

**BIOEFFICACY, PERSISTENCE TOXICITY AND RESIDUES OF  
REDUCED RISK INSECTICIDES AGAINST POMEGRANATE  
THRIPS, *Scirtothrips dorsalis* Hood.**

**By**

**DHIRAJKUMAR RAJARAM KADAM**

**Reg. No. 08/30**

**A thesis submitted to the**

**MAHATMA PHULE KRISHI VIDYAPEETH,  
RAHURI-413 722, DIST. AHMEDNAGAR  
MAHARASHTRA STATE (INDIA)**

**in partial fulfilment of the requirements  
for the degree**

**of**

**DOCTOR OF PHILOSOPHY (AGRICULTURE)**

**In**

**AGRICULTURAL ENTOMOLOGY**

**DEPARTMENT OF AGRIL. ENTOMOLOGY  
POST GRADUATE INSTITUTE  
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**2011**

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**Approved by**

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## **CANDIDATE'S DECLARATION**

I hereby declare that this thesis or a part thereof has not been submitted by me or any other person to any other University or Institute for a Degree or Diploma

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## CERTIFICATE

This is to certify that the thesis entitled “BIOEFFICACY, PERSISTENCE TOXICITY AND RESIDUES OF REDUCED RISK INSECTICIDES AGAINST POMEGRANATE THRIPS (*Scirtothrips dorsalis* Hood)” submitted to the Faculty of Agriculture, Mahatma Phule Krishi Vidyapeeth, Rahuri, Dist. Ahmednagar, Maharashtra State, India, in partial fulfilment of the requirements for the degree of DOCTOR OF PHILOSOPHY (AGRICULTURE) in AGRICULTURAL ENTOMOLOGY, embodies the results of piece of bonafide research work carried out by SHRI. DHIRAJKUMAR R. KADAM, under my guidance and supervision and that no part of the thesis has been submitted to any other University for degree or diploma or publication in other form.

The assistance and help received during the course of this investigation and sources of reference have been duly acknowledged.

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Place: MPKV, Rahuri

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Affectionately Dedicated  
To My  
Beloved Mother  
Smt.Prabhavatidevi  
And Father  
Late Adv.Rajaram D. Kadam



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## List of abbreviations

%	Per cent
/	Per
@	At the rate of
<	Less than
>	Greater than
≈	Equivalent to
=	Equal to
+	Plus
-	Minus
±	Plus or minus
√	Square root of
°C	Degree Celsius
a.i.	Active ingredient
a.m.	<i>Ante meridian</i> (before noon)
CDFA	California Department of Food and Agriculture
cm	Centimeter(s)
Conc.	Concentration
Cv.	Cultivar
DAS	Days after spraying
EC	Emulsifiable concentrate
EPA	Environmental Protection Agency
EU	European Union
e.g.	<i>Exempli gratia</i> or for example
<i>et al.</i>	<i>Et alia</i> , and others
etc.	<i>Et cetera</i> , and so on
Fig.	Figure(s)
g	Gram

ha	Hectare(s)
ha <sup>-1</sup>	Per hectare
hr	Hour
HPLC	High Performance Liquid Chromatograph
i.d.	Internal diameter
i.e.	<i>Id est</i> , that is
kg	Kilogram(s)
kg <sup>-1</sup>	Per kilogram
L	Litre(s)
Ltd.	Limited
m	Metres
max.	maximum
min.	minimum
mg	Miligram(s)
ml	Mililiter(s)
mm	Milimeter(s)
MRL	Maximum residue limit
MT	Metric tones
MS	Maharashtra State
MW	Meteorological week
ng	Nanogram(s)
No.	Number
p.m.	<i>Post meridian</i> (afternoon)
ppm	Parts per million
q	Quintal(s)
r	Correlation coefficient
RBD	Randomised Block Design
RH	Relative humidity

RL <sub>50</sub>	Time required (for residues) to reach half of initial amount
SC	Soluble concentrate
S.E.	Standard error
SL	Soluble liquid
sp	Species
SRM	Single Residue Method
t	Tonnes (s)
Temp.	Temperature
T <sub>BDL</sub>	Time required (for residues) to reach below detection limit
T <sub>MRL</sub>	Time required (for residues) to reach below maximum residue limit
µg	Microgram(s)
µl	Microlitre(s)
USA	United States of America
Viz.,	Namely
WSC	Water Soluble Concentrate

## ABSTRACT

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Research Guide : Dr. V.D. Kale  
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### ABSTRACT

The present investigations were undertaken at Department of Agril. Entomology, MPKV, Rahuri to study the bioefficacy of reduced risk insecticides against pomegranate thrips *Scirtothrips dorsalis* (H.) (Thysanoptera : Thripidae). Various methods of insecticide residue analysis were compared to validate appropriate method for the analysis of residues on pomegranate fruits. The dissipation of insecticides in pomegranate fruits and soil was also studied. Studies were extended further to find out

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Abstract (contd...)

D.R. Kadam

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residues of insecticides in soil when used in stem pasting.

Bioefficacy studies with test insecticides against pomegranate thrips revealed that spinosad 45 SC @ 56.25 g a.i. ha<sup>-1</sup> was the best treatment in minimizing thrips count both on fruit and shoots. The next best treatment was fipronil 5 SC @ 25 g a.i. ha<sup>-1</sup> and it was at par with spinosad 45 SC @ 56.25 g a.i. ha<sup>-1</sup>. The persistence toxicity of spinosad 45 SC @ 56.25 g a.i. ha<sup>-1</sup> and fipronil 5 SC @ 25 g a.i. ha<sup>-1</sup> lasted up to 14 DAS (days after sprays), since, most of the times thrips count in these treatments was less than 5.0 thrips/fruit. Treatments comprising imidacloprid 17.8 SL @ 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 5 EC @ 12.5 g a.i. ha<sup>-1</sup> were not found as effective as spinosad 45 SC @ 56.25 g a.i. ha<sup>-1</sup> and fipronil 5 SC @ 25 g a.i. ha<sup>-1</sup>. Imidacloprid 17.8 SL @ 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 5 EC @ 12.5 g a.i. ha<sup>-1</sup> did not persist beyond 10 days. This indicated that the interval between successive sprays, therefore, should be reduced to 10 days whereas spinosad 45 SC @ 56.25 g a.i. ha<sup>-1</sup> and fipronil 5 SC @ 56.25 g a.i. ha<sup>-1</sup> can be rotated at an interval of 15 days. The laboratory experiment on persistence of insecticides against thrips on fruits and shoots of pomegranate revealed that spinosad 56.25 g a.i. ha<sup>-1</sup> was the most persistent insecticide followed by fipronil 25 g a.i. ha<sup>-1</sup>, whereas, imidacloprid 27 g a.i. ha<sup>-1</sup> was the least persistent treatment.

The recovery of imidacloprid ranged from 75 to 100 % when estimated from pomegranate arils, whole fruits and peel by

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Abstract (contd...)

D.R. Kadam

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three methods of residue analysis viz. California Department of Food and Agriculture (CDFA), QuEChERS and Single Residue Method (SRM). Spinosad recