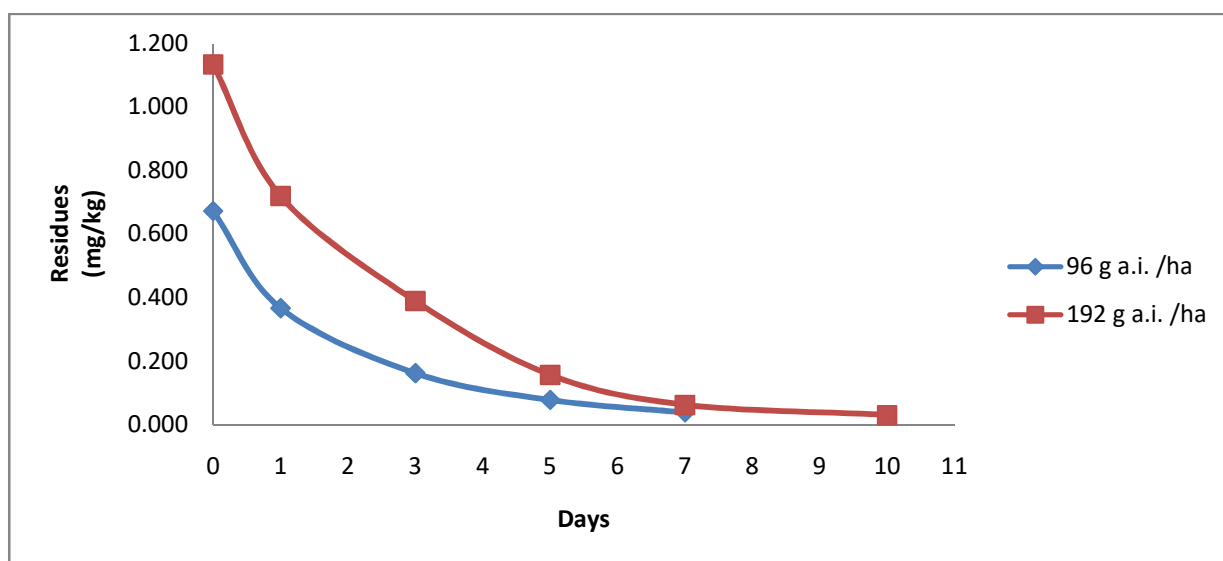


Fig 4.25 Dissipation pattern of spiromesifen (@ 96 g a.i./ha and 192 g a.i./ha) in/on brinjal fruits

4.4.2.2 Initial deposits and persistence of fenazaquin in/on brinjal fruits

At single dose (125 g a.i./ha) and double dose (250 g a.i./ha) the initial deposits of fenazaquin on brinjal fruits were found to be 0.457 mg/kg and 0.761 mg/kg, respectively (Table 4.49 and 4.50). In brinjal fruits the initial deposits of fenazaquin at single dose were 1.66 times lower than that of twice the single dose. The initial deposits of fenazaquin at X dose (125 g a.i./ha) dissipated to 0.332, 0.279, 0.133, 0.069 and 0.024 mg/kg at 1, 3, 5, 7 and 10 days interval with a per cent dissipation of 27.37, 38.91, 70.88, 84.96 and 94.82 per cent, respectively and at 2X dose (250 g a.i./ha) residues dissipated to 0.588, 0.487, 0.276, 0.177, 0.079 and 0.020 mg/kg with per cent dissipation of 22.69, 36.01, 63.78, 76.78, 89.66 and 97.33 per cent at 1, 3, 5, 7, 10 and 15 days intervals, respectively (Fig.4.26).

At application rate of 25, 50 and 125 g a.i./ha during 1st and 2nd year, initial residues of fenazaquin on brinjal fruits were recorded as 0.046, 0.098, 0.174 and 0.048, 0.102, 0.170

mg kg, respectively. After three, five and seven days at each of the three treatment rates, residues on brinjal were below the LOQ (<0.01 mg/kg) (Kaur et al. 2022b). The results of Singh (2021) were similar to our results who also reported that average initial deposits of fenazaquin on tomato fruits when sprayed at the application rate of 125 g a.i./ha and 250 g a.i./ha were 0.431 mg/kg and 0.721 mg/kg which dissipated to 85.92 and 92.69 per cent after 5 and 7 days, respectively. Duhan et al. (2010) recorded the average initial deposits of fenazaquin on okra to be 0.770 and 1.070 mg/kg at single (125 g a.i./ha) and double dose (250 g a.i./ha), respectively.

Table 4.49 Persistence of fenazaquin (@ 125 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.467	0.447	0.456	0.457±0.010	-
1	0.321	0.342	0.332	0.332±0.011	27.37
3	0.285	0.278	0.274	0.279±0.006	38.91
5	0.132	0.145	0.122	0.133±0.012	70.88
7	0.061	0.076	0.069	0.069±0.008	84.96
10	0.031	0.022	0.018	0.024±0.007	94.82
15	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Table 4.50 Persistence of fenazaquin (@ 250 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.743	0.768	0.772	0.761±0.016	-
1	0.587	0.601	0.577	0.588±0.012	22.69
3	0.487	0.476	0.498	0.487±0.011	36.01
5	0.267	0.279	0.281	0.276±0.008	63.78
7	0.172	0.203	0.155	0.177±0.024	76.78
10	0.087	0.066	0.083	0.079±0.011	89.66
15	0.011	0.021	0.029	0.020±0.009	97.33
20	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

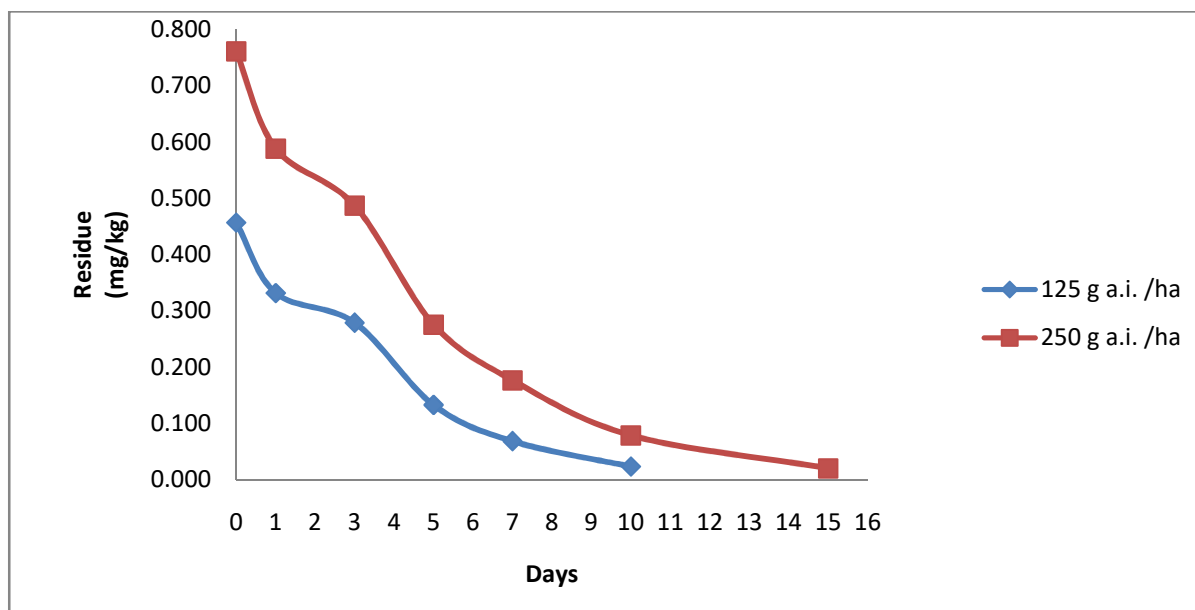


Fig 4.26 Dissipation pattern of fenazaquin (@ 125 g a.i./ha and 250 g a.i./ha) in/on brinjal fruits

4.4.2.3 Initial deposits and persistence of chlorantraniliprole in/on brinjal fruits

The data in Table 4.51 and Table 4.52 depicts that at single dose (40 g a.i./ha) and double dose (80 g a.i./ha) the initial deposits of chlorantraniliprole on brinjal fruits were found to be 0.867 mg/ kg and 1.433 mg/ kg, respectively. Initial chlorantraniliprole deposits in brinjal fruits were 1.65 times lower when a single dosage compared to a double dose. Initial residues of chlorantraniliprole on brinjal fruits dropped from 0.579 to 0.033 mg/kg in 1 to 10 days, resulting in a dissipation of 33.28 to 96.16 per cent at X dose. Chlorantraniliprole residues at 2X dose in brinjal fruits dissipated from 0.891 to 0.022 mg/kg in 1 to 15 days with per cent dissipation from 37.79 to 98.46 per cent (Fig. 4.27). After 10 and 15 days, the residues of chlorantraniliprole at 40 g a.i./ha and 80 g a.i./ha on brinjal fruits reduced below LOQ (<0.01 mg/kg), respectively.

Similarity to our results, Vijayasree et al. (2015) also reported that the initial residues of chlorantraniliprole were 0.72 mg/kg and 1.48 mg/kg at single (30 g a.i./ha) and double (60 g a.i./ha) doses which decreased by 95.37 and 93.92 per cent, respectively on brinjal fruits. Initial deposits of chlorantraniliprole were 0.21 mg/kg in okra fruits at the recommended dosage (25 g a.i./ha) and 0.46 mg/kg at twice the recommended dosage (50 g a.i./ha). The initial residues of chlorantraniliprole in okra fruits at X and 2X dose declined by 28.57 and 41.30 per cent within 24 h, respectively following reduction on 7th day which ranged from 85.71 and 89.13 per cent and reached below detection level at 10th and 15th day for X and 2X

dose, respectively (Singla et al. 2020). With a single dose of 0.20 ml/L and a double dose of 0.40 ml/L, the initial deposits of chlorantraniliprole residues in cabbage heads were determined to be 0.81 mg/kg and 2.00 mg/kg, respectively. By the third day, no residues were found with 100.00 per cent dissipation of the chlorantraniliprole at both dosages in cabbage heads (Kabadad and Gali 2018).

Table 4.51 Persistence of chlorantraniliprole (@ 40 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.854	0.887	0.861	0.867±0.017	-
1	0.582	0.555	0.599	0.579±0.022	33.28
3	0.273	0.263	0.266	0.267±0.005	69.18
5	0.176	0.169	0.192	0.179±0.012	79.36
7	0.061	0.058	0.049	0.056±0.006	93.54
10	0.031	0.026	0.033	0.033±0.003	96.16
15	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Table 4.52 Persistence of chlorantraniliprole (@ 80 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	1.442	1.423	1.433	1.433±0.010	-
1	0.914	0.928	0.832	0.891±0.052	37.79
3	0.462	0.472	0.459	0.464±0.007	67.59
5	0.246	0.253	0.249	0.249±0.004	82.60
7	0.122	0.118	0.117	0.119±0.003	91.69
10	0.061	0.059	0.056	0.059±0.003	95.91
15	0.021	0.028	0.017	0.022±0.006	98.46
20	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

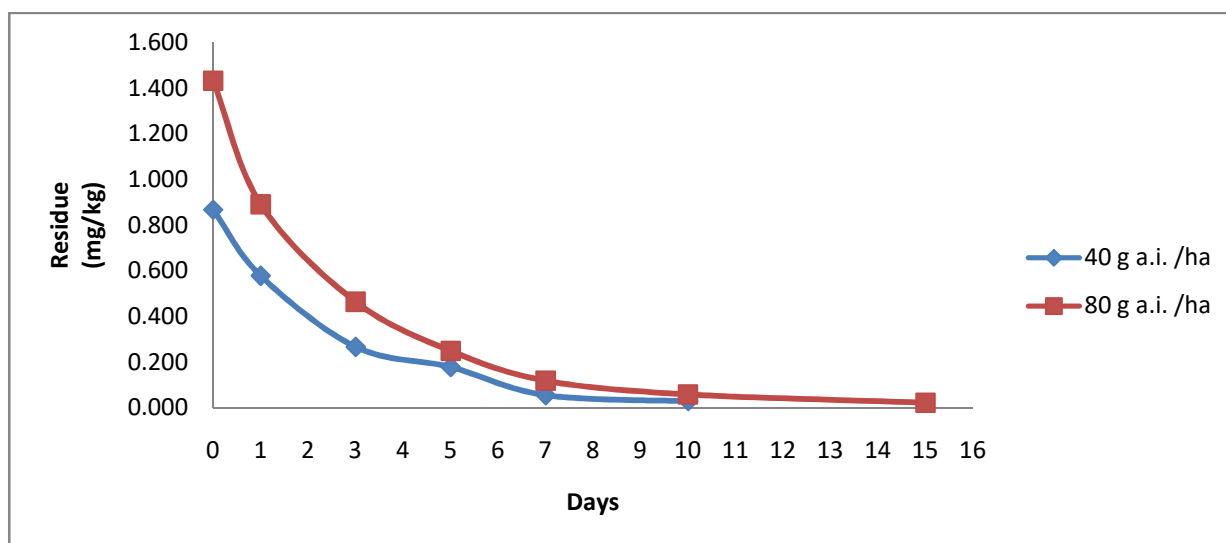


Fig 4.27 Dissipation pattern of chlorantraniliprole (@ 40 g a.i./ha and 80 g a.i./ha) in/on brinjal fruits

4.4.2.4 Initial deposits and persistence of fenvalerate in/on brinjal fruits

The data shown in Table 4.53 and Table 4.54 showed that the initial deposits of fenvalerate on brinjal fruits at single dose (75 g a.i./ha) were found to be 0.587 mg/ kg which dissipated to 0.424, 0.322, 0.120, 0.077 and 0.041 mg/kg at 1, 3, 5, 7 and 10 days, respectively whereas at double dose (150 g a.i./ ha) the initial deposits of 1.233 mg/ kg dissipated to 0.954, 0.698, 0.312, 0.189, 0.069 and 0.029 mg/kg at 1, 3, 5, 7, 10 and 15 days, respectively. The per cent dissipation values ranged between 27.81 to 93.02 per cent and 22.62 to 97.62 per cent at X and 2X dose, respectively (Fig.4.28). The fenvalerate residues reduced to below LOQ (< 0.02 mg/kg) after 10 days at single dose and 15 days at twice the single dose on brinjal fruits.

Table 4.53 Persistence of fenvalerate (@ 75 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.582	0.592	0.588	0.587±0.005	-
1	0.424	0.436	0.412	0.424±0.012	27.81
3	0.316	0.327	0.324	0.322±0.006	45.12
5	0.129	0.118	0.112	0.120±0.009	79.63
7	0.072	0.079	0.081	0.077±0.005	86.83
10	0.041	0.035	0.047	0.041±0.006	93.02
15	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Similar results were observed by Duara et al. (2003), who concluded that when fenvalerate was sprayed on brinjal at the rates of 60 and 112.5 g a.i./ha, respectively, the initial deposits on the fruit were 0.55 and 0.94 mg/kg and on the seventh day, the residues of fenvalerate were below the maximum residual limit (mg/kg). Nath et al. (2018) demonstrated the initial residue deposits of 0.330 and 0.540 mg/kg (peak I + peak II) for fenvalerate on okra fruit which dissipated by 86.00 and 91.85 per cent on the 7th day when sprayed at rates of 75 and 150 g a.i./ha, respectively. According to Bansal (2022), the initial residues of fenvalerate on broccoli heads at 60 g a.i./ha were 1.23 times lower than those at 75 g a.i./ha. The initial residues on broccoli heads decreased to 0.035 mg/kg and 0.029 mg/kg in 7 and 10 days, resulting in 89.86 and 93.14 per cent dissipation at X and 1.25X dose. Gupta and Singh (2001) also conducted a study on dissipation pattern of fenvalerate on cauliflower curds and found that when fenvalerate was applied at the X dose (75 g a.i./ha), the initial deposits dissipated to a level of 45.74 per cent on the first day and 98.45 per cent on the seventh day. Initial deposits of 2.25 mg/kg at the 2X dose (150 g a.i./ha) dissipated to 56.44 per cent on the first day and 99.20 per cent on the tenth day on cauliflower curds. At the X dose and the 2X dose, the fenvalerate residues were below the limit of quantification (LOQ) on 10 and 15 days, respectively.

Table 4.54 Persistence of fenvalerate (@ 150 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	1.280	1.243	1.176	1.233±0.053	-
1	1.023	0.916	0.924	0.954±0.060	22.62
3	0.734	0.712	0.648	0.698±0.045	43.40
5	0.365	0.348	0.224	0.312±0.077	74.67
7	0.178	0.198	0.192	0.189±0.010	84.65
10	0.071	0.073	0.062	0.069±0.006	94.43
15	0.031	0.025	0.032	0.029±0.006	97.62
20	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

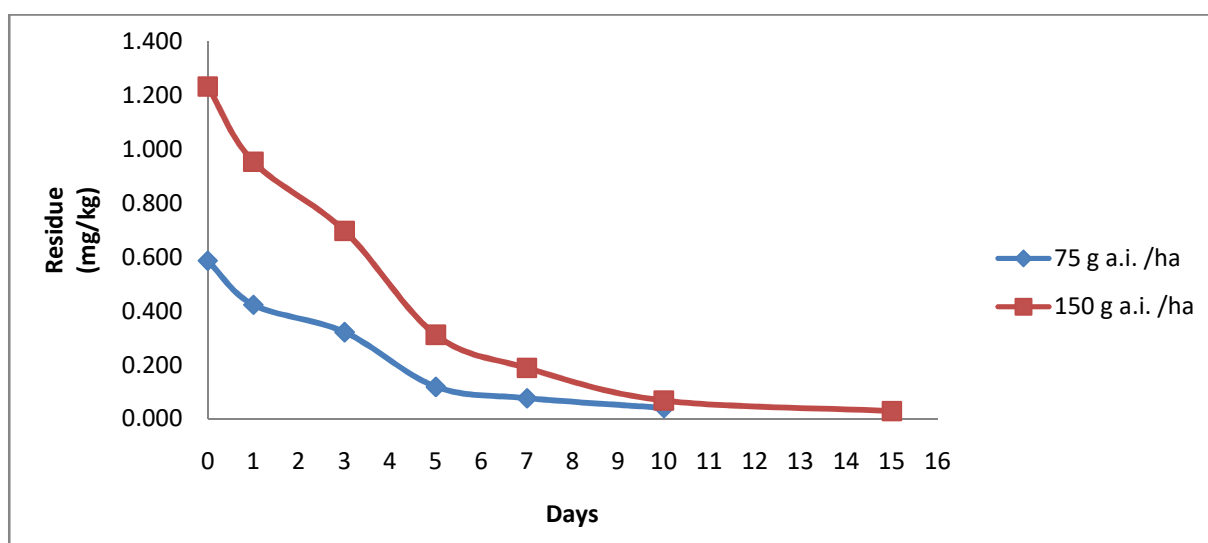


Fig 4.28 Dissipation pattern of fenvalerate (@ 75 g a.i./ha and 150 g a.i./ha) in/on brinjal fruits

4.4.2.5 Initial deposits and persistence of chlorpyrifos in/on brinjal fruits

The initial deposits of chlorpyrifos on brinjal fruits at single dose (200 g a.i./ha) were found to be 0.918 mg/ kg and 1.825 mg/ kg at double dose (400 g a.i./ ha) which reduced to 0.033 and 0.025 mg /kg in 7 days with a dissipation of 96.37 (in 7 days) and 98.64 (in 10 days) per cent at X and 2X dose, respectively (Table 4.55 and 4.56). Persistence data showed (Fig. 4.29) that the chlorpyrifos residues reduced to below LOQ (< 0.01 mg/kg) after 10 days at single dose and 15 days at twice the single dose on brinjal fruits. The findings of the present investigation were consistent with those recorded by Brar (2018) who revealed that the initial residues of chlorpyrifos on brinjal were 1.096 mg/kg and 1.982 mg/kg with a per cent dissipation of 92.25 and 95.72 per cent at 7 and 10 days interval at application rate of 300 and 600 g a.i./ha, respectively. Another study conducted by Singh et al. (2019b) on persistence of chlorpyrifos on cucumber fruits revealed that the initial chlorpyrifos deposits of 0.980

mg/kg and 1.860 mg/kg decreased to 0.059 mg/kg after 7 days of spraying at the single dose (300 g a.i./ha) and 0.057 mg/kg in 10 days at double dose (600 g a.i./ha), respectively. According to Chandra et al. (2014), when treated at 100, 200 and 300 g a.i./ha, respectively, the mean first deposits of chlorpyrifos on okra were 0.389, 0.696 and 0.874 mg/kg. According to Katna et al. (2018), the initial residue levels of chlorpyrifos in french bean at doses X (3.083 mg/kg) and 2X (6.017 mg/kg) were reduced to 0.065 and 0.073 mg/kg on 10 and 15 days respectively, indicating 98 and 99 per cent degradation rate during this time. They also came to the conclusion that by 15 and 20 days, respectively, residues declined below the determination limit of 0.05 mg/kg.

Table 4.55 Persistence of chlorpyrifos (@ 200 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.922	0.915	0.917	0.918±0.004	-
1	0.547	0.558	0.567	0.557±0.010	39.29
3	0.285	0.298	0.29	0.291±0.007	68.30
5	0.068	0.074	0.061	0.068±0.007	92.63
7	0.035	0.029	0.036	0.033±0.004	96.37
10	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Table 4.56 Persistence of chlorpyrifos (@ 400 g a.i./ha) in/on brinjal fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	1.862	1.854	1.799	1.825±0.034	-
1	1.116	1.129	1.104	1.116±0.013	39.27
3	0.582	0.575	0.590	0.582±0.008	68.32
5	0.218	0.233	0.220	0.224±0.008	87.83
7	0.091	0.088	0.079	0.086±0.006	95.32
10	0.029	0.019	0.027	0.025±0.005	98.64
15	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

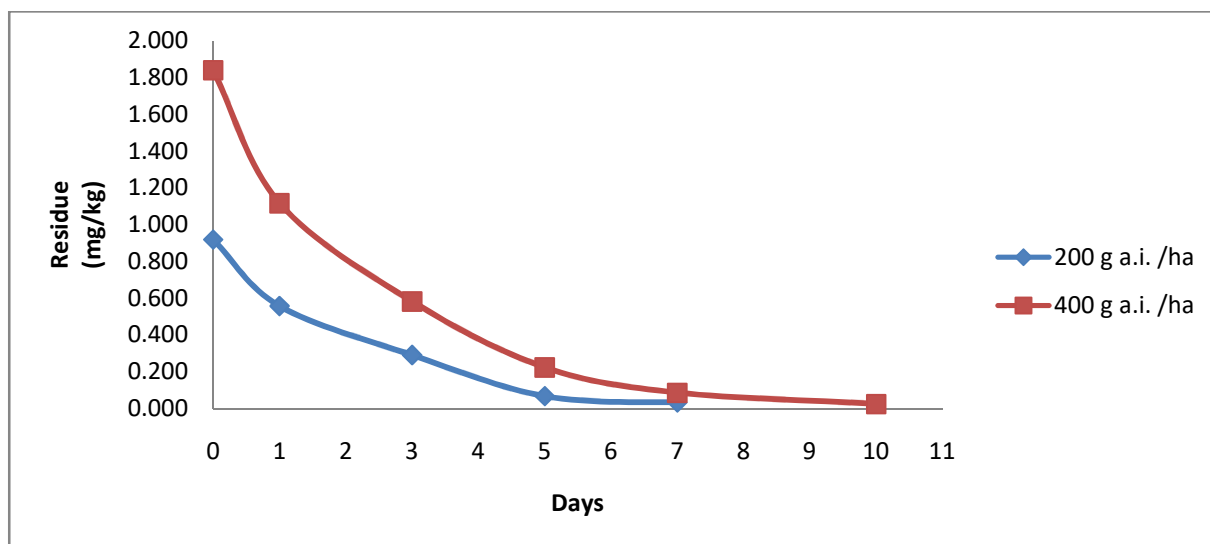


Fig 4.29 Dissipation pattern of chlorpyrifos (@ 200 g a.i./ha and 400 g a.i./ha) in/on brinjal fruits

4.5 Persistence study of pesticides in/on chilli

4.5.1 Recovery studies in/on chilli fruits (green and red) and field soil

The recovery studies of fenazaquin were estimated by spiking the chilli fruits (green and red) and soil at five different fortification levels *viz.* 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg in GC-MS/MS and 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg of cyantraniliprole, flubendiamide, spirotetramat and imidacloprid in LC-MS/MS.

4.5.1.1 Recovery of cyantraniliprole from fortified chilli fruits (green and red) and field soil

The average cyantraniliprole recovery from green and red chilli fruits fortified at different levels *viz.*, 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg was 95.00, 96.56, 102.48, 91.60, 98.50 per cent and 89.00, 96.96, 96.44, 89.04 and 97.02 per cent with a relative standard deviation ranged from 1.43-6.49 and 1.26-4.95 per cent, respectively (Table 4.57 and 4.58). Average recovery from fortified field soil ranged from 94.84 to 101.00 per cent with a relative deviation from 2.56-4.95 per cent, as indicated in Table 4.59. The average recovery of cyantraniliprole from fortified cabbage samples were in the range of 89.80-97.52 per cent at different concentration levels ranged from 0.005 to 0.5 mg/kg with per cent RSD in the range of 0.67-5.33 per cent, whereas in soil recoveries ranged from 91.25-100.11 per cent with per cent RSD of 0.46-5.76 per cent, respectively (Kumar et al. 2021). Five replicates of the recovery trials were done by Sun et al. (2012) with various spiking levels (0.01, 0.05 and 0.1

mg/kg) in various substrates. The average recoveries of cyantraniliprole in the pakchoi and soil samples were 83.3-102.4 per cent and 81.5-100.4 per cent, respectively with relative standard deviations (RSD) ranged between 1.6-6.3 per cent and 7.2- 7.9 per cent, respectively. The recovery rate ranged from 91.90 to 103.70 per cent for cyantraniliprole in proso millet at the fortification level of 0.5 mg/kg (Lee et al. 2019a).

Table 4.57 Recovery of cyantraniliprole from fortified chilli green fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0094	0.0091	0.0097	0.0094	0.0099	0.0095	95.00	3.24
0.025	0.0236	0.0242	0.0238	0.0248	0.0243	0.0241	96.56	1.93
0.05	0.0521	0.0515	0.0514	0.0501	0.0511	0.0512	102.48	1.43
0.1	0.0990	0.0840	0.0960	0.0900	0.0890	0.0916	91.60	6.49
0.2	0.1880	0.1970	0.2050	0.1990	0.1960	0.1970	98.50	3.11

Table 4.58 Recovery of cyantraniliprole from fortified red chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0084	0.0091	0.0087	0.0094	0.0089	0.0089	89.00	4.28
0.025	0.0246	0.0244	0.0238	0.0243	0.0241	0.0242	96.96	1.26
0.05	0.0489	0.0479	0.0482	0.0474	0.0487	0.0482	96.44	1.26
0.1	0.0877	0.0923	0.0848	0.0912	0.0892	0.0890	89.04	3.33
0.2	0.2001	0.1997	0.1847	0.1826	0.2031	0.1940	97.02	4.95

Table 4.59 Recovery of cyantraniliprole from fortified chilli field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0104	0.0099	0.0107	0.0096	0.0099	0.0101	101.00	4.37
0.025	0.0256	0.0234	0.0248	0.0253	0.0231	0.0244	97.76	4.62
0.05	0.0499	0.0479	0.0492	0.0511	0.0518	0.0500	99.96	3.08
0.1	0.0897	0.0973	0.0898	0.0982	0.0992	0.0948	94.84	4.95
0.2	0.2011	0.1949	0.1947	0.1996	0.2071	0.1995	99.74	2.56

4.5.1.2 Recovery of imidacloprid from fortified chilli fruits (green and red) and field soil

The average recoveries of imidacloprid from fortified green chilli fruits was 90.60, 96.48, 98.00, 93.00 and 98.40 per cent with a relative standard deviation from 1.08-4.25 per cent at different fortification levels viz., 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg, respectively (Table 4.60). The average recoveries of imidacloprid from fortified red chilli fruits and field soil was in the range of 89.00-96.10 per cent and 93.84-103.00 per cent with a relative standard deviation ranged from 1.27-6.55 and 1.74-5.72 per cent, respectively (Table 4.61 and Table 4.62).

At fortification levels of 0.05, 0.25 and 0.5 mg/kg, the average mean recovery of imidacloprid in chilli was 97.4, 94.4 and 84.1 per cent, respectively (Mathew et al. 2012). Varghese et al. (2015) reported the mean recovery from chilli fruits at fortification level 0.01, 0.05 and 0.1 mg/kg as 93.30, 113.00 and 88.00 per cent with per cent RSD as 9.17, 4.08 and 8.58 per cent, respectively. Pandit et al. (2016) found that 87.33–89.0 per cent of imidacloprid was recovered from okra field soil at fortification levels of 0.5, 1.0 and 2.0 mg/kg.

Table 4.60 Recovery of imidacloprid from fortified green chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0088	0.0091	0.0096	0.0086	0.0092	0.0103	90.60	4.25
0.025	0.0245	0.0245	0.0234	0.0240	0.0242	0.0480	96.48	1.89
0.05	0.0497	0.0492	0.0483	0.0491	0.0487	0.1010	98.00	1.08
0.1	0.0920	0.0940	0.0960	0.0910	0.0920	0.2510	93.00	2.15
0.2	0.1980	0.1990	0.2020	0.1890	0.1960	0.5030	98.40	2.47

Table 4.61 Recovery of imidacloprid from fortified red chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0082	0.0090	0.0092	0.0086	0.0095	0.0089	89.00	5.73
0.025	0.0240	0.0228	0.0231	0.0239	0.0246	0.0237	94.72	3.07
0.05	0.0477	0.0472	0.0470	0.0461	0.0467	0.0469	93.88	1.27
0.1	0.0820	0.0840	0.0960	0.0910	0.0920	0.0890	89.00	6.55
0.2	0.1880	0.1990	0.1940	0.1890	0.1910	0.1922	96.10	2.31

Table 4.62 Recovery of imidacloprid from fortified chilli field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0108	0.0099	0.0107	0.0096	0.0105	0.0103	103.00	5.09
0.025	0.0252	0.0267	0.0247	0.0254	0.0248	0.0254	101.44	3.16
0.05	0.0488	0.0479	0.0508	0.0502	0.0495	0.0494	98.88	2.31
0.1	0.0988	0.0976	0.0897	0.0866	0.0965	0.0938	93.84	5.72
0.2	0.1976	0.1996	0.2055	0.1965	0.1994	0.1997	99.86	1.74

4.5.1.3 Recovery of spirotetramat from fortified chilli fruits (green and red) and field soil

The data in Table 4.63 depicts the average recoveries of spirotetramat from fortified green chilli fruits at different levels of fortification viz., 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg was 88.60, 98.16, 97.96, 93.10 and 98.89 per cent with a relative standard deviation ranged from 1.25-5.72 per cent, respectively. The average recoveries of spirotetramat from fortified red chilli fruits and soil ranged from 91.20-95.56 per cent and 97.30-101.33 per cent with a

relative standard deviation ranged from 1.95-6.71 per cent and 2.43-5.94 per cent, respectively (Table 4.64 and Table 4.65).

Mathew et al. (2012) conducted a study at three fortification levels (0.05, 0.25 and 0.5 mg/kg) in chilli and concluded that the recovery of spirotetramat in chilli fruits was 104.7, 102.3 and 82.1 per cent, respectively. At fortification levels of 0.01 to 0.30 mg/kg, the mean per cent recoveries of spirotetramat from samples of chilli fruit ranged from 84.63 to 89.06 per cent with the per cent RSD in the range of 3.06- 5.22 per cent (Chahil et al. 2015). According to Singh et al. (2013), average recovery of spirotetramat in chilli field soil was 92.03, 97.20, 95.10 and 90.50 per cent at fortification levels of 1.00, 0.30, 0.15 and 0.03 mg/kg, respectively. Sharma (2020a) also recorded average recoveries of spirotetramat in cabbage heads at fortification levels of 0.05, 0.10, 0.25, 0.50 and 1.00 mg/kg and found per cent recovery of 94.00, 95.00, 96.00, 94.60 and 96.20 per cent, respectively.

Table 4.63 Recovery of spirotetramat from fortified green chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0087	0.0083	0.0088	0.0092	0.0093	0.0089	88.60	4.56
0.025	0.0248	0.0254	0.0243	0.0239	0.0243	0.0245	98.16	2.35
0.05	0.0493	0.0497	0.0482	0.0485	0.0492	0.0490	97.96	1.25
0.1	0.0894	0.0992	0.0861	0.0942	0.0966	0.0931	93.10	5.72
0.2	0.1999	0.1967	0.1889	0.2022	0.2012	0.1978	98.89	2.72

Table 4.64 Recovery of spirotetramat from fortified red chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0097	0.0093	0.0088	0.0092	0.0086	0.0091	91.20	4.74
0.025	0.0238	0.0244	0.0241	0.0234	0.0233	0.0238	95.20	1.95
0.05	0.0453	0.0477	0.0482	0.0495	0.0482	0.0478	95.56	3.22
0.1	0.0824	0.0922	0.0891	0.0982	0.0956	0.0915	91.50	6.71
0.2	0.1899	0.1897	0.1789	0.1866	0.1967	0.1884	94.18	3.42

Table 4.65 Recovery of spirotetramat from fortified chilli field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0107	0.0103	0.0098	0.0092	0.0096	0.0099	99.20	5.94
0.025	0.0258	0.0251	0.0239	0.0244	0.0255	0.0249	99.76	3.14
0.05	0.0493	0.0447	0.0508	0.0511	0.0492	0.0490	98.04	5.23
0.1	0.0924	0.0982	0.0991	0.0989	0.0979	0.0973	97.30	2.86
0.2	0.2012	0.2113	0.1989	0.2006	0.2013	0.2027	101.33	2.43

4.5.1.4 Recovery of flubendiamide from fortified chilli fruits (green and red) and field soil

Recoveries of flubendiamide from fortified green chilli fruits at different levels of fortification, *viz.*, 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg, was in the range of 88.40 to 102.68 per cent with a relative standard deviation ranged from 1.64-5.69 per cent (Table 4.66). At five different fortification levels, 0.01, 0.025, 0.05, 0.1 and 0.2 mg/kg, the recovery of flubendiamide from red chilli fruits and field soil was reported to be 86.40, 98.16, 97.92, 94.64 and 96.56 per cent and 102.60, 103.12, 98.92, 93.10 and 95.35 per cent with a relative standard deviation values ranged from 1.60 to 5.47 per cent and 2.27 to 6.34 per cent, respectively (Table 4.67 and Table 4.68). In a similar study conducted by Akshima (2019) on flubendiamide in chilli fruits and soil concluded that at different fortification levels *viz.*, 0.05, 0.10, 0.25, 0.50 and 1.00 mg/kg the average recoveries were found in the range between 93.20– 98.72 and 94.40 – 103.62 per cent, respectively. Average recoveries of flubendiamide from fortified okra fruits and soil at fortification level ranged from 0.05-1.00 mg/kg were in range of 92.40 - 99.00 and 94.96 - 102.58 per cent, respectively (Gautam 2019). At fortification levels of 0.05-0.5 mg/kg, the mean flubendiamide recoveries (five replicates) ranged from 77.8-89.60 per cent in chillies to 81.2-91.10 per cent in soil (Sharma et al. 2011). When chilli fruits and soil were fortified at a level of 0.01-0.2 mg/kg, average flubendiamide recoveries ranged between 85.00 and 93.00 per cent in chillies and from 86.00 to 97.50 per cent in soil, respectively (Sahoo et al. 2009).

Table 4.66 Recovery of flubendiamide from fortified green chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0091	0.0096	0.0085	0.0084	0.0086	0.0088	88.40	5.69
0.025	0.0242	0.0255	0.0232	0.0249	0.0246	0.0245	97.92	3.51
0.05	0.0489	0.0509	0.0494	0.0502	0.0492	0.0497	99.44	1.64
0.1	0.1036	0.1004	0.1047	0.1035	0.1012	0.1027	102.68	1.75
0.2	0.2102	0.1898	0.2004	0.1989	0.1863	0.1971	98.56	4.78

Table 4.67 Recovery of flubendiamide from fortified red chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0081	0.0086	0.0085	0.0094	0.0086	0.0086	86.40	5.47
0.025	0.0242	0.025	0.0242	0.0243	0.025	0.0245	98.16	1.72
0.05	0.0499	0.0481	0.0494	0.0482	0.0492	0.0490	97.92	1.60
0.1	0.0966	0.0925	0.0878	0.0974	0.0989	0.0946	94.64	4.75
0.2	0.2002	0.1993	0.1899	0.1969	0.1793	0.1931	96.56	4.51

Table 4.68 Recovery of flubendiamide from fortified chilli field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0101	0.0099	0.0113	0.0104	0.0096	0.0103	102.60	6.34
0.025	0.0252	0.0265	0.0262	0.0252	0.0258	0.0258	103.12	2.27
0.05	0.0507	0.0511	0.0474	0.0499	0.0482	0.0495	98.92	3.24
0.1	0.0988	0.0916	0.0987	0.0897	0.0867	0.0931	93.10	5.85
0.2	0.1996	0.1998	0.1877	0.1865	0.1799	0.1907	95.35	4.58

4.5.1.5 Recovery of fenazaquin from fortified chilli fruits (green and red) and field soil

From Table 4.69, it was concluded that the average recoveries of fenazaquin from green chilli fruits ranged from 93.44 to 99.60 per cent at various levels of fortification, viz., 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg, with a relative standard deviation ranged between 2.80 and 5.00 per cent, respectively. The recovery of fenazaquin from red chilli fruits and field soil was reported to be 95.20, 98.64, 96.00, 91.92 and 96.26 per cent and 99.80, 97.52, 94.08, 93.18, 98.80 per cent at five different fortification levels, namely 0.01, 0.05, 0.1, 0.25 and 0.5 mg/kg with a relative standard deviation ranged from 2.54-5.98 and 2.47-5.94 per cent, respectively (Table 4.70 and Table 4.71).

Table 4.69 Recovery of fenazaquin from fortified green chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0099	0.0095	0.0099	0.0108	0.0097	0.0100	99.60	5.00
0.05	0.0251	0.0249	0.0258	0.0239	0.0246	0.0249	99.44	2.80
0.1	0.0499	0.0498	0.0462	0.0494	0.0487	0.0488	97.60	3.13
0.25	0.0977	0.0953	0.0948	0.0912	0.0882	0.0934	93.44	4.00
0.5	0.2001	0.1897	0.1887	0.1896	0.2011	0.1938	96.92	3.20

Nasr et al. (2009) found that fortified tomato fruits at 0.1 ppm with fenazaquin had an average recovery of 89.20 per cent. Duhan et al. (2010) measured 94.80 and 100.70 per cent of fenazaquin recovery from fortified okra fruit samples at concentration level of 0.1 and 0.2 mg/kg, respectively. With an RSD of 0.98 to 1.90 per cent, the average fenazaquin recoveries from apple fruit samples at fortification levels of 0.01, 0.1 and 0.2 µg/g ranged from 80.00 to 94.50 per cent (Yaqoob et al. 2021).

Table 4.70 Recovery of fenazaquin from fortified red chilli fruits

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0093	0.0091	0.0099	0.0096	0.0097	0.0095	95.20	3.35
0.05	0.0248	0.0254	0.0245	0.0249	0.0237	0.0247	98.64	2.54
0.1	0.0468	0.0479	0.0501	0.0486	0.0466	0.0480	96.00	2.98
0.25	0.0897	0.0976	0.0889	0.0856	0.0978	0.0919	91.92	5.98
0.5	0.1995	0.1896	0.1994	0.1866	0.1875	0.1925	96.26	3.33

Table 4.71 Recovery of fenazaquin from fortified chilli field soil

Fortification levels (mg/kg)	Recovery (mg/kg)						Average recovery (%)	% RSD
	R ₁	R ₂	R ₃	R ₄	R ₅	Mean		
0.01	0.0093	0.0105	0.0097	0.0097	0.0107	0.0100	99.80	5.94
0.05	0.0251	0.0249	0.0233	0.0242	0.0244	0.0244	97.52	2.89
0.1	0.0477	0.0487	0.0465	0.0448	0.0475	0.0470	94.08	3.14
0.25	0.0888	0.0986	0.0945	0.0963	0.0877	0.0932	93.18	5.09
0.5	0.2004	0.1997	0.1992	0.1889	0.1998	0.1976	98.80	2.47

4.5.2 Initial deposits and persistence of test pesticide (s) in/on chilli fruits

4.5.2.1 Initial deposits and persistence of cyantraniliprole in/on chilli fruits

Average initial deposits of cyantraniliprole on chilli fruits were found to be 0.886 mg/kg and 1.525 mg/kg, respectively, when cyantraniliprole was applied to chilli at a single dose (@ 60 g a.i./ha) and twice the single dose (@ 120 g a.i./ha). The initial cyantraniliprole deposits of double dose were 1.72 times higher than those produced by the single dose (Table 4.72 and 4.73). According to persistence data, the cyantraniliprole residues on chilli fruits decreased from 0.663 to 0.023 mg/kg in 1 to 10 days, resulting in a single dosage dissipation of 25.13 to 97.37 per cent. With double dose, cyantraniliprole residues on chilli fruits decreased from 0.974 to 0.019 mg/kg in 1 to 15 days and showed a dissipation of 36.15 to 98.78 per cent (Fig. 4.30). After 10 and 15 days, respectively, the residues of cyantraniliprole at single dose and double dose on chilli fruits reduced below LOQ (<0.01 mg/kg).

The initial deposits of cyantraniliprole in cabbage were found to be 0.403 and 1.195 mg/kg which reduced to 0.087 and 0.384 mg/kg on 7th day and to 0.032 and 0.141 mg/kg on 15th day at X (60 g a.i./ha) and 2X (120 g a.i./ha) doses, respectively (Kumar et al. 2021). Sun et al. (2012) reported the initial concentration of cyantraniliprole in pakchoi from Guangdong and Shanghai was 1.58 and 0.95 mg/kg in 2009 and 1.43 and 0.70 mg/kg in 2010. The initial residues of cyantraniliprole in okra were 0.23 and 0.42 mg/kg at single and double dose (Cyantraniliprole 7.3 % w/w + Diafenthiuron 36.4 % w/w SC @ 60 + 300 g a.i./ha), respectively. At 7th and 10th day of application residues were below the limit of quantification of 0.01 mg/kg at X and 2X dose, respectively (Sharma et al. 2022).

Table 4.72 Persistence of cyantraniliprole (@ 60 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.871	0.903	0.884	0.886±0.016	-
1	0.675	0.662	0.653	0.663±0.011	25.13
3	0.262	0.277	0.281	0.273±0.010	69.15
5	0.172	0.168	0.161	0.167±0.006	81.15
7	0.061	0.051	0.046	0.053±0.008	94.06
10	0.032	0.016	0.022	0.023±0.008	97.37
15	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Table 4.73 Persistence of cyantraniliprole (@ 120 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	1.527	1.533	1.516	1.525 ±0.009	-
1	0.965	0.973	0.984	0.974±0.010	36.15
3	0.69	0.673	0.683	0.682±0.009	55.29
5	0.414	0.418	0.422	0.418±0.004	72.60
7	0.198	0.203	0.211	0.204±0.007	86.63
10	0.083	0.071	0.065	0.073±0.009	95.21
15	0.018	0.011	0.027	0.019±0.008	98.78
20	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

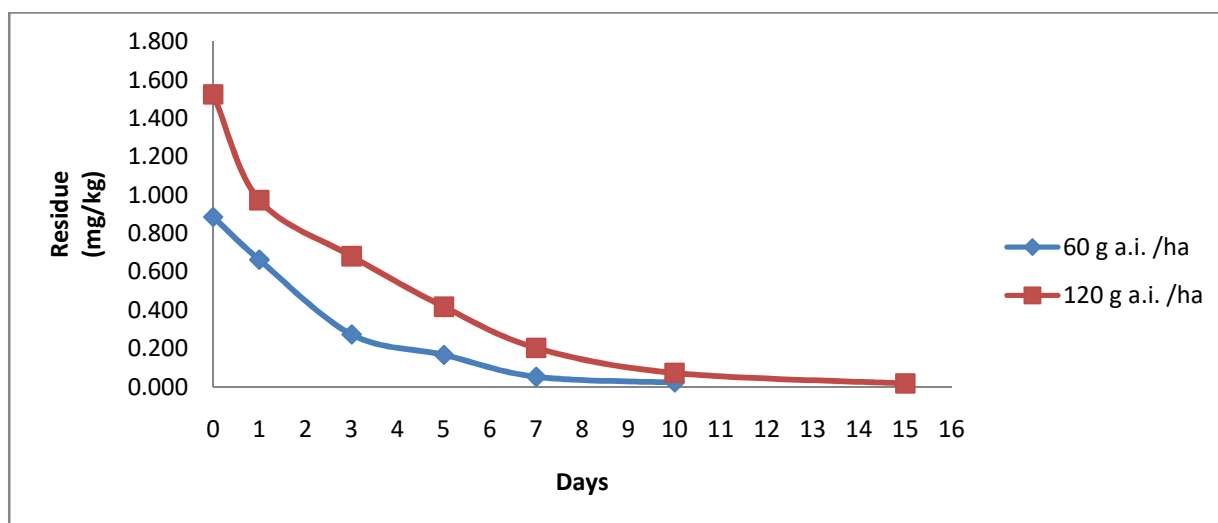


Fig 4.30 Dissipation pattern of cyantraniliprole (@ 60 g a.i./ha and 120 g a.i./ha) in/on chilli fruits

4.5.2.2 Initial deposits and persistence of imidacloprid in/on chilli fruits

The average initial deposits of imidacloprid on chilli fruits were found to be 0.869 mg/kg and 1.301 mg/kg when applied at the rate of 25 g a.i./ha and 50 g a.i./ha, respectively. In chilli fruits the initial imidacloprid deposits at double dose were 1.49 times higher than that of single dose. The imidacloprid initial residues reduced from 0.613-0.039 mg/kg in 1 to 10 days

at single dose and at double it reduced from 0.883-0.033 mg/kg in 1 to 15 days, respectively (Table 4.74 and 4.75, Fig. 4.31). After 10 and 15 days, the residues of imidacloprid were below LOQ (<0.01 mg/kg) when applied at 25 g a.i./ha and 50 g a.i./ha, respectively.

Our findings were in close proximity with the findings conducted by Chahil et al. (2015) who reported the average initial deposits of imidacloprid on green chilli fruits as 0.73 and 1.49 mg/kg, respectively, following three applications of a combination mixture of spirotetramat 12 % + imidacloprid 12 % at 120 and 240 g a.i./ha. At recommended and double the recommended dosages, imidacloprid residues were below LOQ of 0.01 mg/kg after 7 and 10 days, respectively. As per the studies conducted by Varghese et al. (2015), spraying of imidacloprid at 20 g a.i./ha, left an average initial residue of 1.27 mg/kg on chilli fruits. On the 9th day after spraying there were no detectable imidacloprid residues on chilli fruits. The mean initial deposits of imidacloprid in green chilli fruits were 2.53 and 3.15 mg/kg at single (120 g a.i./ha) and double dose (240 g a.i./ha), respectively (Mathew et al. 2012). Initial imidacloprid deposits on cabbage heads were determined by Bhartiya (2018) and recorded residues as 0.392 and 0.795 mg/kg when applied at rates of 25 and 50 g a.i./ha, respectively. The residues persisted for 3 and 5 days with a dissipation of 72.96 and 87.92 per cent at X and 2X dosage, respectively.

Table 4.74 Persistence of imidacloprid (@ 25 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.836	0.867	0.884	0.869±0.014	-
1	0.632	0.616	0.592	0.613±0.020	29.42
3	0.365	0.379	0.374	0.373±0.007	57.12
5	0.119	0.125	0.133	0.126±0.007	85.54
7	0.085	0.078	0.069	0.077±0.008	91.10
10	0.042	0.045	0.031	0.039±0.007	95.47
15	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Table 4.75 Persistence of imidacloprid (@ 50 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	1.295	1.318	1.291	1.301±0.015	-
1	0.868	0.893	0.888	0.883±0.013	32.15
3	0.585	0.574	0.592	0.584±0.009	55.15
5	0.338	0.352	0.364	0.351±0.013	73.00
7	0.142	0.135	0.152	0.143±0.009	89.01
10	0.072	0.061	0.075	0.069±0.007	94.67
15	0.039	0.028	0.031	0.033±0.006	97.49
20	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

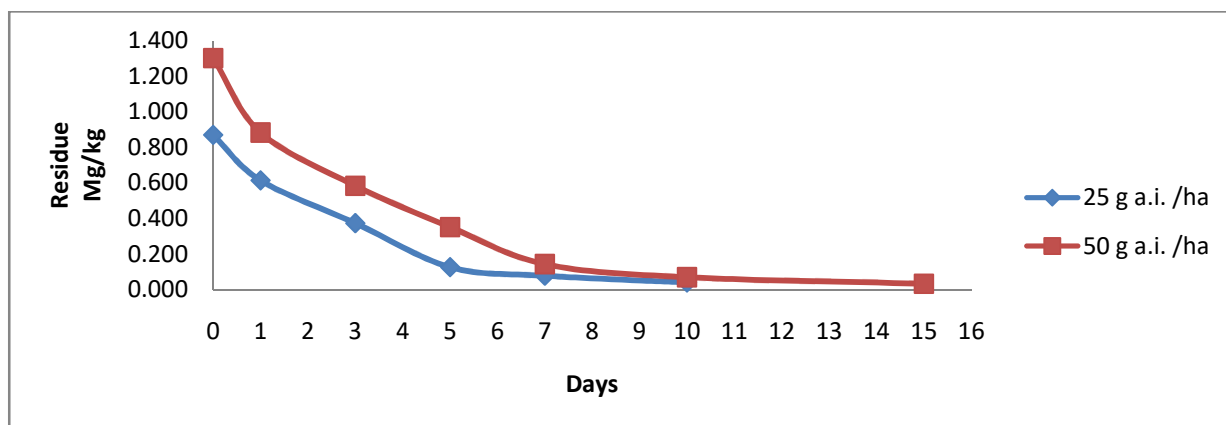


Fig 4.31 Dissipation pattern of imidacloprid (@ 25 g a.i./ha and 50 g a.i./ha) in/on chilli fruits

4.5.2.3 Initial deposits of spirotetramat in/on chilli fruits

The data given in Table 4.76 and Table 4.77 depicts that at single dose (60 g a.i./ha) the initial deposits of spirotetramat on chilli fruits were found to be 0.258 mg/ kg and 0.524 mg/kg at double dose (120 g a.i./ ha). Initial deposits of recommended and double the recommended dose decreased to 0.156, 0.066 and 0.023 mg/kg at 1, 3 and 5 days and 0.362, 0.152, 0.068 and 0.027 mg/kg at 1, 3, 5 and 7 days, respectively. The per cent dissipation values for a recommended dose were found to be 39.74, 74.58 and 90.97 per cent at intervals of 1, 3 and 5 days and for double the recommended dose, they were found to be 31.02, 70.95, 87.03 and 94.79 per cent, respectively, at an intervals of 1, 3, 5 and 7 days (Fig.4.32). Residues of spirotetramat were below LOQ (<0.01 mg/kg) after 5 and 7 days when applied at the rate of 60 g a.i./ha and 120 g a.i./ha, respectively.

Present findings are supported by Chahil et al. (2015) who found that after one day; the initial deposits in chilli fruits at X (0.55 mg/kg) and 2X (1.22 mg/kg) doses reduced to 0.25 and 0.58 mg/kg, respectively, suggesting a loss of more than 50 per cent. Spirotetramat residues were below the limit of quantification (LOQ) of 0.03 mg/kg in 5 and 7 days at X and 2X dosages, respectively. The initial deposits of spirotetramat in green chillies at the rate 60 and 120 g a.i./ha was found to be 2.52 and 3.39 µg/g and 2.29 and 3.11 µg/g from the first and second field experiment, respectively (Vinothkumar et al. 2012). Sharma (2020a) found the initial residues of spirotetramat on cabbage heads as 0.327 and 0.726 mg/kg at application rates of 90 g a.i./ha and 180 g a.i./ha, respectively. Initial deposits of spirotetramat on brinjal were reported to be 0.80 and 1.16 mg/kg from X and 2X dosages, respectively, according to Bhardwaj et al. (2016). The initial concentrations of spirotetramat in the parsley (0.612 mg/kg), dill (0.558 mg/kg) and radish leaves (0.616 mg/kg) were reported to have reduced to

the minimum levels of 0.003 mg/kg, 0.004 mg/kg and 0.001 mg/kg, respectively, at dissipation rates of 99% (Łozowieka et al. 2017).

Table 4.76 Persistence of spirotetramat (@ 60 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.258	0.268	0.249	0.258±0.010	-
1	0.166	0.158	0.143	0.156±0.012	39.74
3	0.059	0.062	0.076	0.066±0.009	74.58
5	0.015	0.022	0.033	0.023±0.009	90.97
7	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Table 4.77 Persistence of spirotetramat (@ 120 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.532	0.513	0.528	0.524±0.010	-
1	0.361	0.346	0.378	0.362±0.016	31.02
3	0.133	0.156	0.168	0.152±0.018	70.95
5	0.065	0.058	0.081	0.068±0.012	87.03
7	0.021	0.032	0.029	0.027±0.006	94.79
10	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

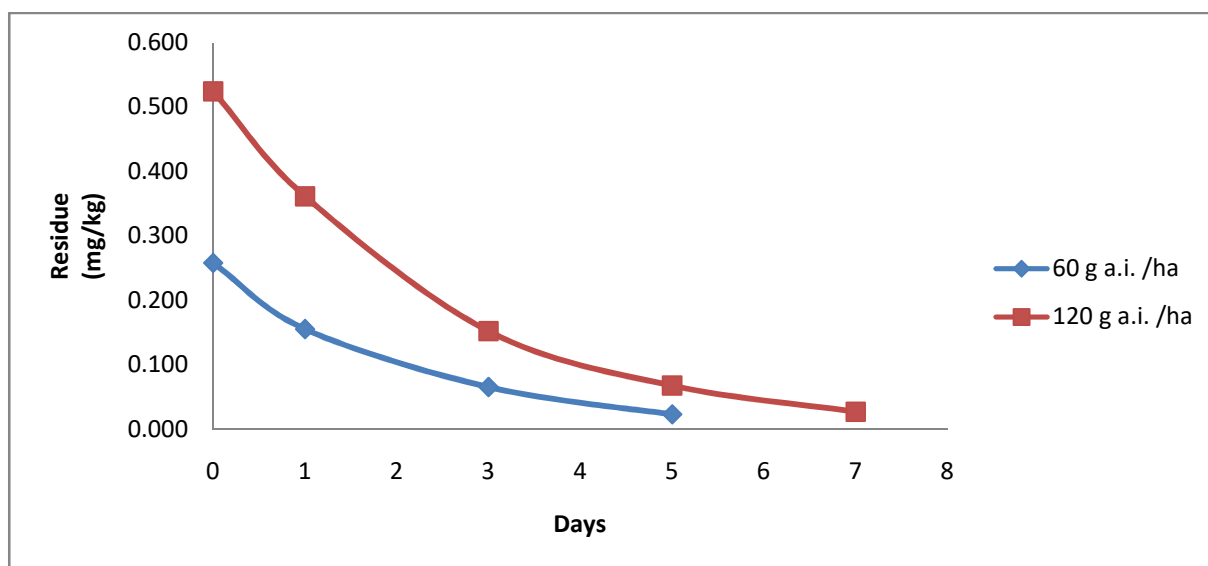


Fig 4.32 Dissipation pattern of spirotetramat (@ 60 g a.i./ha and 120 g a.i./ha) in/on chilli fruits

4.5.2.4 Initial deposits and persistence of flubendiamide in/on chilli

Initial deposits of flubendiamide on chilli fruits at single (50 g a.i./ha) and double dose (100 g a.i./ha) were found to be 0.578 mg/kg and 0.840 mg/kg, respectively. The initial

deposits at recommended dose dissipated to 0.348, 0.174, 0.075 and 0.028 mg/kg at 1, 3, 5 and 7 days with per cent dissipation ranged between 39.83-92.05 per cent and at double the recommended dose the initial deposits dissipated to 0.538, 0.268, 0.101, 0.066 and 0.025 mg/kg at 1, 3, 5, 7 and 10 days with per cent dissipation of 35.91-95.42 per cent, respectively (Table 4.78 and 4.79, Fig.4.33). From the persistence data it was concluded that the flubendiamide residues reduced to below LOQ (< 0.01 mg/kg) after 7 and 10 days at recommended and double the recommended dose on chilli fruits.

Our results were in close proximity with study conducted by Akshima (2019) who concluded that after application of flubendiamide in combi product @ 36 and 72 g a.i./ha, initial deposits of 0.423 mg/kg and 0.815 mg/kg were recorded in chilli. Following two treatments of flubendiamide @ 60 and 120 g a.i./ha, respectively, at a 10-day interval, Sahoo et al. (2009) observed average initial deposits of flubendiamide on chilli as 1.06 and 2.00 mg/kg, respectively. The residues persisted for 5 and 7 days with per cent dissipation of 85.88 and 94.15 per cent at X and 2X doses, respectively. Buddidathi et al. (2015) reported initial deposits of 0.665 and 1.545 mg/kg, respectively, on capsicum after applying flubendiamide at 48 and 96 g a.i./ha. Gautam (2019) recorded the initial deposits (0.535 and 0.921 mg/kg) of flubendiamide on okra fruits at application rates of 36 and 72 g a.i./ha which further dissipated to 87.42 and 84.21 per cent after the 10th day of treatment, respectively.

Table 4.78 Persistence of flubendiamide (@ 50 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.564	0.594	0.577	0.578±0.015	-
1	0.354	0.348	0.342	0.348±0.006	39.83
3	0.182	0.162	0.178	0.174±0.011	69.91
5	0.063	0.077	0.084	0.075±0.011	87.09
7	0.036	0.028	0.019	0.028±0.009	92.05
10	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Table 4.79 Persistence of flubendiamide (@ 100 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	0.841	0.832	0.847	0.840±0.008	-
1	0.542	0.546	0.527	0.538±0.010	35.91
3	0.278	0.265	0.261	0.268±0.009	68.10
5	0.103	0.101	0.098	0.101±0.013	88.02
7	0.075	0.069	0.053	0.066±0.011	92.18
10	0.031	0.018	0.025	0.025±0.007	95.42
15	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

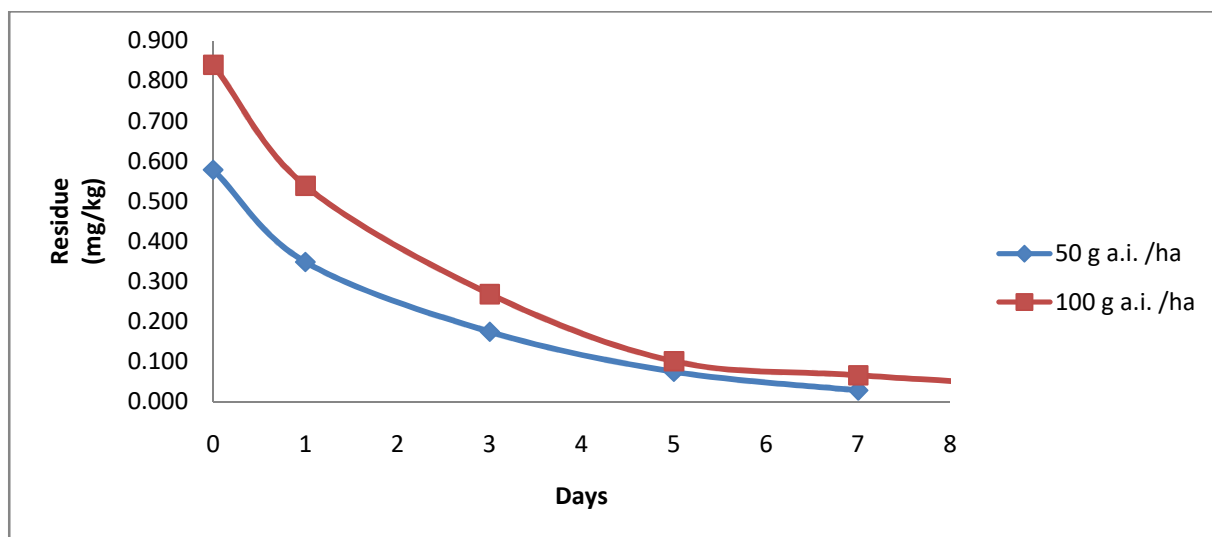


Fig 4.33 Dissipation pattern of flubendiamide (@ 50 g a.i./ha and 100 g a.i./ha) in/on chilli fruits

4.5.2.5 Initial deposits of fenazaquin in/on chilli fruits

The initial residues of fenazaquin on chilli fruits were 1.549 and 2.555 mg/kg at the application rate of 125 g a.i./ha and 250 g a.i./ha, respectively (Table 4.80 and 4.81). In chilli fruits the initial fenazaquin deposits at recommended dose were 1.64 times lower than that of double the recommended dose. Initial residues of fenazaquin on chilli fruits reduced from 1.133-0.047 mg/kg in 1 to 15 days, resulting in a dissipation of 26.83-96.94 per cent at application rate of 125 g a.i./ha. Fenazaquin residues at the application rate of 250 g a.i./ha dissipated from 1.978-0.042 mg/kg in 1 to 20 days with per cent dissipation of 22.58-98.34 per cent. From the persistence data it was concluded that the initial residues of fenazaquin were below LOQ (<0.01 mg/kg) after 15 and 20 days at single and double dose, respectively (Fig. 4.34). Our results were in close proximity with the study conducted by Patil and his co-workers (Patil et al. 2019) who applied fenazaquin (50 ml a.i./ha) on chilli fruits and observed 2.33 mg/kg initial deposits which dissipated to 91.80 per cent after 15 days of application. However, Nasr et al. (2014) reported 0.520 mg/kg initial deposits of fenazaquin (300ml/100L) on chilli fruits. Singh (2021) reported average initial fenazaquin deposits of 0.617 mg/kg and 1.221 mg/kg at 125 g a.i./ha and 250 g a.i./ha on capsicum, respectively. When sprayed at 125 g a.i./ha and 250 g a.i./ha on okra fruits, the initial deposits were gradually decreased to 0.120 mg/kg and 0.010 mg/kg after 15 and 30 days (Kaur et al. 2022a). After three, five and seven days at each of the three treatment rates (25, 50 and 125 g a.i./ha), residues on brinjal were below the LOQ (0.01 mg/kg) (Kaur et al. 2022b).

Table 4.80 Persistence of fenazaquin (@ 125 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ± SD	
0	1.556	1.543	1.548	1.549±0.007	-
1	1.121	1.133	1.146	1.133±0.013	26.83
3	0.872	0.858	0.872	0.867±0.008	44.01
5	0.617	0.611	0.621	0.616±0.005	60.21
7	0.416	0.423	0.418	0.419±0.004	72.95
10	0.213	0.204	0.209	0.209±0.005	86.53
15	0.052	0.049	0.041	0.047±0.006	96.94
20	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

Table 4.81 Persistence of fenazaquin (@ 250 g a.i./ha) in/on chilli fruits

Interval (Days)	Residues (mg/kg)				Dissipation (%)
	R ₁	R ₂	R ₃	Mean ±SD	
0	2.534	2.567	2.565	2.555±0.019	-
1	1.976	1.964	1.995	1.978±0.016	22.58
3	1.483	1.493	1.475	1.484±0.009	41.94
5	1.165	1.175	1.147	1.162±0.014	54.51
7	0.806	0.817	0.827	0.817±0.011	68.04
10	0.512	0.522	0.531	0.522±0.010	79.59
15	0.132	0.142	0.155	0.143±0.012	94.40
20	0.041	0.037	0.049	0.042±0.006	98.34
25	<LOQ	<LOQ	<LOQ	<LOQ	-
Control	ND	ND	ND	ND	-

LOQ = Limit of Quantification; ND = Not Detected

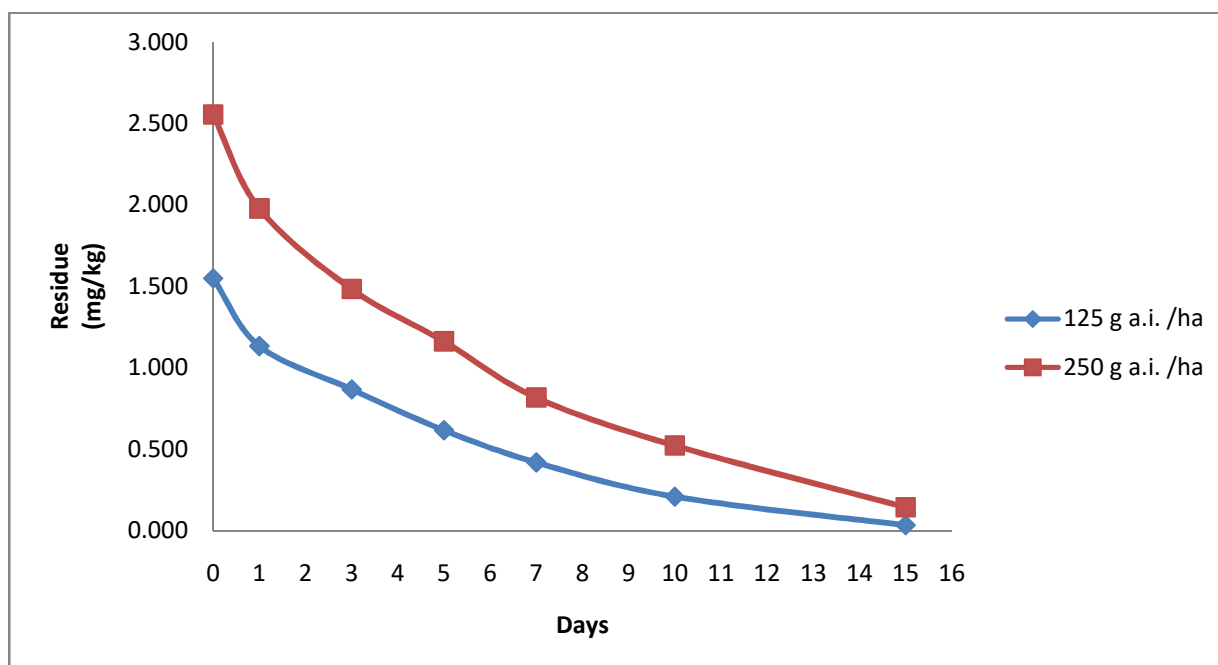


Fig 4.34 Dissipation pattern of fenazaquin (@ 125 g a.i./ha and 250 g a.i./ha) in/on chilli fruits

4.5.3 Residues of pesticides in red chilli

In red chilli fruits, the residues of cyantraniliprole, imidacloprid, spirotetramat, flubendiamide and fenazaquin were observed to be below limit of quantification (<0.01 mg/kg) at harvest (48 days) after application at single and double dose.

When the combination mix (spirotetramat 120+imidacloprid 120) - 240 w/v SC was applied at two doses of 120+120 and 240+240 g.ai./ha, no residues of imidacloprid and spirotetramat beyond the limit of quantification could be found in red chillies at harvest (Mathew et al. 2012). When treated at 1000 and 2000 ml/ha, red chilli samples taken 20 days following the last application failed to detect spirotetramat and imidacloprid at their respective detection limits (Chahil et al. 2015). After being applied at 60 and 120 a.i./ha, red chillies collected after 20 days did not show the presence of flubendiamide (Parmar et al. 2012).

4.6 Statistical constants of pesticides

The statistical constants indicating regression equations, correlation coefficients, residue half lives and waiting periods based on MRL due to the analysis of persistence data processed in accordance with Hoskins (1961). Calculations of all the pesticides under investigation in/on brinjal and chilli are presented in Tables 4.82 and 4.83.

4.6.1 Residue half life and waiting period

4.6.1.1 Residue half life and waiting period of pesticides in brinjal

4.6.1.1.1 Spiromesifen

Spiromesifen deposits from brinjal fruits dissipated to half at X dose (96 g a.i./ha) in 1.81 days and 1.85 days at 2X dose (192 g a.i./ha). The preharvest interval (PHI) for spiromesifen was determined to be 0.77 and 2.18 days at X dose (96 g a.i./ha) and 2X dose (192 g a.i./ha), respectively, for safe consumption of brinjal (Table 4.82). The findings of Vinothkumar et al. (2018), who came to the conclusion that spiromesifen dissipation followed first order reaction kinetics and that the computed half lives were 1.32 and 2.18 days with a safe waiting period of 1.40 and 2.18 days for brinjal at the rate of 96 g a.i./ha and 192 g a.i./ha dose, respectively which were in the close proximity of our investigations. Spiromesifen half-lives on brinjal were 3.64 and 4.10 days at recommended (96 g a.i./ha) and double the recommended dose (192 g a.i./ha), respectively with a safe waiting period of 1 day (Singh et al. 2021). Dubey et al. (2021) recorded half-life of spiromesifen as 1.6, 1.8, 1.9 and 1.7 days

with a safe harvesting interval of 8.9, 5.2, 6.0 and 6.9 days, respectively for okra, chilli, capsicum and brinjal. The half-life of spiromesifen on cabbage, according to Bhartiya (2018), was determined to be 1.83 and 1.89 days with a safe waiting period of 8.94 and 11.33 days at application rates of 125 and 250 g a.i./ha, respectively.

4.6.1.1.2 Fenazaquin

The initial fenazaquin deposits in brinjal fruits dissipated to half in 2.36 days at X dose (125 g a.i./ha) and 2.87 days at 2X dose (250 g a.i./ha). For the safe harvesting of brinjal fruits the waiting periods for fenazaquin were determined as 13.02 and 17.93 days following spray application at X and 2X doses, respectively (Table 4.82). Our findings are comparable to those of Nasr et al. (2009), who found that fenazaquin residues dissipated to half in 2.4 days with a suggested waiting period of 1 day for safe harvesting of tomatoes after the application at a rate of 300mL/100L. Fenazaquin had a 1.79 days half-life at the X dose (125 g a.i./ha) and a 1.85 days at 2X dose (250 g a.i./ha) with a safe consumption of tomatoes after 12.29 (X dose) and 13.07 days (2X dose), respectively (Singh 2021). At treatment rates of 125 g a.i./ha and 250 g a.i./ha, respectively, Duhan et al. (2010) reported half-life periods of 3.13 and 4.43 days on okra fruits. The 4 day waiting period for fenazaquin on brinjal was recommended by Kaur et al. (2022b).

4.6.1.1.3 Chlorantraniliprole

The data given in Table 4.82 shows that the initial deposits of chlorantraniliprole dissipated to half in 2.02 and 2.48 days when applied at the rate of 40 g a.i./ha and 80 g a.i./ha, respectively. The waiting period of 1.07 (X dose) and 3.11 days (2X dose) was suggested for chlorantraniliprole on brinjal.

The half-life of chlorantraniliprole at 30 and 60 g a.i./ha on brinjal was 1.58 and 1.80 days, but on okra, the values were 1.60 and 1.70 days and suggested a waiting period of 0.69 and 2.38 days on brinjal and 0 and 1.20 days on okra respectively (Vijayasree et al. 2015). In chilli fruits, the half-life of chlorantraniliprole was found to be 1.18 and 2.05 days at 30 and 60 g a.i./ha, respectively (Ahlawat et al. 2019). Persistence studies by Singla et al. (2020) showed that the half-lives ($t_{1/2}$) of chlorantraniliprole in okra were 2.27 and 2.45 days with a safe waiting period of 0 and 1 day when applied at application rate of 25 and 50 g a.i./ha, respectively.

4.6.1.1.4 Fenvalerate

At X dose (75 g a.i./ha) and 2 X dose (150 g a.i./ha) on brinjal, the half-lives were 2.51 and 2.65 days, respectively (Table 4.82). Since the initial deposit of fenvalerate at X dose (0.587 mg/kg) and 2X (1.233 mg/kg) was less than the FSSAI MRL (2 mg/kg), no waiting period was calculated.

When sprayed at 60 kg a.i./ha, the half-life of fenvalerate in brinjal fruits was 3.26 days (Duara et al. 2003). The findings of Nath et al. (2018), who calculated that the half-lives of fenvalerate on okra fruits varied from 2.62 and 2.24 days when applied at X dose (0.075 kg a.i./ha) and 2X dose (0.150 kg a.i./ha), respectively, are almost identical to the results of our experiment. According to Gupta and Singh (2001), the half-life of fenvalerate on cauliflower curds was 1.19 and 1.46 days at the recommended application dose of 75 g a.i./ha and double that dose (150 g a.i./ha), respectively. Bansal (2022) found that fenvalerate residues dissipated to half in 2.29 and 2.67 days when applied at application rate of 60 and 75 g a.i./ha on cabbage heads.

4.6.1.1.5 Chlorpyrifos

The data given in Table 4.82 show that chlorpyrifos residues dissipated to half (RL_{50}) at X dose (200 g a.i./ha) in 1.42 days and to 1.61 days at 2X dose (400 g a.i./ha) from brinjal fruits. For safe consumption of brinjal fruits a safe harvesting period of 3.13 and 5.15 days was suggested at X and 2X dose, respectively.

Present findings were in similarity with the study conducted by Brar (2018), who reported the dissipated half life of chlorpyrifos on brinjal as 1.55 and 2.15 days with a safe waiting period of 3.81 days and 7.13 days for single dose (300 g a.i./ha) and double dose (600 g a.i./ha), respectively. Katna et al. (2018), reported residual half-lives of chlorpyrifos in french beans as 1.86 and 2.29 days at X and 2X doses and suggested a safe waiting period of 5 days. When used as a ready-mix formulation in okra fruits, Samriti et al. (2012) observed that the half-life values of chlorpyrifos were 0.58 and 0.61 days at X dose (250 g a.i./ha) and 2X dose (500 g a.i./ha). Whereas, Singh et al. (2019b) advised waiting period of 7.05 and 9.98 days before eating any chlorpyrifos treated cucumbers at X dose (300 g a.i./ha) and 2X dose (600 g a.i./ha), respectively.

Table 4.82 Statistical constants of tested insecticides on brinjal fruits

Pesticides	Dose (g a.i. ha ⁻¹)	Statistical Constants			
		Regression equation	Correlation coefficient (R ²)	RL ₅₀ (Days)	Waiting period (Days)
Spiromesifen	96	y = -0.166-0.240x	0.986	1.81	0.77
	192	y= -0.163+0.033x	0.991	1.85	2.18
Fenazaquin	125	y= -0.127-0.287x	0.977	2.36	13.02
	250	y= -0.105-0.067x	0.991	2.87	17.93
Chlorantraniliprole	40	y= -0.149-0.085x	0.983	2.02	1.07
	80	y= -0.122+0.048x	0.981	2.48	3.11
Fenvalerate*	75	y= -0.120-0.234x	0.978	2.51	-
	150	y= -0.114+0.094x	0.986	2.65	-
Chlorpyrifos	200	y= -0.211-0.018x	0.985	1.42	3.13
	400	y= -0.187+0.271x	0.998	1.61	5.15

*Since, the initial deposits were less than the FSSAI MRL for fenvalerate on brinjal, waiting period has not been calculated.

4.6.1.2 Residue half life and waiting period of pesticides in chilli

4.6.1.2.1 Cyantraniliprole

At X dose (60 g a.i./ha), cyantraniliprole initial deposits from chilli fruits dissipated to half in 1.85 days and in 2.37 days at 2X dose (120 g a.i./ha). For the safe consumption of chilli, the preharvest interval of cyantraniliprole was found to be 1.53 and 3.81 days at X dose (60 g a.i./ha) and 2X dose (120 g a.i./ha), respectively (Table 4.83). The half-lives of cyantraniliprole dissipation in cabbage were found to be 3.5-4.2 days and 3.9-4.8 days, respectively, at application rates of 60 g a.i./ha and 120 g a.i./ha (Kumar et al. 2021). For safe consumption of okra, waiting period of 10 days is suggested for cyantraniliprole when combi product (Cyantraniliprole 7.3 % w/w + Diafenthiuron 36.4 % w/w SC) was applied @ 60 + 300 g a.i./ha (Sharma et al. 2022).

4.6.1.2.2 Imidacloprid

The data shown in Table 4.83 depicts that the half lives of imidacloprid at X dose (25 g a.i./ha) and 2 X dose (50 g a.i./ha) on chilli were 2.15 and 2.34 days with a safe waiting period of 3.30 and 4.94 days, respectively. In a study conducted by Varghese et al. (2015) dissipated half life of 2.08 days with a safe waiting period of 11.26 days for imidacloprid on chilli (@ 20 g a.i./ha) was recorded. Another study on chilli was conducted by Chahil et al. (2015) who recorded a half life 1.91 and 1.30 days at application rate of 1000 and 2000 ml/ha, respectively. For the safe harvesting of cabbage heads following spray application at single (25 g a.i./ha) and double dosage (50 g a.i./ha), the waiting period for imidacloprid have been

determined as 4.73 and 6.53 days, respectively (Bhartiya 2018). The findings of the current investigations nearly agree with those of Mandal et al. (2010) who determined the half-lives of imidacloprid on brinjal to be 2.31 and 2.18 days, at application rates of 60 and 120 g a.i./ha, respectively.

4.6.1.2.3 Spirotetramat

The information in the Table 4.83, demonstrates that the initial deposition of spirotetramat, when applied at rates of 60 g a.i./ha and 120 g a.i./ha, respectively, dissipated to half in 1.46 and 1.64 days. Since the initial deposit of spirotetramat at X dose (0.258 mg/kg) and 2X dose (0.524 mg/kg) was less than the FSSAI MRL (2 mg/kg), no waiting period was calculated.

The outcome of the current research is consistent with that of Chahil et al. (2015), who found that spirotetramat half-lives on chilli fruits were 1.91 and 1.30 days when applied at 1000 and 2000 ml/ha, respectively. Mathew et al. (2012) also conducted a study on dissipation kinetics of spirotetramat on chilli and found that residues of spirotetramat dissipated to half in 2.01 and 3.09 days at application rate of 120 and 240 g a.i./ha, respectively. Sharma (2020a) concluded in his study that residues of spirotetramat dissipated to half in 2.4 and 2.3 days when applied at 90 and 180 g a.i./ha, respectively on cabbage heads.

4.6.1.2.4 Flubendiamide

According to the data given in Table 4.83, flubendiamide residues reduced to half at X dose (50 g a.i./ha) in 1.64 days and to 1.96 days at 2X dose (100 g a.i./ha) from chilli fruits. Based on the FSSAI MRL, the safe waiting periods for flubendiamide on chilli were calculated as 7.95 and 10.58 days following pesticide treatment at X dose (50 g a.i./ha) and 2X dose (100 g a.i./ha), respectively. The findings were similar to the study conducted by Akshima (2019) on dissipation kinetics of flubendiamide on chilli and found that the half life values of flubendiamide deposits at single and double doses were 1.85 and 1.72 days with a safe waiting period of 5.71 and 6.94, respectively. According to Vemuri et al. (2016), flubendiamide half-life on capsicum fruits was 6.02 days at rate of 48 g a.i./ha. Flubendiamide half-life on tomato was determined by Paramasivam and Banerjee (2011) to be 1.64 and 1.98 days after application at 50 and 100 g a.i./ha, respectively. The flubendiamide deposits dissipated to half in 3.34 and 3.69 days with a safe waiting period of 4.74 and 8.13 days at application rate of 36 and 72 g a.i./ha from okra fruits (Gautam 2019).

4.6.1.2.5 Fenazaquin

The half lives of fenazaquin on chilli fruits were 3.10 and 3.47 days when applied at the application rate of 125 g a.i./ha and 250 g a.i./ha, respectively. The waiting periods for the safe picking of chilli fruits after spray application at X and 2X doses were calculated as 5.06 and 8.16 days, respectively (Table 4.83).

Table 4.83 Statistical constants of tested pesticides on chilli fruits

Pesticides	Dose (g a.i./ha)	Statistical Constants			
		Regression equation	Correlation coefficient (R ²)	RL ₅₀ (Days)	Waiting period (Days)
Cyantraniliprole	60	y= -0.163-0.042x	0.990	1.85	1.53
	120	y= -0.127+0.185x	0.995	2.37	3.81
Imidacloprid	25	y=-0.140-0.080x	0.980	2.15	3.30
	50	y= -0.129+0.061x	0.977	2.34	4.94
Spirotetramat*	60	y= -0.206-0.588x	0.999	1.46	-
	120	y= -0.183-0.268x	0.999	1.64	-
Flubendamide	50	y= -0.184-0.240x	0.996	1.64	7.95
	100	y= -0.153-0.119x	0.990	1.96	10.58
Fenazaquin	125	y=0.097+0.224x	0.983	3.10	5.06
	250	y= -0.087+0.456x	0.985	3.47	8.16

*Since, the initial deposits were less than the FSSAI MRL for spirotetramat on chilli; waiting period has not been calculated.

Present findings were in close proximity with Duhan et al. (2010) who found that okra fruits had half-lives of 3.13 and 4.43 days at application rates of 125 g a.i./ha and 250 g a.i./ha, respectively. When applied at the application rate of 50 g a.i./ha, Patil et al. (2019) obtained half life values of 6.57 days on chilli fruits. Singh (2021) conducted a study on persistence of fenazaquin on capsicum and concluded that the residues of fenazaquin dissipated to half in 2.06 and 2.37 days with a safe waiting period of 9.11 and 10.17 days at X dose (125 g a.i. /ha) and 2 X dose (250 g a.i./ha), respectively.

4.7 Persistence study of pesticides in soil

Nowadays, soil deterioration is regarded as one of agriculture biggest environmental problems (Squire et al. 2015). Agrochemicals are used to treat seeds and suppress weeds as well as to spray aerial plant parts, treated foliage fall to the ground and transfer polluted water on the soil surface and deeper into the soil profile which reach the soil (Chaplain et al. 2011). These chemicals are moved by leaching and surface runoff after becoming deposited in the soil. They can interact with the living portion of the soil and be biodegraded, or they can go through chemical processes such hydrolysis, photolysis and chemical degradation (Kookana et

al. 1998). Agrochemicals are more persistent in the soil and have a negative impact on the soil microbes when used heavily (Campos et al. 2019). Pesticides impact soil fertility and, eventually, plant growth through generating qualitative and quantitative changes in the soil microbiota (Hartmann et al. 2015).

4.7.1 Residues of pesticides in brinjal field soil

After being applied at X dose and 2X dose of all the five pesticides used in the investigation *viz.*, chlorantraniliprole, spiromesifen, fenazaquin, chlorpyrifos and fenvalerate residues in brinjal field soil were found to be below the limit of quantification (0.01 mg/kg) at harvest (30 days).

Present results were supported by many studies. When spiromesifen was applied at 96 g a.i./ha and 192 g a.i./ha, residues evaluated from brinjal field soil at the 0 (2 hr) day and the 10th day were below the limit of quantification (LOQ) (Singh et al. 2021). According to Siddamalliah and Mohapatra (2016), there were no spiromesifen remains in the soil of the cabbage crop during harvest (30 days after analysis). After 15 days of fenazaquin applied at the application rates of 25, 50, and 125 g a.i./ha, Kaur et al. (2022a) observed that the residues of fenazaquin in okra cropped soil were below the limit of quantification. According to Raha et al. (1993), residual levels at both the standard (0.015 %) and double (0.030 %) doses of fenvalerate 20 EC were below the level of determination in a soil sample taken from the treated brinjal field on the 15th day following the spraying. After 15 days of spraying, the chlorantraniliprole residues in the soil of the okra field were below the limit of quantification (LOQ) when administered at rates of 25 and 50 g a.i./ha (Singla et al. 2020).

4.7.2 Residues of pesticides in chilli field soil

In chilli field soil, residues of cyantraniliprole, fenazaquin, flubendiamide, imidacloprid and spirotetramat were found to be below the limit of quantification (<0.01 mg/kg) at harvest (48 days) after being applied at X doses and 2X doses.

In okra and chilli field soil the residues of flubendiamide were found to be below determination level (0.05 mg/kg) after 20 days of application of combination product of flubendiamide + deltamethrin (Fame Quick) at standard (36 + 24 g a.i./ha) and double dose (72 + 48 g a.i./ha) (Gautam 2019; Akshima 2019). According to Das et al. (2012), flubendiamide residues at single (24 g a.i./ha) and double (48 g a.i./ha) doses were found below detection

limit in soil samples taken from the treated okra field on the fifteenth day following the last spray. Sharma (2020a) found no residues of spirotetramat in cabbage cropped soil when application of 90 and 180 g a.i./ha was applied in cabbage crop. Patyal et al. (2018) recorded that spirotetramat residues in apple tree basin soil at different locations in H.P. and J. & K were below the LOQ level of 0.03 mg/kg. After 90 days of treatment, imidacloprid residues in sugarcane at single (20 g a.i./ha) and double (80 g a.i./ha) doses decreased to below the detectable level in soil (Sharma and Singh 2013). No traceable residues of imidacloprid in cucumber field soil were found when crop was sprayed at application rate of 105 and 210 g a.i./ha (Sharma 2020b).

4.8 Risk assessment

All risk associated with the use of pesticides that affects human health is a result of the manifestation of hazard and pesticide exposure. If the impending threat to human health is less and fixed, then risk found to be proportional to exposure period, which can be reduced to low and irregular (Bates 2002). The real exposure of pesticide residues can be estimated by analysing consumer's diet.

Consumer risk assessment of the chlorantraniliprole, fenvalerate, spiromesifen, chlorpyrifos, fenazaquin in brinjal fruits and cyantraniliprole, fenazaquin, imidacloprid, spirotetramat, flubendiamide in chilli fruits was performed using consumption of food, ADI values. The values of average body weight for different age groups were taken from Indian Council of Medical Research report on nutrient requirements and recommended dietary allowance (ICMR 2010).

Table 4.84 Consumption of brinjal by different age groups in rural and urban areas

Age group (years)	Average Body Weight (kg)	National capita intake (kg/person/month)		Daily intake (kg/person/day)		Consumption of brinjal (kg)	
		Rural	Urban	Rural	Urban	Rural	Urban
Men	60.0	0.428	0.358	0.143	0.012	0.00024	0.00019
Women	55.0	0.392	0.328	0.131	0.011	0.00024	0.00019
Children	1-3	0.179	0.150	0.003	0.003	0.00024	0.00019
	4-6	0.128	0.107	0.004	0.004	0.00024	0.00019
	7-9	0.092	0.077	0.006	0.005	0.00024	0.00019
Boys	10-12	0.395	0.331	0.008	0.007	0.00024	0.00019
	13-15	0.340	0.284	0.011	0.009	0.00024	0.00019
	16-18	0.245	0.205	0.013	0.011	0.00024	0.00019
Girls	10-12	0.372	0.311	0.008	0.007	0.00024	0.00019
	13-15	0.332	0.278	0.011	0.009	0.00024	0.00019
	16-18	0.250	0.209	0.012	0.010	0.00024	0.00019

The consumption data for brinjal and chilli was used in calculation of dietary risk assessment. A typical Indian adult weighing 60 kg consumes 0.428 kg and 0.358 kg of brinjal and 0.152 kg and 0.166 kg of chilli, every 30 days in the rural and urban areas, respectively, according to the National Sample Survey Office study (NSSO 2014) (Table 4.84 and Table 4.85).

Table 4.85 Consumption of chilli by different age groups in rural and urban areas

Age group (years)	Average Body Weight (kg)	National capita intake (kg/person/month)		Daily intake (kg/person/day)		Consumption of chilli (kg)		
		Rural	Urban	Rural	Urban	Rural	Urban	
Men	60.0	0.152	0.166	0.005	0.005	0.00008	0.00009	
Women	55.0	0.139	0.152	0.004	0.005	0.00008	0.00009	
Children	1-3	12.9	0.033	0.036	0.001	0.001	0.00008	0.00009
	4-6	18.0	0.046	0.050	0.001	0.002	0.00008	0.00009
	7-9	25.1	0.064	0.069	0.002	0.002	0.00008	0.00009
Boys	10-12	34.3	0.087	0.095	0.003	0.003	0.00008	0.00009
	13-15	47.6	0.121	0.132	0.004	0.004	0.00008	0.00009
	16-18	55.4	0.140	0.153	0.005	0.005	0.00008	0.00009
Girls	10-12	35.0	0.089	0.097	0.003	0.003	0.00008	0.00009
	13-15	46.6	0.118	0.129	0.004	0.004	0.00008	0.00009
	16-18	52.1	0.132	0.144	0.004	0.005	0.00008	0.00009

The average consumption of crop was calculated by converting the consumption per day. Similarly, for every age group with different average body weights the average consumption was calculated (Table 4.84 and 4.85). Risk analysis was done by considering the worst-case scenario at the highest residues of the persistence data (Tripathy et al. 2021). The MRL values and ADI values of tested pesticides are mentioned in Table 4.86 and 4.87.

Table 4.86 Risk assessment of tested pesticides in brinjal

Insecticides	Dosage (g a.i./ha)	ADI (mg/kg b.w./day)	MRL (mg/kg)	Dietary intake (kg/person/month)	
				Rural	Urban
Spiromesifen	96	0.03 (JMPR, 2005)	0.5	0.428	0.358
	192				
Fenazaquin	125	0.05 (JMPR, 2017)	0.01		
	250				
Chlorantraniliprole	40	2.00 (JMPR, 2008)	0.6		
	80				
Fenvalerate	75	0.02 (JMPR, 2012)	2		
	150				
Chlorpyrifos	200	0.01 (JMPR, 2004)	0.2		
	400				

Table 4.87 Risk assessment of tested pesticides in chilli

Insecticides	Dosage (g a.i./ha)	ADI (mg/kg b.w./day)	MRL (mg/kg)	Dietary intake (kg/person/month)	
				Rural	Urban
Cyantraniliprole	60	0.03 (JMPR, 2013)	0.5	0.152	0.166
	120				
Imidacloprid	25	0.06 (JMPR, 2008)	0.3		
	50				
Spirotetramat	60	0.05 (JMPR, 2008)	2		
	120				
Flubendiamide	50	0.02 (JMPR, 2010)	0.02		
	100				
Fenazaquin	125	0.05 (JMPR, 2017)	0.5		
	250				

4.8.1 Risk Assessment by using Hazard Quotient in brinjal

The risk evaluation in the current study estimates the hazard quotient for chlorantraniliprole, spiromesifen, chlorpyrifos and fenazaquin in brinjal fruits. Since, initial deposits obtained for fenvalerate were already less than the present MRL, pesticide is considered safe and hence, no hazard quotient has been worked out.

The results shown in Table 4.88 showed that for all the age groups with varied body weights, the EDI values of spiromesifen (@ 96 g a.i./ha) ranged between 0.145×10^{-5} - 0.675×10^{-5} and 0.121×10^{-5} - 0.565×10^{-5} mg/kg b.w./day for rural and urban habitat types, respectively. For rural and urban locations, respectively, the values of HQ were found to fall within the ranges of 0.484×10^{-4} - 2.251×10^{-4} and 0.405×10^{-4} - 1.883×10^{-4} . For children aged 1-3 and men, the highest and lowest values of HQ were seen in rural and urban areas, respectively. Spiromesifen applied at 96 g a.i./ha on brinjal was found to be safe to use because the HQ value for all age groups was found to be much lower than 1.

Table 4.88 Risk assessment of spiromesifen (@ 96 g a.i./ha) using hazard quotient

Age group (years)	Average Body weight (kg)	EDI ($\times 10^{-5}$ mg/kg b.w./day)		HQ $\times 10^{-4}$		
		Rural	Urban	Rural	Urban	
Men	60.0	0.145	0.121	0.484	0.405	
Women	55.0	0.158	0.132	0.528	0.442	
Children	1-3	12.9	0.675	0.565	2.251	1.883
	4-6	18.0	0.484	0.405	1.613	1.349
	7-9	25.1	0.347	0.290	1.157	0.968
Boys	10-12	34.3	0.254	0.212	0.847	0.708
	13-15	47.6	0.183	0.153	0.610	0.510
	16-18	55.4	0.157	0.132	0.524	0.438
Girls	10-12	35.0	0.249	0.208	0.830	0.694
	13-15	46.6	0.187	0.156	0.623	0.521
	16-18	52.1	0.167	0.140	0.557	0.466

EDI- Estimated daily intake; HQ- Hazard quotient

The EDI values of spiromesifen (@ 192 g a.i./ha) for all mentioned age groups with different body weights were ranged between 0.154×10^{-5} – 0.717×10^{-5} and 0.129×10^{-5} – 0.600×10^{-5} mg/kg b.w./day for rural and urban habitat type, respectively. The values of HQ were found in the range of 0.514×10^{-4} – 2.390×10^{-4} and 0.430×10^{-4} – 1.999×10^{-4} for rural and urban habitat type, respectively. For rural and urban, the maximum and minimum value of HQ was observed for children of 1-3 years and men, respectively (Table 4.89). The HQ value for all the age groups were found to be far less than 1, revealed that spiromesifen applied at 192 g a.i./ha on brinjal is safe to use.

Table 4.89 Risk assessment of spiromesifen (@ 192 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-5}$ mg/kg b.w./day)		HQ $\times 10^{-4}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.154	0.129	0.514	0.430
Women		55.0	0.168	0.141	0.561	0.469
Children	1-3	12.9	0.717	0.600	2.390	1.999
	4-6	18.0	0.514	0.430	1.713	1.433
	7-9	25.1	0.369	0.308	1.228	1.027
Boys	10-12	34.3	0.270	0.226	0.899	0.752
	13-15	47.6	0.194	0.163	0.648	0.542
	16-18	55.4	0.167	0.140	0.557	0.466
Girls	10-12	35.0	0.264	0.221	0.881	0.737
	13-15	46.6	0.198	0.166	0.662	0.553
	16-18	52.1	0.178	0.148	0.592	0.495

The EDI values for both the doses of fenazaquin (@125 g a.i./ha and 250 g a.i./ha) for all mentioned age groups were same and were ranged between 0.040×10^{-6} – 0.184×10^{-6} and 0.033×10^{-6} – 0.154×10^{-6} mg/kg b.w./day for rural and urban habitat type, respectively. The values of HQ were estimated in the range of 0.079×10^{-5} – 0.369×10^{-5} and 0.066×10^{-5} – 0.308×10^{-3} for rural and urban habitat type, respectively. For rural and urban, the maximum and minimum value of HQ was observed for children of 1-3 years and men, respectively. The HQ value for all the age groups were recorded to be far less than 1, showed that fenazaquin (@ 125 g a.i./ha) and fenazaquin (@ 250 g a.i./ha) sprayed on brinjal crop is safe to use (Table 4.90 and 4.91).

Table 4.90 Risk assessment of fenazaquin (@ 125 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.040	0.033	0.079	0.066
Women		55.0	0.043	0.036	0.086	0.072
Children	1-3	12.9	0.184	0.154	0.369	0.308
	4-6	18.0	0.132	0.110	0.264	0.221
	7-9	25.1	0.095	0.079	0.189	0.158
Boys	10-12	34.3	0.069	0.058	0.139	0.116
	13-15	47.6	0.050	0.042	0.100	0.084
	16-18	55.4	0.043	0.036	0.086	0.072
Girls	10-12	35.0	0.068	0.057	0.136	0.114
	13-15	46.6	0.051	0.043	0.102	0.085
	16-18	52.1	0.046	0.038	0.091	0.076

Table 4.91 Risk assessment of fenazaquin (@ 250 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.040	0.033	0.079	0.066
Women		55.0	0.043	0.036	0.086	0.072
Children	1-3	12.9	0.184	0.154	0.369	0.308
	4-6	18.0	0.132	0.110	0.264	0.221
	7-9	25.1	0.095	0.079	0.189	0.158
Boys	10-12	34.3	0.069	0.058	0.139	0.116
	13-15	47.6	0.050	0.042	0.100	0.084
	16-18	55.4	0.043	0.036	0.086	0.072
Girls	10-12	35.0	0.068	0.057	0.136	0.114
	13-15	46.6	0.051	0.043	0.102	0.085
	16-18	52.1	0.046	0.038	0.091	0.076

The EDI values of chlorantraniliprole (@ 40 g a.i./ha) in rural habitat ranged from 0.106×10^{-5} - 0.493×10^{-5} mg/kg b.w./day for the various age groups specified. The values of HQ were reported to be between 0.053×10^{-5} - 0.246×10^{-5} . In contrast, the EDI values of chlorantraniliprole in urban habitat ranged from 0.089×10^{-5} - 0.412×10^{-5} mg/kg b.w./day. The values of HQ were found to be between 0.044×10^{-5} - 0.206×10^{-5} . Children aged 1-3 years and men were found to have the highest and lowest values of HQ in both rural and urban habitats, as indicated in Table 4.92. The fact that all age groups HQ values were significantly below 1 indicated that using chlorantraniliprole on brinjal at a rate of 40 g a.i./ha was safe.

Table 4.92 Risk assessment of chlorantraniliprole (@ 40 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-5}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.106	0.089	0.053	0.044
Women		55.0	0.116	0.097	0.058	0.048
Children	1-3	12.9	0.493	0.412	0.246	0.206
	4-6	18.0	0.353	0.295	0.177	0.148
	7-9	25.1	0.253	0.212	0.127	0.106
Boys	10-12	34.3	0.185	0.155	0.093	0.078
	13-15	47.6	0.134	0.112	0.067	0.056
	16-18	55.4	0.115	0.096	0.057	0.048
Girls	10-12	35.0	0.182	0.152	0.091	0.076
	13-15	46.6	0.136	0.114	0.068	0.057
	16-18	52.1	0.122	0.102	0.061	0.051

In rural habitat type, the EDI values of chlorantraniliprole (@ 80 g a.i./ha) for different mentioned age groups were ranged between 0.099×10^{-5} – 0.459×10^{-5} mg/kg b.w./day. The values of HQ were found in the range of 0.040×10^{-5} – 0.229×10^{-5} as represented in Table 4.93. Whereas in case of urban type of habitat, the EDI values of chlorantraniliprole were ranged between 0.083×10^{-5} – 0.384×10^{-5} mg/kg b.w./day. The values of HQ were found in the range of 0.041×10^{-5} – 0.192×10^{-5} . The maximum and minimum values of HQ in rural and urban habitat were observed for children of 1-3 years and men, respectively. The HQ value for all the age groups were found to be far less than 1, suggested that chlorantraniliprole applied at 80 g a.i./ha on brinjal is not causing risk to consumers.

Table 4.93 Risk assessment of chlorantraniliprole (@80 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-5}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.099	0.083	0.049	0.041
Women		55.0	0.108	0.090	0.054	0.045
Children	1-3	12.9	0.459	0.384	0.229	0.192
	4-6	18.0	0.329	0.275	0.164	0.138
	7-9	25.1	0.236	0.197	0.118	0.099
Boys	10-12	34.3	0.173	0.144	0.086	0.072
	13-15	47.6	0.124	0.104	0.062	0.052
	16-18	55.4	0.107	0.089	0.053	0.045
Girls	10-12	35.0	0.169	0.141	0.085	0.071
	13-15	46.6	0.127	0.106	0.064	0.053
	16-18	52.1	0.114	0.095	0.057	0.048

The data presented in the Table 4.94 revealed that the EDI values of chlorpyrifos (@ 200 g a.i./ha) for all mentioned age groups were ranged between 0.027×10^{-5} – 0.125×10^{-5} and 0.022×10^{-5} – 0.104×10^{-5} mg/kg b.w./day for rural and urban habitat type, respectively. The values of HQ were estimated in the range of 2.682×10^{-5} – 12.473×10^{-5} and 2.243×10^{-5} –

10.433×10⁻⁵ for rural and urban habitat type, respectively. For rural and urban, the maximum and minimum value of HQ was observed for children of 1-3 years and men, respectively. The HQ value for all the age groups were recorded to be far less than 1, showed that chlorpyrifos (@ 200 g a.i./ha) sprayed on brinjal crop is safe to use.

Table 4.94 Risk assessment of chlorpyrifos (@ 200 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI (×10 ⁻⁵ mg/kg b.w./day)		HQ ×10 ⁻⁵	
			Rural	Urban	Rural	Urban
Men		60.0	0.027	0.022	2.682	2.243
Women		55.0	0.029	0.024	2.925	2.447
Children	1-3	12.9	0.125	0.104	12.473	10.433
	4-6	18.0	0.089	0.075	8.939	7.477
	7-9	25.1	0.064	0.054	6.410	5.362
Boys	10-12	34.3	0.047	0.039	4.691	3.924
	13-15	47.6	0.034	0.028	3.380	2.827
	16-18	55.4	0.029	0.024	2.904	2.429
Girls	10-12	35.0	0.046	0.038	4.597	3.845
	13-15	46.6	0.035	0.029	3.453	2.888
	16-18	52.1	0.031	0.026	3.088	2.583

In accordance with the data presented in Table 4.95, the EDI on chlorpyrifos (@ 400 g a.i./ha) was found to be in the range between 0.034 ×10⁻⁵ and 0.159 ×10⁻⁵ and 0.029 ×10⁻⁵ and 0.133 ×10⁻⁵ mg/kg b.w./day for rural and urban habitat types, respectively. For the urban and rural habitat types, the values of HQ were calculated to be between 2.851 ×10⁻⁵ - 13.259 ×10⁻⁵ and 3.408 ×10⁻⁵ - 15.852 ×10⁻⁵, respectively. For adults and children aged 1-3, the highest and lowest values of HQ were seen in rural and urban areas, respectively. The HQ values for all age groups were found to be much lower than 1, demonstrating the safety of using chlorpyrifos at a rate of 400 g a.i./ha on brinjal crop.

Table 4.95 Risk assessment of chlorpyrifos (@ 400 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI (×10 ⁻⁵ mg/kg b.w./day)		HQ ×10 ⁻⁵	
			Rural	Urban	Rural	Urban
Men		60.0	0.034	0.029	3.408	2.851
Women		55.0	0.037	0.031	3.718	3.110
Children	1-3	12.9	0.159	0.133	15.852	13.259
	4-6	18.0	0.114	0.095	11.360	9.502
	7-9	25.1	0.081	0.068	8.147	6.815
Boys	10-12	34.3	0.060	0.050	5.962	4.987
	13-15	47.6	0.043	0.036	4.296	3.593
	16-18	55.4	0.037	0.031	3.691	3.087
Girls	10-12	35.0	0.058	0.049	5.843	4.887
	13-15	46.6	0.044	0.037	4.388	3.670
	16-18	52.1	0.039	0.033	3.925	3.283

4.8.2 Risk Assessment by using TMDI (theoretical maximum daily intake)

Risk assessment of all five pesticides that were investigated in this experiment was also evaluated using TMDI values. The MPI (maximum permitted intake) value is greater than the TMDI (theoretical maximum daily intake) value calculated for chlorantraniliprole, chlorpyrifos, fenvalerate, fenazaquin and spiromesifen for all age groups. Hence, all of the pesticides indicated above can be used on the brinjal crop in terms of consumer safety.

The TMDI for spiromesifen in rural and urban areas was 1.189×10^{-4} and 0.994×10^{-4} mg/person/day, respectively. For various age categories, the MPI values ranged from 0.387 to 1.800 mg/person/day in both rural and urban areas (Table 4.96). The fact that the value of TMDI was found to be lower than MPI values demonstrated that spiromesifen is safe for use in both rural and urban areas for all of the indicated age groups.

Table 4.96 Risk assessment of spiromesifen (@ 96 and 192 g a.i./ha) using TMDI

Age group (years)		Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
				Rural	Urban
Men		60.0	1.800	1.189	0.994
Women		55.0	1.650	1.189	0.994
Children	1-3	12.9	0.387	1.189	0.994
	4-6	18.0	0.540	1.189	0.994
	7-9	25.1	0.753	1.189	0.994
Boys	10-12	34.3	1.029	1.189	0.994
	13-15	47.6	1.428	1.189	0.994
	16-18	55.4	1.662	1.189	0.994
Girls	10-12	35.0	1.050	1.189	0.994
	13-15	46.6	1.398	1.189	0.994
	16-18	52.1	1.563	1.189	0.994

Table 4.97 Risk assessment of fenazaquin (@ 125 and 250 g a.i./ha) using TMDI

Age group (years)		Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
				Rural	Urban
Men		60.0	3.000	0.024	0.020
Women		55.0	2.750	0.024	0.020
Children	1-3	12.9	0.645	0.024	0.020
	4-6	18.0	0.900	0.024	0.020
	7-9	25.1	1.255	0.024	0.020
Boys	10-12	34.3	1.715	0.024	0.020
	13-15	47.6	2.380	0.024	0.020
	16-18	55.4	2.770	0.024	0.020
Girls	10-12	35.0	1.750	0.024	0.020
	13-15	46.6	2.330	0.024	0.020
	16-18	52.1	2.605	0.024	0.020

The values of TMDI for fenazaquin were 0.024×10^{-4} and 0.020×10^{-4} mg/person/day for rural and urban habitat types, respectively. For various age groups in rural and urban areas, the MPI values ranged between 0.645 – 3.000 mg/person/day as shown in Table 4.97. It was reported that the value of TMDI is smaller than MPI values, indicating that the risk associated with fenazaquin for all specified age groups in rural and urban areas is acceptable.

For rural and urban areas, the TMDI values for chlorantraniliprole were 1.427×10^{-4} and 1.193×10^{-4} mg/person/day, respectively. In both rural and urban locations, the MPI values ranged from 25.80 to 120.00 mg/person/day for various age categories. It was determined that chlorantraniliprole falls under the acceptable risk range for all specified age groups in both rural and urban locations because the value of TMDI is smaller than MPI values (Table 4.98).

Table 4.98 Risk assessment of chlorantraniliprole (@ 40 and 80 g a.i./ha) using TMDI

Age group (years)	Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
			Rural	Urban
Men	60.0	120.00	1.427	1.193
Women	55.0	110.00	1.427	1.193
Children	1-3	12.9	1.427	1.193
	4-6	18.0	1.427	1.193
	7-9	25.1	1.427	1.193
Boys	10-12	34.3	1.427	1.193
	13-15	47.6	1.427	1.193
	16-18	55.4	1.427	1.193
Girls	10-12	35.0	1.427	1.193
	13-15	46.6	1.427	1.193
	16-18	52.1	1.427	1.193

Table 4.99 Risk assessment of fenvalerate (@ 75 and 150 g a.i./ha) using TMDI

Age group (years)	Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
			Rural	Urban
Men	60.0	1.200	1.189	0.994
Women	55.0	1.100	1.189	0.994
Children	1-3	12.9	1.189	0.994
	4-6	18.0	1.189	0.994
	7-9	25.1	1.189	0.994
Boys	10-12	34.3	1.189	0.994
	13-15	47.6	1.189	0.994
	16-18	55.4	1.189	0.994
Girls	10-12	35.0	1.189	0.994
	13-15	46.6	1.189	0.994
	16-18	52.1	1.042	0.994

The values of TMDI for rural and urban habitat types for fenvalerate were 1.189×10^{-4} and 0.994×10^{-4} mg/person/day, respectively. The MPI values ranged between 0.258-1.200 mg/person/day for various age groups in rural and urban areas, as shown in Table 4.99. The

risk associated with fenvalerate for all specified age groups in rural and urban areas is acceptable as TMDI is smaller than MPI values.

For rural and urban areas, the TMDI values for chlorpyrifos were 0.476×10^{-4} and 0.398×10^{-4} mg/person/day, respectively. In both rural and urban locations, the MPI values ranged from 0.129 to 0.600 mg/person/day for various age categories. It was determined that chlorpyrifos falls under the acceptable risk range for all specified age groups in both rural and urban locations because the value of TMDI is smaller than MPI values (Table 4.100).

Table 4.100 Risk assessment of chlorpyrifos (@ 200 and 400 g a.i./ha) using TMDI

Age group (years)	Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
			Rural	Urban
Men	60.0	0.600	0.476	0.398
Women	55.0	0.550	0.476	0.398
Children	1-3	12.9	0.129	0.398
	4-6	18.0	0.180	0.398
	7-9	25.1	0.251	0.398
Boys	10-12	34.3	0.343	0.398
	13-15	47.6	0.476	0.398
	16-18	55.4	0.554	0.398
Girls	10-12	35.0	0.350	0.398
	13-15	46.6	0.466	0.398
	16-18	52.1	0.521	0.476

Paramasivam (2020) estimated the dietary risk of chlorantraniliprole in tomato fruit at 30 g a.i./ha on 0, 1, 3, 5 and 7 days interval, as its EDI value came out in the range of 0.0001-0.0034 mg/kg b.w./day and the HQ value in range of 0.00003-0.0021 for adult, indicating that chlorantraniliprole did not pose a significant health risk. The cumulative dietary risk quotient (RQ) calculated based on the collective pesticide residues for chlorantraniliprole in pigeon pea present in the combi-product (Chlorantraniliprole 9.26 % + λ -cyhalothrin 4.63 % ZC) was less than 1 from 0 day (2hr) at single (30 g a.i./ha) and double dose (60 g a.i./ha) indicating no risk to consumer (Kansara et al. 2021). Sharma et al. (2014b) estimated MPI as 1.21 mg/person/day. The TMRC (Theoretical maximum residue contribution) values on day 0 were found to be 0.033, 0.014, 0.044 and 0.042 mg/kg b.w./day, as TMRC value was less than MPI value spiromesifen falls under the acceptable risk range based on data reflecting maximum residues that may occur under worst conditions on recommended dose (150 g a.i./ha). Based on the HQ values, the safety of spiromesifen has also been evaluated. The HQ was found to be 0.01, 0.004, 0.014 and 0.009 per cent, respectively, for the recommended dose (144 g a.i./ha) in okra, chilli, capsicum and brinjal. Being below the 100 % limit, this finding implies no

danger or harmful effects related to dietary residue exposure to spiromesifen (Dubey et al. 2021).

4.8.3 Risk Assessment by using Hazard Quotient in chilli

The hazard quotient for the chemicals *viz.*, cyantraniliprole, flubendiamide, fenazaquin, imidacloprid and spirotetramat in chilli fruits is estimated by the risk evaluation in the current study. Fenvalerate is regarded as safe because the initial deposits acquired for it were already below the current MRL; hence, no hazard quotient has been calculated.

For the different age groups given, the EDI values of cyantraniliprole (@ 60 g a.i./ha) in rural habitat varied from 0.384×10^{-6} – 1.787×10^{-6} mg/kg b.w./day. According to data (Table 4.101), the values of HQ ranged from 1.281×10^{-5} – 5.957×10^{-5} . In contrast, the range of cyantraniliprole EDI values in urban environments was between 0.420×10^{-6} – 1.952×10^{-6} and mg/kg b.w./day. The range of HQ values was determined to be 1.399×10^{-5} – 6.506×10^{-5} . According to Table 4.101, children aged 1-3 years and men had the highest and lowest HQ values in both rural and urban settings, respectively. Because the HQ values for all age groups were significantly lower than 1, it was determined that utilising cyantraniliprole on chilli at a rate of 60 g a.i./ha was not hazardous.

Table 4.101 Risk assessment of cyantraniliprole (@ 60 g a.i./ha) using hazard quotient

Age group (years)	Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$		
		Rural	Urban	Rural	Urban	
Men	60.0	0.384	0.420	1.281	1.399	
Women	55.0	0.419	0.458	1.397	1.526	
Children	1-3	12.9	1.787	1.952	5.957	6.506
	4-6	18.0	1.281	1.399	4.269	4.662
	7-9	25.1	0.918	1.003	3.062	3.344
Boys	10-12	34.3	0.672	0.734	2.240	2.447
	13-15	47.6	0.484	0.529	1.614	1.763
	16-18	55.4	0.416	0.454	1.387	1.515
Girls	10-12	35.0	0.659	0.719	2.196	2.398
	13-15	46.6	0.495	0.540	1.649	1.801
	16-18	52.1	0.442	0.483	1.475	1.611

The EDI values of cyantraniliprole (@ 120 g a.i./ha) for the various age groups were in the range of 0.588×10^{-6} – 2.736×10^{-6} mg/kg b.w./day in rural habitat type. As shown in Table 4.102, the values of HQ were obtained in the range of 1.961×10^{-5} – 9.121×10^{-5} . Contrarily, in urban habitats, the EDI values of cyantraniliprole varied from 0.642×10^{-6} – 2.988×10^{-6} mg/kg b.w./day. The range of HQ values was found to be between 2.142×10^{-5} – 9.961×10^{-5} . For

children aged 1-3 and men, the highest and lowest levels of HQ were found in rural and urban environments, respectively. The HQ value for all the age groups were found to be far less than 1, suggested that cyantraniliprole applied at 120 g a.i./ha on chilli will not cause risk to consumers.

Table 4.102 Risk assessment of cyantraniliprole (@ 120 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.588	0.642	1.961	2.142
Women		55.0	0.642	0.701	2.139	2.336
Children	1-3	12.9	2.736	2.988	9.121	9.961
	4-6	18.0	1.961	2.142	6.537	7.139
	7-9	25.1	1.406	1.536	4.688	5.119
Boys	10-12	34.3	1.029	1.124	3.430	3.746
	13-15	47.6	0.742	0.810	2.472	2.700
	16-18	55.4	0.637	0.696	2.124	2.319
Girls	10-12	35.0	1.009	1.101	3.362	3.671
	13-15	46.6	0.757	0.827	2.525	2.757
	16-18	52.1	0.678	0.740	2.258	2.466

The data in Table 4.103, demonstrated that for rural and urban habitat types, respectively, the EDI values of imidacloprid (@ 25 g a.i./ha) varied between 0.177×10^{-6} and 0.825×10^{-6} and 0.194×10^{-6} and 0.901×10^{-6} mg/kg b.w./day for all age categories. The values of HQ were determined to be between 0.296×10^{-5} – 1.375×10^{-5} and 0.323×10^{-5} – 1.501×10^{-5} for rural and urban habitat categories, respectively. The highest and lowest values of HQ were seen in rural and urban locations, respectively, for children ages 1-3 and men. The safety of utilizing imidacloprid (@ 25 g a.i./ha) on the chilli crop was proved by the fact that the HQ value for all age groups was reported to be substantially lower than 1.

Table 4.103 Risk assessment of imidacloprid (@ 25 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.177	0.194	0.296	0.323
Women		55.0	0.193	0.211	0.322	0.352
Children	1-3	12.9	0.825	0.901	1.375	1.501
	4-6	18.0	0.591	0.646	0.985	1.076
	7-9	25.1	0.424	0.463	0.707	0.772
Boys	10-12	34.3	0.310	0.339	0.517	0.565
	13-15	47.6	0.224	0.244	0.373	0.407
	16-18	55.4	0.192	0.210	0.320	0.350
Girls	10-12	35.0	0.304	0.332	0.507	0.553
	13-15	46.6	0.228	0.249	0.381	0.416
	16-18	52.1	0.204	0.223	0.340	0.372

According to the data in Table 4.104, the rural and urban habitat types respective EDIs for imidacloprid (@ 50 g a.i./ha) were determined to be between 0.494×10^{-6} – 2.298×10^{-6}

mg/kg b.w./day and $0.540 \times 10^{-6} - 2.509 \times 10^{-6}$ mg/kg a.i./ha, respectively. The values of HQ were determined to be between $0.823 \times 10^{-5} - 3.829 \times 10^{-5}$ and $0.899 \times 10^{-5} - 4.182 \times 10^{-5}$ for the rural and urban habitat categories, respectively. Urban and rural locations, respectively, had the greatest and lowest levels of HQ for children ages 1-3 and men. Imidacloprid can be used safely on chilli crop at a rate of 50 g a.i./ha because the HQ values for all age groups were found to be substantially lower than 1, supporting this claim.

Table 4.104 Risk assessment of imidacloprid (@ 50 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.494	0.540	0.823	0.899
Women		55.0	0.539	0.589	0.898	0.981
Children	1-3	12.9	2.298	2.509	3.829	4.182
	4-6	18.0	1.647	1.798	2.744	2.997
	7-9	25.1	1.181	1.290	1.968	2.149
Boys	10-12	34.3	0.864	0.944	1.440	1.573
	13-15	47.6	0.623	0.680	1.038	1.133
	16-18	55.4	0.535	0.584	0.892	0.974
Girls	10-12	35.0	0.847	0.925	1.411	1.541
	13-15	46.6	0.636	0.695	1.060	1.158
	16-18	52.1	0.569	0.621	0.948	1.036

According to the results presented in Table 4.105 and 4.106, the EDI values of both flubendiamide (@ 50 g a.i./ha) and flubendiamide (@ 100 g a.i./ha) for all age groups with varying body weights were same and ranged between $0.014 \times 10^{-6} - 0.065 \times 10^{-6}$ and $0.015 \times 10^{-5} - 0.071 \times 10^{-6}$ mg/kg b.w./day for rural and urban habitat types, respectively.

Table 4.105 Risk assessment of flubendiamide (@ 50 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.014	0.015	0.070	0.077
Women		55.0	0.015	0.017	0.077	0.084
Children	1-3	12.9	0.065	0.071	0.327	0.357
	4-6	18.0	0.047	0.051	0.235	0.256
	7-9	25.1	0.034	0.037	0.168	0.184
Boys	10-12	34.3	0.025	0.027	0.123	0.134
	13-15	47.6	0.018	0.019	0.089	0.097
	16-18	55.4	0.015	0.017	0.076	0.083
Girls	10-12	35.0	0.024	0.026	0.121	0.132
	13-15	46.6	0.018	0.020	0.091	0.099
	16-18	52.1	0.016	0.018	0.081	0.089

The values of HQ were discovered to fall within the ranges of $0.070 \times 10^{-5} - 0.327 \times 10^{-5}$ and $0.077 \times 10^{-5} - 0.357 \times 10^{-5}$ for rural and urban areas, respectively. The highest and lowest levels of HQ were found in rural and urban locations, respectively, for children ages 1-3 and males. Since the HQ value for all age groups was substantially lower than 1, flubendiamide applied at 50 g a.i./ha and 100 g a.i./ha on chilli was determined to be safe to use.

Table 4.106 Risk assessment of flubendiamide (@ 100 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.014	0.015	0.070	0.077
Women		55.0	0.015	0.017	0.077	0.084
Children	1-3	12.9	0.065	0.071	0.327	0.357
	4-6	18.0	0.047	0.051	0.235	0.256
	7-9	25.1	0.034	0.037	0.168	0.184
Boys	10-12	34.3	0.025	0.027	0.123	0.134
	13-15	47.6	0.018	0.019	0.089	0.097
	16-18	55.4	0.015	0.017	0.076	0.083
Girls	10-12	35.0	0.024	0.026	0.121	0.132
	13-15	46.6	0.018	0.020	0.091	0.099
	16-18	52.1	0.016	0.018	0.081	0.089

The EDI values for fenazaquin (@ 125 g a.i./ha) for all mentioned age groups were ranged between $0.590 \times 10^{-6} - 2.743 \times 10^{-6}$ and $0.644 \times 10^{-6} - 2.995 \times 10^{-6}$ mg/kg b.w./day for rural and urban habitat type, respectively. The values of HQ were estimated in the range of $1.179 \times 10^{-5} - 5.486 \times 10^{-5}$ and $1.288 \times 10^{-5} - 5.991 \times 10^{-5}$ for rural and urban habitat type, respectively (Table 4.107). For rural and urban, the maximum and minimum value of HQ was observed for children of 1-3 years and men, respectively. The HQ value for all the age groups were recorded to be far less than 1, showed that fenazaquin (@ 125 g a.i./ha) sprayed on chilli crop is safe to use.

Table 4.107 Risk assessment of fenazaquin (@ 125 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.590	0.644	1.179	1.288
Women		55.0	0.643	0.703	1.287	1.405
Children	1-3	12.9	2.743	2.995	5.486	5.991
	4-6	18.0	1.966	2.147	3.931	4.293
	7-9	25.1	1.410	1.539	2.819	3.079
Boys	10-12	34.3	1.032	1.127	2.063	2.253
	13-15	47.6	0.743	0.812	1.487	1.624
	16-18	55.4	0.639	0.697	1.277	1.395
Girls	10-12	35.0	1.011	1.104	2.022	2.208
	13-15	46.6	0.759	0.829	1.519	1.658
	16-18	52.1	0.679	0.742	1.358	1.483

The data in Table 4.108 showed that the EDI values for fenazaquin (@ 250 g a.i./ha) for all mentioned age groups were ranged between 0.734×10^{-6} – 3.415×10^{-6} and 0.802×10^{-6} – 3.729×10^{-6} mg/kg b.w./day for rural and urban habitat type, respectively. The values of HQ were estimated in the range of 1.468×10^{-5} – 6.830×10^{-5} and 1.604×10^{-5} – 7.459×10^{-5} for rural and urban habitat type, respectively. For rural and urban, the maximum and minimum value of HQ was observed for children of 1-3 years and men, respectively. The HQ value for all the age groups were recorded to be far less than 1, showed that fenazaquin (@ 250 g a.i./ha) sprayed on chilli crop is safe to use.

Table 4.108 Risk assessment of fenazaquin (@ 250 g a.i./ha) using hazard quotient

Age group (years)		Average Body weight (kg)	EDI ($\times 10^{-6}$ mg/kg b.w./day)		HQ $\times 10^{-5}$	
			Rural	Urban	Rural	Urban
Men		60.0	0.734	0.802	1.468	1.604
Women		55.0	0.801	0.875	1.602	1.749
Children	1-3	12.9	3.415	3.729	6.830	7.459
	4-6	18.0	2.447	2.673	4.895	5.345
	7-9	25.1	1.755	1.917	3.510	3.833
Boys	10-12	34.3	1.284	1.403	2.569	2.805
	13-15	47.6	0.925	1.011	1.851	2.021
	16-18	55.4	0.795	0.868	1.590	1.737
Girls	10-12	35.0	1.259	1.375	2.517	2.749
	13-15	46.6	0.945	1.032	1.891	2.065
	16-18	52.1	0.846	0.923	1.691	1.847

4.8.4 Risk Assessment by using TMDI (theoretical maximum daily intake)

Using TMDI values, the risk associated with each of the five pesticides examined in this trial was assessed. All age groups have an MPI value that is higher than the TMDI value for cyantraniliprole, flubendiamide, imidacloprid and fenazaquin. In light of the safety of consumers, all of the pesticides mentioned above may be applied to the chilli crop.

Table 4.109 Risk assessment of cyantraniliprole (@ 60 and 120 g a.i./ha) using TMDI

Age group (years)		Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
				Rural	Urban
Men		60.0	1.800	0.422	0.461
Women		55.0	1.650	0.422	0.461
Children	1-3	12.9	0.387	0.422	0.461
	4-6	18.0	0.540	0.422	0.461
	7-9	25.1	0.753	0.422	0.461
Boys	10-12	34.3	1.029	0.422	0.461
	13-15	47.6	1.428	0.422	0.461
	16-18	55.4	1.662	0.422	0.461
Girls	10-12	35.0	1.050	0.422	0.461
	13-15	46.6	1.398	0.422	0.461
	16-18	52.1	1.563	0.422	0.461

The TMDI values for cyantranilprole in rural and urban areas 0.422×10^{-4} and 0.461×10^{-4} mg/person/day, respectively. For different age groups, the MPI values in both rural and urban areas ranged from 0.387 to 1.800 mg/person/day. Because the value of TMDI is lower than MPI values, it has been established that cyantranilprole is below the acceptable risk range for all specified age groups in both rural and urban areas (Table 4.109).

Table 4.110 Risk assessment of imidacloprid (@ 25 and 50 g a.i./ha) using TMDI

Age group (years)	Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
			Rural	Urban
Men	60.0	3.600	0.253	0.277
Women	55.0	3.300	0.253	0.277
Children	1-3	12.9	0.774	0.253
	4-6	18.0	1.080	0.253
	7-9	25.1	1.506	0.253
Boys	10-12	34.3	2.058	0.253
	13-15	47.6	2.856	0.253
	16-18	55.4	3.324	0.253
Girls	10-12	35.0	2.100	0.253
	13-15	46.6	2.796	0.253
	16-18	52.1	3.126	0.253

According to the data given in Table 4.110, the TMDI values for imidacloprid in rural and urban areas were 0.253×10^{-4} and 0.277×10^{-4} mg/person/day, respectively. For different age groups, the MPI values in both rural and urban areas ranged from 0.774 to 3.600 mg/person/day. Because the value of TMDI is lower than MPI values, it has been established that imidacloprid is below the acceptable risk range for all specified age groups in both rural and urban areas.

Table 4.111 Risk assessment of spirotetramat (@ 60 and 120 g a.i./ha) using TMDI

Age group (years)	Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
			Rural	Urban
Men	60.0	3.000	0.422	0.461
Women	55.0	2.750	0.422	0.461
Children	1-3	12.9	0.645	0.422
	4-6	18.0	0.900	0.422
	7-9	25.1	1.255	0.422
Boys	10-12	34.3	1.715	0.422
	13-15	47.6	2.380	0.422
	16-18	55.4	2.770	0.422
Girls	10-12	35.0	1.750	0.422
	13-15	46.6	2.330	0.422
	16-18	52.1	2.605	0.422

For rural and urban habitat categories, the TMDI for spirotetramat were same as that of fenazaquin i.e. 0.422×10^{-4} and 0.461×10^{-4} mg/person/day, respectively. The MPI values ranged from 0.645 to 3.000 mg/person/day for different age groups in rural and urban locations, as shown in Table 4.111. The risk associated with spirotetramat for all specified age groups in rural and urban areas was reported to be acceptable because the value of TMDI is smaller than MPI values.

Table 4.112 Risk assessment of flubendiamide (@ 50 and 100 g a.i./ha) using TMDI

Age group (years)		Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
				Rural	Urban
Men		60.0	1.200	0.017	0.018
Women		55.0	1.100	0.017	0.018
Children	1-3	12.9	0.258	0.017	0.018
	4-6	18.0	0.360	0.017	0.018
	7-9	25.1	0.502	0.017	0.018
Boys	10-12	34.3	0.686	0.017	0.018
	13-15	47.6	0.952	0.017	0.018
	16-18	55.4	1.108	0.017	0.018
Girls	10-12	35.0	0.700	0.017	0.018
	13-15	46.6	0.932	0.017	0.018
	16-18	52.1	1.042	0.017	0.018

The TMDI for flubendiamide was 0.017×10^{-4} and 0.018×10^{-4} mg/person/day in rural and urban area, respectively. In both rural and urban locations, the MPI values for various age groups ranged from 0.360 to 1.200 mg/person/day (Table 4.112). It was shown that flubendiamide is safe for usage in both rural and urban regions for all of the stated age groups because the value of TMDI was determined to be lower than MPI values.

Table 4.113 Risk assessment of fenazaquin (@ 125 and 250 g a.i./ha) using TMDI

Age group (years)		Average Body weight (kg)	MPI (mg/person/day)	TMDI ($\times 10^{-4}$ mg/person/day)	
				Rural	Urban
Men		60.0	3.000	0.422	0.461
Women		55.0	2.750	0.422	0.461
Children	1-3	12.9	0.645	0.422	0.461
	4-6	18.0	0.900	0.422	0.461
	7-9	25.1	1.255	0.422	0.461
Boys	10-12	34.3	1.715	0.422	0.461
	13-15	47.6	2.380	0.422	0.461
	16-18	55.4	2.770	0.422	0.461
Girls	10-12	35.0	1.750	0.422	0.461
	13-15	46.6	2.330	0.422	0.461
	16-18	52.1	2.605	0.422	0.461

For rural and urban habitat categories, the TMDI for fenazaquin were 0.422×10^{-4} and 0.461×10^{-4} mg/person/day, respectively. The MPI values ranged from 0.645 to 3.000 mg/person/day for different age groups in rural and urban locations, as shown in Table 4.113. The risk associated with fenazaquin for all specified age groups in rural and urban areas was reported to be acceptable because the value of TMDI is smaller than MPI values.

According to Kumar et al. (2021), cyantraniliprole in cabbage head poses an estimated dietary risk of 0.0001-0.0015 mg/kg b.w./day at single dose (60 g a.i./ha) and 0.0005-0.0043 mg/kg b.w./day at double dose (120 g a.i./ha). Risk quotient (RQ) values ranged from 0.2902 to 0.0116 at X dose and from 0.4676 to 0.0295 at 2X dose. RQ values in every case were substantially lower than 1, demonstrating that even after two subsequent applications of cyantraniliprole on cabbage, there is virtually minimal danger of food exposure for people. Chawla et al. (2018) assess the dietary risk of beta-cyfluthrin and imidacloprid as parts of a combi product in/on chickpea. HQ for beta-cyfluthrin was 0.0010-0.0011 for standard dose and 0.0013-0.0015 for double dose while the corresponding values for imidacloprid were 0.0015-0.0018 and 0.0016-0.0018, respectively. The results showed that the use of beta-cyfluthrin and imidacloprid as a combi-product on chickpea was safe provided that proper PHI was followed. According to Dikshit et al. (2003), the use of beta-cyfluthrin and imidacloprid on tomato crops was safe because their TMDI values (0.046 mg/person/day for beta-cyfluthrin and 0.10 mg/person/day for imidacloprid) were substantially lower than their MPI values, making them suitable for usage.

Chapter-5

SUMMARY AND CONCLUSION

The present investigation “**Bioefficacy and residue dynamics of some pesticides used against insect pests of brinjal and chilli**” was carried out in the Department of Entomology, Dr. Y.S. Parmar University of Horticulture and Forestry, Nauni, Solan (H.P.). The obtained experimental results are summarized as:

- The results of bioefficacy study on brinjal revealed that treatment T₆ (fenazaquin 10% EC @ 250 g a.i./ha) was most effective against jassids with 81.98 and 82.80 per cent reduction in 2021 and 2022, respectively. Treatment T₁₀ (fenvaterate 20% EC @ 60 g a.i./ha) was the least effective against jassids with 34.33 and 37.65 per cent reduction during 2021 and 2022, respectively .
- Bioefficacy studies carried out against brinjal shoot and fruit borer revealed that treatment T₉ (chlorantraniliprole 18.5% SC @ 80 g a.i./ha) recorded minimum shoot infestation during both the years (2021 and 2022) with 2.22 and 2.45 per cent infestation, respectively. Whereas, maximum infestation was observed in untreated control with 21.00 and 16.30 per cent infestation during 2021 and 2022, respectively. The minimum fruit damage was found in the plots treated with T₉ (chlorantraniliprole 18.5% SC @ 80 g a.i./ha) with 6.78 and 6.13 per cent. Whereas, maximum in the untreated control i.e. 35.97 and 33.32 per cent during 2021 and 2022, respectively.
- The bioefficacy studies on chilli thrips revealed that treatment T₃ (cyantraniliprole 10.26% OD @ 120 g a.i./ha) was the most effective in both the years (2021 and 2022) providing 83.06 and 85.27 per cent overall reduction, respectively, whereas, treatment T₁₀ (flubendiamide 20% WG @ 38 g a.i./ha) was the least effective against chilli thrips during both the years with 33.24 and 35.80 per cent reduction, respectively.
- The results of both the years revealed that there were no phytotoxicity symptoms like leaf injury, wilting, vein clearing, necrosis, epinasty, hyponasty were observed on brinjal and chilli crop after application of pesticides.
- Brinjal crop treated with different pesticides showed that the maximum population of coccinellids after control was recorded in chlorantraniliprole 18.5%SC (@ 30 g a.i./ha) with a count of 0.71 and 0.65 and minimum in chlorpyrifos 20% EC (@ 400 g a.i./ha) with a count of 0.22 and 0.27 during 2021 and 2022, respectively.

- In case of chilli, the maximum population of coccinellids after control was recorded in flubendiamide (20% WG) (<X) with a count of 0.73 and 0.61 and minimum in Imidacloprid (17.8% SL) (2X) with a count of 0.27 and 0.26 in 2021 and 2022, respectively.
- Highest benefit cost ratio of 4.22:1 and 4.29:1 was recorded in the brinjal plots treated with chlorantraniliprole 18.5% SC @ 40 g a.i./ha whereas lowest benefit cost ratio was in the control during 2021 and 2022, respectively. In case of chilli, highest benefit cost ratio of 2.98:1 and 3.11:1 was obtained in the treatment cyantraniliprole 10.26% OD @ 60 g a.i./ha, whereas lowest benefit cost ratio in the control during 2021 and 2022, respectively.
- The efficiency of QuEChERS analytical method was validated for the analysis of pesticides in brinjal and chilli using parameters *viz.*, system precision, linearity, accuracy, repeatability, reproducibility, ruggedness and the measurement uncertainty according to the set guidelines by SANCO. The per cent recovery and RSD were within the acceptance range. Hence, the validated QuEChERS method qualified all the requisite analytical parameters and was adopted to study the persistence of chlorantraniliprole, spiromesifen, chlorpyrifos, fenvalerate and fenazaquin on brinjal and cyantraniliprole, flubendiamide, fenazaquin, spirotetramat and imidacloprid on chilli.
- The average initial deposits of spiromesifen on brinjal fruits were 0.672 and 1.133 mg/kg @ 96 and 192 g a.i./ha which dissipated to 0.045 and 0.026 mg/kg, respectively after 7 and 10 days of spray, respectively.
- At the application rates of 125 and 250 g a.i./ha of fenazaquin on brinjal fruits, the average initial deposits were 0.457 and 0.761 mg/kg which dissipated to 0.024 and 0.020 mg/kg after 10 and 15 days of spray, respectively
- On brinjal fruits, the average initial deposits of chlorantraniliprole @ 40 and 80 g a.i./ha were 0.867 and 1.433 mg/kg which dissipated to 0.033 and 0.022 mg/kg after 10 and 15 days of spray, respectively.
- The average initial deposits of fenvalerate on brinjal fruits were 0.587 and 1.233 mg/kg @ 75 and 150 g a.i./ha which dissipated to 0.041 and 0.029 mg/kg after 10 and 15 days of spray, respectively.
- On brinjal fruits, the average initial deposits of chlorpyrifos @ 200 and 400 g a.i./ha were 0.918 and 1.825 mg/kg which reduced to 0.033 and 0.025 after 7 and 10 days of spray, respectively.

- On chilli fruits, the average initial deposits were 0.886 and 1.525 mg/kg after application of cyantraniliprole @ 60 and 120 g a.i./ha which dissipated to 0.023 and 0.019 mg/kg after 10 and 15 days of spray, respectively.
- The average initial deposits of imidacloprid @ 25 and 50 g a.i./ha were 0.869 and 1.301 mg/kg which dissipated to 0.039 and 0.033 mg/kg after 10 and 15 days of spray in chilli, respectively.
- After application of spirotetramat @ 60 and 120 g a.i./ha the initial deposits on chilli fruits were 0.258 and 0.524 mg/kg which dissipated to 0.023 and 0.027 mg/kg after 5 and 7 days, respectively.
- On chilli fruits the initial residues of flubendiamide @ 50 and 100 g a.i./ha were 0.578 and 0.840 mg/kg which dissipated to 0.028 and 0.025 after 7 and 10 days of application, respectively.
- The average initial deposits of fenazaquin @ 125 and 250 g a.i./ha were 1.549 and 2.555 mg/kg which dissipated to 0.047 and 0.042 mg/kg after 15 and 20 days of application on chilli fruits, respectively.
- The residues of cyantraniliprole, imidacloprid, spirotetramat, flubendiamide and fenazaquin in red chilli were observed below the limit of quantification (LOQ) of 0.01 mg/kg at harvest (48 days) when applied at recommended and double the recommended dose.
- The half-life calculated for spiromesifen (@ 96 and 192 g a.i./ha), fenazaquin (@ 125 and 250 g a.i./ha), chlorantraniliprole (@ 40 and 80 g a.i./ha), fenvalerate (@ 75 and 150 g a.i./ha) and chlorpyrifos (@ 200 and 400 g a.i./ha) were 1.81 and 1.85, 2.36 and 2.87, 2.02 and 2.48, 2.51 and 2.65, 2.36 and 2.87 days, respectively on brinjal fruits.
- The safe waiting period suggested for spiromesifen (@ 96 and 192 g a.i./ha), fenazaquin (@ 125 and 250 g a.i./ha), chlorantraniliprole (@ 40 and 80 g a.i./ha) and chlorpyrifos (@ 200 and 400 g a.i./ha) were 0.77 and 2.18, 13.02 and 17.93, 1.07 and 3.11, 3.13 and 5.15 days, respectively on brinjal fruits. The waiting period of fenvalerate was not calculated as the initial residues of fenvalerate on brinjal were less than the FSSAI MRL.
- The half-life calculated for cyantraniliprole (@ 60 and 120 g a.i./ha), imidacloprid (@ 25 and 50 g a.i./ha), spirotetramat (@ 60 and 120 g a.i./ha), flubendiamide (@ 50 and 100 g a.i./ha) and fenazaquin (@ 125 and 250 g a.i./ha) were 1.85 and 2.37, 2.15 and 2.34, 1.46 and 1.64, 1.64 and 1.96, 3.10 and 3.47 days, respectively on chilli fruits.

- The safe waiting period suggested for cyantraniliprole (@ 60 and 120 g a.i./ha), imidacloprid (@ 25 and 50 g a.i./ha), flubendiamide (@ 50 and 100 g a.i./ha) and fenazaquin (@ 125 and 250 g a.i./ha) was 1.53 and 3.81, 3.30 and 4.94, 7.95 and 10.58, 5.06 and 8.16 days, respectively on chilli fruits. Since the initial deposits of spirotetramat in chilli were less than the FSSAI MRL, so, waiting period has not been calculated.
- The residues of chlorantraniliprole, spiromesifen, chlorpyrifos, fenvalerate and fenazaquin in brinjal field soil and cyantraniliprole, flubendiamide, fenazaquin, spirotetramat and imidacloprid in chilli field soil were observed below the limit of quantification (LOQ) at harvest, as applied at the recommended and two times the recommended dose.
- The risk assessment of chlorantraniliprole, spiromesifen, chlorpyrifos, fenvalerate and fenazaquin on brinjal and cyantraniliprole, flubendiamide, fenazaquin, spirotetramat and imidacloprid on chilli calculated as hazard quotient was less than 1 for all different age categories in both urban and rural areas, thereby implying the safety of all tested insecticides on brinjal and chilli crop. Another approach of risk assessment is theoretical maximum daily intake used in current study for all tested insecticides were observed to be less than maximum permissible intake, thus indicating the tested insecticides were safe when proper PHI is followed.

CONCLUSIONS

- From the bioefficacy study of different pesticides against jassids in brinjal, it was concluded that fenazaquin @ 192 g a.i./ha was the most effective in reducing the jassids population and in case of shoot and fruit borer, chlorantraniliprole @ 80 g a.i./ha was found more significant in reducing the infestation caused by the borer. Among all the pesticides used in chilli crop against thrips, cyantraniliprole @ 120 g a.i./ha proved to be more effective in reducing the thrips population. The pesticides at recommended and double the recommended dose on both the crops did not show any phytotoxic symptoms. All the pesticides used in the study proved to be safer for natural enemies (coccinellids) on both the crops.
- Validation of QuEChERS method employed in the laboratory fulfilled all analytical parameters for all the pesticides with respect to specificity, recovery, accuracy, linearity and precisions which were within the acceptance range.

- Dissipation studies in brinjal and chilli showed that all the pesticides followed first order kinetics. The residues of chlorantraniliprole, spiromesifen, chlorpyrifos, fenvalerate and fenazaquin on brinjal persisted between 10 – 15 days at X dose and 15 – 20 days at 2X dose with a half lives in the range of 1.42 – 2.51 days and 1.61 – 2.87 days at single and double dose, respectively.
- In case of green chilli fruits, residues of cyantraniliprole, flubendiamide, fenazaquin, spirotetramat and imidacloprid on chilli fruits persisted between 7 – 20 days at X dose and 15 – 25 days at 2X dose with a half life in the range between 1.46 – 3.47 days (X dose) and 1.64 – 3.47 days (2X dose). However the residues were below LOQ in red chilli fruits at harvest.
- In brinjal and chilli field soil the residues detected were below limit of quantification at harvest after last application at both X and 2X dose for all the tested pesticides.
- From the present investigation it was concluded that brinjal fruits should be harvested following the safe waiting period of 2-3 days for all the tested pesticides viz., spiromesifen, fenazaquin, chlorantraniliprole and chlorpyrifos. Whereas, preharvest interval (PHI) of 5-11 days should be followed for harvesting chilli fruits when tested with cyantraniliprole, imidacloprid, spirotetramat and flubendiamide.
- Risk assessment studies showed that risk for the all tested pesticides in brinjal and chilli is considered safe for all age groups in both rural and urban regions.

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APPENDIX –I

Bioefficacy of pesticides against jassids on brinjal after first spray in 2021

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	4	256.255
Factor B	14	514.143
Interaction A X B	56	181.792
Error	148	6.199
Total	224	

APPENDIX –II

Bioefficacy of pesticides against jassids on brinjal after second spray in 2021

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	4	457.003
Factor B	14	1254.641
Interaction A X B	56	24.444
Error	148	9.051
Total	224	

APPENDIX –III

Bioefficacy of pesticides against jassids on brinjal after first spray in 2022

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	14	425.817
Factor B	4	361.841
Interaction A X B	56	190.02
Error	148	4.349
Total	224	

APPENDIX –IV

Bioefficacy of pesticides against jassids on brinjal after second spray in 2022

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	14	459.901
Factor B	4	358.332
Interaction A X B	56	212.835
Error	148	5.283
Total	224	

APPENDIX –V

Effect of different pesticides treatments on shoot infestation by shoot and fruit borer of brinjal after first spray during 2021

Source of Variation	df	Mean Sum of Squares (MSS)	
		5 th day	10 th day
Replication	2	0.132	0.045
Treatment	15	1.006	1.589
Error	30	0.036	0.071
Total	47		

APPENDIX –VI

Effect of different pesticides treatments on shoot infestation by shoot and fruit borer of brinjal after second spray during 2021

Source of Variation	df	Mean Sum of Squares (MSS)	
		5 th day	10 th day
Replication	2	0.132	0.045
Treatment	15	1.006	1.589
Error	30	0.036	0.071
Total	47		

APPENDIX –VII

Effect of different pesticides treatments on shoot infestation by shoot and fruit borer of brinjal after first spray during 2022

Source of Variation	df	Mean Sum of Squares (MSS)	
		5 th day	10 th day
Replication	2	0.016	0.007
Treatment	15	0.619	1.462
Error	30	0.022	0.025
Total	47		

APPENDIX –VIII

Effect of different pesticides treatments on shoot infestation by shoot and fruit borer of brinjal after second spray during 2022

Source of Variation	df	Mean Sum of Squares (MSS)	
		5 th day	10 th day
Replication	2	0.004	0.128
Treatment	15	1.375	1.995
Error	30	0.036	0.038
Total	47		

APPENDIX –IX

Effect of different pesticides treatments on fruit infestation by shoot and fruit borer of brinjal after first and second spray during 2021

Source of Variation	df	Mean Sum of Squares (MSS)	
		1 st spray	2 nd spray
Replication	2	0.318	0.070
Treatment	15	1.751	2.911
Error	30	0.058	0.045
Total	47		

APPENDIX –X

Effect of different pesticides treatments on fruit infestation by shoot and fruit borer of brinjal after first and second spray during 2022

Source of Variation	df	Mean Sum of Squares (MSS)	
		1 st spray	2 nd spray
Replication	2	0.176	0.182
Treatment	15	1.642	2.643
Error	30	0.103	0.060
Total	47		

APPENDIX –XI

Effect of pesticides on the population of coccinellids after first spray in brinjal during 2021

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	15	0.073
Factor B	4	0.003
Interaction A X B	60	0.030
Error	158	0.006
Total	239	

APPENDIX –XII

Effect of pesticides on the population of coccinellids after second spray in brinjal during 2021

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	15	0.069
Factor B	4	0.005
Interaction A X B	60	0.034
Error	158	0.006
Total	239	

APPENDIX –XIII

Effect of pesticides on the population of coccinellids after first spray in brinjal during 2022

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	15	0.045
Factor B	4	0.001
Interaction A X B	60	0.023
Error	158	0.004
Total	239	

APPENDIX –XIV

Effect of pesticides on the population of coccinellids after second spray in brinjal during 2022

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	15	0.076
Factor B	4	0.001
Interaction A X B	60	0.031
Error	158	0.005
Total	239	

APPENDIX –XV

Bioefficacy of pesticides against thrips on chilli after first spray during 2021

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	14	511.311
Factor B	4	312.202
Interaction A X B	56	214.774
Error	148	5.217
Total	224	

APPENDIX –XVI

Bioefficacy of pesticides against thrips on chilli after second spray during 2021

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	14	661.153
Factor B	4	272.441
Interaction A X B	56	213.057
Error	148	5.847
Total	224	

APPENDIX –XVII

Bioefficacy of pesticides against thrips on chilli after first spray during 2022

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	14	622.91
Factor B	4	233.289
Interaction A X B	56	206.878
Error	148	3.377
Total	224	

APPENDIX –XVIII

Bioefficacy of pesticides against thrips on chilli after second spray during 2022

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	14	601.948
Factor B	4	306.149
Interaction A X B	56	198.873
Error	148	5.46
Total	224	

APPENDIX –XIX

Effect of pesticides on the population of coccinellids after first spray in chilli during 2021

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	15	0.028
Factor B	4	0.005
Interaction A X B	60	0.025
Error	158	0.005
Total	239	

APPENDIX –XX

Effect of pesticides on the population of coccinellids after second spray in chilli during 2021

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	15	0.031
Factor B	4	0.002
Interaction A X B	60	0.037
Error	158	0.004
Total	239	

APPENDIX –XXI

Effect of pesticides on the population of coccinellids after first spray in brinjal during 2022

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	15	0.019
Factor B	4	0.001
Interaction A X B	60	0.015
Error	158	0.005
Total	239	

APPENDIX –XXII

Effect of pesticides on the population of coccinellids after second spray in brinjal during 2022

Source of Variation	df	Mean Sum of Squares (MSS)
Replication	2	
Factor A	15	0.023
Factor B	4	0.002
Interaction A X B	60	0.015
Error	158	0.005
Total	239	

APPENDIX –XXIII

Cost of cultivation of brinjal and chilli by different treatments

A.	Fixed cost for all treatments per hectare	Brinjal	Chilli
1.	Field preparation		
	Ploughing with tractor (3hour/ha) @ Rs. 500/hour	1500.00	1500.00
	Land preparation (10 man days) @ Rs. 417.17/man days	4171.70	4171.70
2.	Cost of seed		
	Brinjal (500 g/ha) @Rs. 120/100g	600.00	6000.00
	Chilli (1000 g/ha) @Rs. 6000/1000g		
3.	Sowing cost (10 mandays) @ Rs. 417.17/mandays	4171.70	4171.70
4.	Fertilizer application (30 man days) @ Rs. 417.17/man days	12515.10	12515.10
5.	Pesticides application (10 man days) @ Rs. 417.17/man days	4171.70	4171.70
6.	Interculture (15 man days) @ Rs. 417.17/man days	6257.55	6257.55
7.	Irrigation (20 man days) @ Rs. 417.17/ man days	8343.40	8343.40
8.	Harvesting (20 man days) @ Rs. 417.17/ man days	8343.40	8343.40
9.	Land rental value including interest and depreciation	10000.00	10000.00
	Total	60074.55	65474.55

Variable cost for different treatments in brinjal and chilli

Input cost							
Brinjal				Chilli			
Input	Qty. required	Rate	Amount (Rs.)	Input	Qty. required	Rate	Amount (Rs.)
FYM (q)	100	225 Rs./q	22500.00	FYM (q)	250	225 Rs./q	56250.00
SSP (kg)	375	11.14 Rs./kg	4177.50	SSP (kg)	475	11.14 Rs./kg	5291.50
MOP (kg)	75	34.00 Rs./kg	2550.0	MOP(kg)	90	34.00 Rs./kg	3060.00
Urea (kg)	108.69	5.33 Rs./kg	579.32	Urea (kg)	163.04	5.33 Rs./kg	869.00
Grand total			29806.82				65470.50

Cost of spray in brinjal

Treatment	Pesticides	Dosage/ha (ml)	Cost of 2 sprays (Rs.)
T ₁	Spiromesifen (22.9% SC) (x)	300	3900.0
T ₂	Spiromesifen (22.9% SC) (X)	400	5200.0
T ₃	Spiromesifen (22.9% SC) (2X)	800	10400.0
T ₄	Fenazaquin (10%EC) (x)	940	6166.4
T ₅	Fenazaquin (10%EC) (X)	1250	8200.0
T ₆	Fenazaquin (10%EC) (2X)	2500	16400.0
T ₇	Chlorantraniliprole (18.5% SC) (x)	150	5485.0
T ₈	Chlorantraniliprole (18.5% SC) (X)	200	7313.3
T ₉	Chlorantraniliprole (18.5% SC) (2X)	400	14626.7
T ₁₀	Fenvalerate (20% EC) (x)	290	493.0
T ₁₁	Fenvalerate (20% EC) (X)	375	637.5
T ₁₂	Fenvalerate (20% EC) (2X)	750	1275.0
T ₁₃	Chlorpyrifos (20% EC) (x)	750	870.0
T ₁₄	Chlorpyrifos (20% EC) (X)	1000	1160.0
T ₁₅	Chlorpyrifos (20% EC) (2X)	2000	2320.0

Cost of spray in chilli

Treatment	Pesticides	Dosage/ha (ml)	Cost of 2 sprays (Rs.)
T ₁	Cyantraniliprole (10.26% OD) (x)	450	10134.00
T ₂	Cyantraniliprole (10.26% OD) (X)	600	13512.00
T ₃	Cyantraniliprole (10.26% OD) (2X)	1200	27024.00
T ₄	Imidacloprid (17.8% SL) (x)	94	752.00
T ₅	Imidacloprid (17.8% SL) (X)	125	1000.00
T ₆	Imidacloprid (17.8% SL) (2X)	250	2000.00
T ₇	Spirotetramat (15.31% OD) (x)	300	2610.00
T ₈	Spirotetramat (15.31% OD) (X)	400	3480.00
T ₉	Spirotetramat (15.31% OD) (2X)	800	6960.00
T ₁₀	Flubendiamide (20% WG) (x)	188	3113.28
T ₁₁	Flubendiamide (20% WG) (X)	250	4140.00
T ₁₂	Flubendiamide (20% WG) (2X)	500	8280.00
T ₁₃	Fenazaquin (10%EC) (x)	940	6166.40
T ₁₄	Fenazaquin (10%EC) (X)	1250	8200.00
T ₁₅	Fenazaquin (10%EC) (2X)	2500	16400.00

Total cost of cultivation for different treatments in brinjal

Treatment	Pesticides	Fixed Cost	Variable Cost (Rs.) (Input cost + Cost of 2 spray)	Total cost of cultivation (Rs.) (Fixed cost + Variable Cost)
T ₀	Control	60074.55	29806.82	89881.40
T ₁	Spiromesifen (22.9% SC) (x)	60074.55	29806.82 + 3900.00	93781.40
T ₂	Spiromesifen (22.9% SC) (X)	60074.55	29806.82 + 5200.00	95081.40
T ₃	Spiromesifen (22.9% SC) (2X)	60074.55	29806.82 + 10400.00	100281.40
T ₄	Fenazaquin (10%EC) (x)	60074.55	29806.82 + 6166.40	96047.80
T ₅	Fenazaquin (10%EC) (X)	60074.55	29806.82 + 8200.00	98081.40
T ₆	Fenazaquin (10%EC) (2X)	60074.55	29806.82 + 16400.00	106281.40
T ₇	Chlorantraniliprole (18.5% SC) (x)	60074.55	29806.82 + 5485.00	95366.40
T ₈	Chlorantraniliprole (18.5% SC) (X)	60074.55	29806.82 + 7313.33	97194.70
T ₉	Chlorantraniliprole (18.5% SC) (2X)	60074.55	29806.82 + 14626.67	104508.00
T ₁₀	Fenvalerate (20% EC) (x)	60074.55	29806.82 + 493.00	90374.40
T ₁₁	Fenvalerate (20% EC) (X)	60074.55	29806.82 + 637.50	90518.90
T ₁₂	Fenvalerate (20% EC) (2X)	60074.55	29806.82 + 1275.00	91156.40
T ₁₃	Chlorpyriphos (20% EC) (x)	60074.55	29806.82 + 870.00	90751.40
T ₁₄	Chlorpyriphos (20% EC) (X)	60074.55	29806.82 + 1160.00	91041.40
T ₁₅	Chlorpyriphos (20% EC) (2X)	60074.55	29806.82 + 2320.00	92201.40

Total cost of cultivation for different treatments in chilli

Treatment	Pesticides	Fixed Cost	Variable Cost (Rs.) (Input cost + Cost of 2 spray)	Total cost of cultivation (Rs.) (Fixed cost + Variable Cost)
T ₀	Control	65474.55	65470.50	130945.05
T ₁	Cyantraniliprole (10.26% OD) (x)	65474.55	65470.50 + 10134.00	141079.05
T ₂	Cyantraniliprole (10.26% OD) (X)	65474.55	65470.50 + 13512.00	144457.05
T ₃	Cyantraniliprole (10.26% OD) (2X)	65474.55	65470.50 + 27024.00	157969.05
T ₄	Imidacloprid (17.8% SL) (x)	65474.55	65470.50 + 752.00	131697.05
T ₅	Imidacloprid (17.8% SL) (X)	65474.55	65470.50 + 1000.00	131945.05
T ₆	Imidacloprid (17.8% SL) (2X)	65474.55	65470.50 + 2000.00	132945.05
T ₇	Spirotetramat (15.31% OD) (x)	65474.55	65470.50 + 2610.00	133555.05
T ₈	Spirotetramat (15.31% OD) (X)	65474.55	65470.50 + 3480.00	134425.05
T ₉	Spirotetramat (15.31% OD) (2X)	65474.55	65470.50 + 6960.00	137905.05
T ₁₀	Flubendiamide (20% WG) (x)	65474.55	65470.50 + 3113.28	134058.33
T ₁₁	Flubendiamide (20% WG) (X)	65474.55	65470.50 + 4140.00	135085.05
T ₁₂	Flubendiamide (20% WG) (2X)	65474.55	65470.50 + 8280.00	139225.05
T ₁₃	Fenazaquin (10%EC) (x)	65474.55	65470.50 + 6166.40	137111.45
T ₁₄	Fenazaquin (10%EC) (X)	65474.55	65470.50 + 8200.00	139145.05
T ₁₅	Fenazaquin (10%EC) (2X)	65474.55	65470.50 + 16400.00	147345.05

Gross income for different treatments in brinjal

Treatment	Pesticides	Yield×Selling Price	Gross Income (Rs.) (2021)
T ₀	Control	184.20 × 22 × 100	405240.00
T ₁	Spiromesifen (22.9% SC) (x)	202.60 × 22 × 100	445720.00
T ₂	Spiromesifen (22.9% SC) (X)	205.00 × 22 × 100	451000.00
T ₃	Spiromesifen (22.9% SC) (2X)	215.60 × 22 × 100	474320.00
T ₄	Fenazaquin (10%EC) (x)	211.40 × 22 × 100	465080.00
T ₅	Fenazaquin (10%EC) (X)	217.40 × 22 × 100	478280.00
T ₆	Fenazaquin (10%EC) (2X)	222.40 × 22 × 100	489280.00
T ₇	Chlorantraniliprole (18.5% SC) (x)	206.60 × 22 × 100	454520.00
T ₈	Chlorantraniliprole (18.5% SC) (X)	230.60 × 22 × 100	507320.00
T ₉	Chlorantraniliprole (18.5% SC) (2X)	235.00 × 22 × 100	517000.00
T ₁₀	Fenvalerate (20% EC) (x)	195.20 × 22 × 100	429440.00
T ₁₁	Fenvalerate (20% EC) (X)	204.40 × 22 × 100	449680.00
T ₁₂	Fenvalerate (20% EC) (2X)	209.20 × 22 × 100	460240.00
T ₁₃	Chlorpyrifos (20% EC) (x)	197.80 × 22 × 100	435160.00
T ₁₄	Chlorpyrifos (20% EC) (X)	202.40 × 22 × 100	445280.00
T ₁₅	Chlorpyrifos (20% EC) (2X)	211.20 × 22 × 100	464640.00

Treatment	Pesticides	Yield×Selling Price	Gross Income (Rs.) (2022)
T ₀	Control	175.00 × 22 × 100	385000.00
T ₁	Spiromesifen (22.9% SC) (x)	193.40 × 22 × 100	425480.00
T ₂	Spiromesifen (22.9% SC) (X)	197.60 × 22 × 100	434720.00
T ₃	Spiromesifen (22.9% SC) (2X)	205.00 × 22 × 100	451000.00
T ₄	Fenazaquin (10%EC) (x)	197.60 × 22 × 100	434720.00
T ₅	Fenazaquin (10%EC) (X)	204.60 × 22 × 100	450120.00
T ₆	Fenazaquin (10%EC) (2X)	215.20 × 22 × 100	473440.00
T ₇	Chlorantraniliprole (18.5% SC) (x)	211.20 × 22 × 100	464640.00
T ₈	Chlorantraniliprole (18.5% SC) (X)	233.60 × 22 × 100	513920.00
T ₉	Chlorantraniliprole (18.5% SC) (2X)	239.00 × 22 × 100	525800.00
T ₁₀	Fenvalerate (20% EC) (x)	195.40 × 22 × 100	429880.00
T ₁₁	Fenvalerate (20% EC) (X)	202.20 × 22 × 100	444840.00
T ₁₂	Fenvalerate (20% EC) (2X)	208.60 × 22 × 100	458920.00
T ₁₃	Chlorpyrifos (20% EC) (x)	186.80 × 22 × 100	410960.00
T ₁₄	Chlorpyrifos (20% EC) (X)	197.40 × 22 × 100	434280.00
T ₁₅	Chlorpyrifos (20% EC) (2X)	204.20 × 22 × 100	449240.00

Sale rate of brinjal= Rs. 22/kg

Gross income for different treatments in chilli

Treatment	Pesticides	Yield×Selling Price	Gross Income (Rs.) (2021)
T ₀	Control	115.60 × 35 × 100	404600.00
T ₁	Cyantraniliprole (10.26% OD) (x)	144.20 × 35 × 100	504700.00
T ₂	Cyantraniliprole (10.26% OD) (X)	164.40 × 35 × 100	575400.00
T ₃	Cyantraniliprole (10.26% OD) (2X)	170.80 × 35 × 100	597800.00
T ₄	Imidacloprid (17.8% SL) (x)	124.20 × 35 × 100	434700.00
T ₅	Imidacloprid (17.8% SL) (X)	135.40 × 35 × 100	473900.00
T ₆	Imidacloprid (17.8% SL) (2X)	139.60 × 35 × 100	488600.00
T ₇	Spirotetramat (15.31% OD) (x)	126.60 × 35 × 100	443100.00
T ₈	Spirotetramat (15.31% OD) (X)	137.60 × 35 × 100	481600.00
T ₉	Spirotetramat (15.31% OD) (2X)	142.60 × 35 × 100	499100.00
T ₁₀	Flubendiamide (20% WG) (x)	124.40 × 35 × 100	435400.00
T ₁₁	Flubendiamide (20% WG) (X)	135.40 × 35 × 100	473900.00
T ₁₂	Flubendiamide (20% WG) (2X)	138.20 × 35 × 100	483700.00
T ₁₃	Fenazaquin (10%EC) (x)	143.20 × 35 × 100	501200.00
T ₁₄	Fenazaquin (10%EC) (X)	151.00 × 35 × 100	528500.00
T ₁₅	Fenazaquin (10%EC) (2X)	158.80 × 35 × 100	555800.00

Treatment	Pesticides	Yield×Selling Price	Gross Income (Rs.) (2022)
T ₀	Control	122.60 × 35 × 100	429100.00
T ₁	Cyantraniliprole (10.26% OD) (x)	151.00 × 35 × 100	528500.00
T ₂	Cyantraniliprole (10.26% OD) (X)	169.60 × 35 × 100	593600.00
T ₃	Cyantraniliprole (10.26% OD) (2X)	175.00 × 35 × 100	612500.00
T ₄	Imidacloprid (17.8% SL) (x)	131.20 × 35 × 100	459200.00
T ₅	Imidacloprid (17.8% SL) (X)	139.80 × 35 × 100	489300.00
T ₆	Imidacloprid (17.8% SL) (2X)	144.20 × 35 × 100	504700.00
T ₇	Spirotetramat (15.31% OD) (x)	131.40 × 35 × 100	459900.00
T ₈	Spirotetramat (15.31% OD) (X)	142.40 × 35 × 100	498400.00
T ₉	Spirotetramat (15.31% OD) (2X)	147.00 × 35 × 100	514500.00
T ₁₀	Flubendiamide (20% WG) (x)	129.20 × 35 × 100	452200.00
T ₁₁	Flubendiamide (20% WG) (X)	138.20 × 35 × 100	483700.00
T ₁₂	Flubendiamide (20% WG) (2X)	152.00 × 35 × 100	532000.00
T ₁₃	Fenazaquin (10%EC) (x)	135.40 × 35 × 100	473900.00
T ₁₄	Fenazaquin (10%EC) (X)	144.20 × 35 × 100	504700.00
T ₁₅	Fenazaquin (10%EC) (2X)	148.60 × 35 × 100	520100.00

Sale rate of chilli = Rs. 35/kg

Net income of different treatments in brinjal

Treatment	Pesticides	Net Income (Rs.) (2021)	Net Income (Rs.) (2022)
T ₀	Control	315358.63	295118.63
T ₁	Spiromesifen (22.9% SC) (x)	351938.63	331698.63
T ₂	Spiromesifen (22.9% SC) (X)	355918.63	339638.63
T ₃	Spiromesifen (22.9% SC) (2X)	374038.63	350718.63
T ₄	Fenazaquin (10%EC) (x)	369032.23	338672.23
T ₅	Fenazaquin (10%EC) (X)	380198.63	352038.63
T ₆	Fenazaquin (10%EC) (2X)	382998.63	367158.63
T ₇	Chlorantraniliprole (18.5% SC) (x)	359153.63	369273.63
T ₈	Chlorantraniliprole (18.5% SC) (X)	410125.30	416725.30
T ₉	Chlorantraniliprole (18.5% SC) (2X)	412491.96	421291.96
T ₁₀	Fenvalerate (20% EC) (x)	339065.63	339505.63
T ₁₁	Fenvalerate (20% EC) (X)	359161.13	354321.13
T ₁₂	Fenvalerate (20% EC) (2X)	369083.63	367763.63
T ₁₃	Chlorpyrifos (20% EC) (x)	344408.63	320208.63
T ₁₄	Chlorpyrifos (20% EC) (X)	354238.63	343238.63
T ₁₅	Chlorpyrifos (20% EC) (2X)	372438.63	357038.63

Net income of different treatments in chilli

Treatment	Pesticides	Net Income (Rs.) (2021)	Net Income (Rs.) (2022)
T ₀	Control	273654.95	298154.95
T ₁	Cyantraniliprole (10.26% OD) (x)	363620.95	387420.95
T ₂	Cyantraniliprole (10.26% OD) (X)	430942.95	449142.95
T ₃	Cyantraniliprole (10.26% OD) (2X)	439830.95	454530.95
T ₄	Imidacloprid (17.8% SL) (x)	303002.95	327502.95
T ₅	Imidacloprid (17.8% SL) (X)	341954.95	357354.95
T ₆	Imidacloprid (17.8% SL) (2X)	355654.95	371754.95
T ₇	Spirotetramat (15.31% OD) (x)	309544.95	326344.95
T ₈	Spirotetramat (15.31% OD) (X)	347174.95	363974.95
T ₉	Spirotetramat (15.31% OD) (2X)	361194.95	376594.95
T ₁₀	Flubendiamide (20% WG) (x)	301341.67	318141.67
T ₁₁	Flubendiamide (20% WG) (X)	338814.95	348614.95
T ₁₂	Flubendiamide (20% WG) (2X)	344474.95	392774.95
T ₁₃	Fenazaquin (10%EC) (x)	364088.55	336788.55
T ₁₄	Fenazaquin (10%EC) (X)	389354.95	365554.95
T ₁₅	Fenazaquin (10%EC) (2X)	408454.95	372754.95

Economics of different treatments used against brinjal insect pest during 2021

Treatments	Pesticide	Dosage (g a.i./ha)	Yield (q/ha)	Fixed Cost (Rs.)	Variable Cost (Rs.)	Total Cost (Rs.)	Gross Income (Rs.)	Net Income (Rs.)	B:C
T ₀	Control	-	184.20	60074.55	29806.82	89881.37	405240.00	315358.63	3.51:1
T ₁	Spiromesifen (22.9 % SC) (x)	72	202.60	60074.55	33706.82	93781.37	445720.00	351938.63	3.75:1
T ₂	Spiromesifen (22.9 % SC) (X)	96	205.00	60074.55	35006.82	95081.37	451000.00	355918.63	3.74:1
T ₃	Spiromesifen (22.9 % SC) (2X)	192	215.60	60074.55	40206.82	100281.37	474320.00	374038.63	3.73:1
T ₄	Fenazaquin (10 % EC) (x)	94	211.40	60074.55	35973.22	96047.77	465080.00	369032.23	3.84:1
T ₅	Fenazaquin (10 % EC) (X)	125	217.40	60074.55	38006.82	98081.37	478280.00	380198.63	3.88:1
T ₆	Fenazaquin (10 % EC) (2X)	250	222.40	60074.55	46206.82	106281.37	489280.00	382998.63	3.60:1
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	206.60	60074.55	35291.82	95366.37	454520.00	359153.63	3.77:1
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	230.60	60074.55	37120.15	97194.70	507320.00	410125.30	4.22:1
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	235.00	60074.55	44433.49	104508.04	517000.00	412491.96	3.95:1
T ₁₀	Fenvalerate (20 % EC) (x)	60	195.20	60074.55	30299.82	90374.37	429440.00	339065.63	3.75:1
T ₁₁	Fenvalerate (20 % EC) (X)	75	204.40	60074.55	30444.32	90518.87	449680.00	359161.13	3.97:1
T ₁₂	Fenvalerate (20 % EC) (2X)	150	209.20	60074.55	31081.82	91156.37	460240.00	369083.63	4.05:1
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	197.80	60074.55	30676.82	90751.37	435160.00	344408.63	3.80:1
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	202.40	60074.55	30966.82	91041.37	445280.00	354238.63	3.89:1
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	211.20	60074.55	32126.82	92201.37	464640.00	372438.63	4.04:1

Economics of different treatments used against brinjal insect pest during 2022

Treatments	Pesticide	Dosage (g a.i./ha)	Yield (q/ha)	Fixed Cost (Rs.)	Variable Cost (Rs.)	Total Cost (Rs.)	Gross Income (Rs.)	Net Income (Rs.)	B:C
T ₀	Control	-	175.00	60074.55	29806.82	89881.40	385000.00	295118.63	3.28:1
T ₁	Spiromesifen (22.9 % SC) (x)	72	193.40	60074.55	33706.82	93781.40	425480.00	331698.63	3.54:1
T ₂	Spiromesifen (22.9 % SC) (X)	96	197.60	60074.55	35006.82	95081.40	434720.00	339638.63	3.57:1
T ₃	Spiromesifen (22.9 % SC) (2X)	192	205.00	60074.55	40206.82	100281.40	451000.00	350718.63	3.50:1
T ₄	Fenazaquin (10 % EC) (x)	94	197.60	60074.55	35973.22	96047.80	434720.00	338672.23	3.53:1
T ₅	Fenazaquin (10 % EC) (X)	125	204.60	60074.55	38006.82	98081.40	450120.00	352038.63	3.59:1
T ₆	Fenazaquin (10 % EC) (2X)	250	215.20	60074.55	46206.82	106281.40	473440.00	367158.63	3.45:1
T ₇	Chlorantraniliprole (18.5 % SC) (x)	30	211.20	60074.55	35291.82	95366.40	464640.00	369273.63	3.87:1
T ₈	Chlorantraniliprole (18.5 % SC) (X)	40	233.60	60074.55	37120.15	97194.70	513920.00	416725.30	4.29:1
T ₉	Chlorantraniliprole (18.5 % SC) (2X)	80	239.00	60074.55	44433.49	104508.00	525800.00	421291.96	4.03:1
T ₁₀	Fenvalerate (20 % EC) (x)	60	195.40	60074.55	30299.82	90374.40	429880.00	339505.63	3.76:1
T ₁₁	Fenvalerate (20 % EC) (X)	75	202.20	60074.55	30444.32	90518.90	444840.00	354321.13	3.91:1
T ₁₂	Fenvalerate (20 % EC) (2X)	150	208.60	60074.55	31081.82	91156.40	458920.00	367763.63	4.03:1
T ₁₃	Chlorpyrifos (20 % EC) (x)	150	186.80	60074.55	30676.82	90751.40	410960.00	320208.63	3.53:1
T ₁₄	Chlorpyrifos (20 % EC) (X)	200	197.40	60074.55	30966.82	91041.40	434280.00	343238.63	3.77:1
T ₁₅	Chlorpyrifos (20 % EC) (2X)	400	204.20	60074.55	32126.82	92201.40	449240.00	357038.63	3.87:1

Economics of different treatments used against chilli thrips during 2021

Treatments	Pesticide	Dosage (g a.i./ha)	Yield (q/ha)	Fixed Cost (Rs.)	Variable Cost (Rs.)	Total Cost (Rs.)	Gross Income (Rs.)	Net Income (Rs.)	B:C
T ₀	Control		115.60	65474.55	65470.50	130945.05	404600.00	273654.95	2.09:1
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	144.20	65474.55	75604.50	141079.05	504700.00	363620.95	2.58:1
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	164.40	65474.55	78982.50	144457.05	575400.00	430942.95	2.98:1
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	170.80	65474.55	92494.50	157969.05	597800.00	439830.95	2.78:1
T ₄	Imidacloprid (17.8 % SL) (x)	19	124.20	65474.55	66222.50	131697.05	434700.00	303002.95	2.30:1
T ₅	Imidacloprid (17.8 % SL) (X)	25	135.40	65474.55	66470.50	131945.05	473900.00	341954.95	2.59:1
T ₆	Imidacloprid (17.8 % SL) (2X)	50	139.60	65474.55	67470.50	132945.05	488600.00	355654.95	2.68:1
T ₇	Spirotetramat (15.31 % OD) (x)	45	126.60	65474.55	68080.50	133555.05	443100.00	309544.95	2.32:1
T ₈	Spirotetramat (15.31 % OD) (X)	60	137.60	65474.55	68950.50	134425.05	481600.00	347174.95	2.58:1
T ₉	Spirotetramat (15.31 % OD) (2X)	120	142.60	65474.55	72430.50	137905.05	499100.00	361194.95	2.62:1
T ₁₀	Flubendiamide (20 % WG) (x)	38	124.40	65474.55	68583.78	134058.33	435400.00	301341.67	2.25:1
T ₁₁	Flubendiamide (20 % WG) (X)	50	135.40	65474.55	69610.50	135085.05	473900.00	338814.95	2.51:1
T ₁₂	Flubendiamide (20 % WG) (2X)	100	138.20	65474.55	73750.50	139225.05	483700.00	344474.95	2.47:1
T ₁₃	Fenazaquin (10 % EC) (x)	94	143.20	65474.55	71636.90	137111.45	501200.00	364088.55	2.66:1
T ₁₄	Fenazaquin (10 % EC) (X)	125	151.00	65474.55	73670.50	139145.05	528500.00	389354.95	2.80:1
T ₁₅	Fenazaquin (10 % EC) (2X)	250	158.80	65474.55	81870.50	147345.05	555800.00	408454.95	2.77:1

Economics of different treatments used against chilli thrips during 2022

Treatments	Pesticide	Dosage (g a.i./ha)	Yield (q/ha)	Fixed Cost (Rs.)	Variable Cost (Rs.)	Total Cost (Rs.)	Gross Income (Rs.)	Net Income (Rs.)	B:C
T ₀	Control	-	122.60	65474.55	65470.50	130945.10	429100.00	298154.95	2.28:1
T ₁	Cyantraniliprole (10.26 % OD) (x)	45	151.00	65474.55	75604.50	141079.10	528500.00	387420.95	2.75:1
T ₂	Cyantraniliprole (10.26 % OD) (X)	60	169.60	65474.55	78982.50	144457.10	593600.00	449142.95	3.11:1
T ₃	Cyantraniliprole (10.26 % OD) (2X)	120	175.00	65474.55	92494.50	157969.10	612500.00	454530.95	2.88:1
T ₄	Imidacloprid (17.8 % SL) (x)	19	131.20	65474.55	66222.50	131697.10	459200.00	327502.95	2.49:1
T ₅	Imidacloprid (17.8 % SL) (X)	25	139.80	65474.55	66470.50	131945.10	489300.00	357354.95	2.71:1
T ₆	Imidacloprid (17.8 % SL) (2X)	50	144.20	65474.55	67470.50	132945.10	504700.00	371754.95	2.80:1
T ₇	Spirotetramat (15.31 % OD) (x)	45	131.40	65474.55	68080.50	133555.10	459900.00	326344.95	2.44:1
T ₈	Spirotetramat (15.31 % OD) (X)	60	142.40	65474.55	68950.50	134425.10	498400.00	363974.95	2.71:1
T ₉	Spirotetramat (15.31 % OD) (2X)	120	147.00	65474.55	72430.50	137905.10	514500.00	376594.95	2.73:1
T ₁₀	Flubendiamide (20 % WG) (x)	38	129.20	65474.55	68583.78	134058.30	452200.00	318141.67	2.37:1
T ₁₁	Flubendiamide (20 % WG) (X)	50	138.20	65474.55	69610.50	135085.10	483700.00	348614.95	2.58:1
T ₁₂	Flubendiamide (20 % WG) (2X)	100	152.00	65474.55	73750.50	139225.10	532000.00	392774.95	2.82:1
T ₁₃	Fenazaquin (10 % EC) (x)	94	135.40	65474.55	71636.90	137111.50	473900.00	336788.55	2.46:1
T ₁₄	Fenazaquin (10 % EC) (X)	125	144.20	65474.55	73670.50	139145.10	504700.00	365554.95	2.63:1
T ₁₅	Fenazaquin (10 % EC) (2X)	250	148.60	65474.55	81870.50	147345.10	520100.00	372754.95	2.53:1

Dr. YS PARMAR UNIVERSITY OF HORTICULTURE AND FORESTRY
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Title of thesis : “Bioefficacy and residue dynamics of some pesticides used against insect pests of brinjal and chilli”
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Admission number : H-2018-05-D
Major advisor : Dr. Sapna Katna
Main field : Entomology
Minor field : i) Vegetable Science
ii) Plant Protection
Degree awarded : Ph.D Entomology
Year of degree awarded : 2023
Number of pages in thesis : 236 + xii
Number of words in abstract : 454

ABSTRACT

The present investigation on “Bioefficacy and residue dynamics of some pesticides used against insect pests of brinjal and chilli” was carried out during 2021 and 2022 in the department of Entomology, Dr. YS Parmar University of Horticulture and Forestry, Nauni, Solan. Bioefficacy studies revealed that fenazaquin @ 250 g a.i./ha (81.98% and 82.80%) was most effective in reducing jassids population, whereas, chlorantraniliprole @ 80 g a.i./ha was effective against shoot and fruit borer in reducing shoot infestation (2.22% and 2.45%) and fruit infestation (6.78% and 6.13%) on brinjal crop. In case of thrips in chilli, cyantraniliprole @ 120 g a.i./ha (83.06% and 85.27%) proved to be most effective during 2021 and 2022, respectively. No phytotoxicity symptoms were observed on the brinjal and chilli plants after application of pesticides at given doses. Population of coccinellids after imposing the treatments declined to some extent in a decreasing order *viz.*, chlorantraniliprole > fenvalerate > spiromesifen > fenazaquin > chlorpyrifos in brinjal and flubendiamide > cyantraniliprole > spirotetramat > fenazaquin > imidacloprid in case of chilli. The highest benefit cost ratio of 4.22:1 and 4.29:1 was recorded in the plots treated with chlorantraniliprole @ 40 g a.i./ha in brinjal and 2.98:1 and 3.11:1 in the plots treated with cyantraniliprole @ 60 g a.i./ha in chilli during 2021 and 2022, respectively. Dissipation studies in brinjal and chilli showed that all the pesticides followed first order kinetics. The average initial deposits of spiromesifen (@ 96 and 192 g a.i./ha), fenazaquin (@ 125 and 250 g a.i./ha), chlorantraniliprole (@ 40 and 80 g a.i./ha), fenvalerate (@ 75 and 150 g a.i./ha) and chlorpyrifos (@ 200 and 400 g a.i./ha) on brinjal fruits were 0.672 and 1.133 mg/kg, 0.457 and 0.761mg/kg, 0.867 and 1.433 mg/kg, 0.587 and 1.233 mg/kg and 0.918 and 1.825 mg/kg at single and double dose, respectively. On chilli, the average initial deposits of cyantraniliprole (@ 60 and 120 g a.i./ha), imidacloprid (@ 25 and 50 g a.i./ha), spirotetramat (@ 60 and 120 g a.i./ha), flubendiamide (@ 50 and 100 g a.i./ha) and fenazaquin (@ 125 and 250 g a.i./ha) reduced to half in a range of 1.46 – 3.10 days and 1.64 – 3.47 days at single and double dose, respectively. In brinjal field soil and in red chilli and chilli field soil the residues detected were below limit of quantification at harvest at both X and 2X doses for all the tested pesticides. Risk assessment of all the pesticides calculated as hazard quotient was less than 1 and as theoretical maximum daily intake was less than maximum permissible intake, thus all the tested pesticides on both the crops considered to be safe, provided proper waiting period of 2-3 days in brinjal and 5-11 days in chilli should be followed.

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B Sc Horticulture (Hons)	July, 2016	Dr. YS Parmar University of Horticulture and Forestry, Nauni, Solan, H.P.	Dr. YS Parmar University of Horticulture and Forestry, Nauni, Solan, H.P.	77.50	First
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Publications : 3

Research Papers : 3

Scientific Popular Articles : No

**Visited abroad alongwith duration and
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(Shivani Bhartiya)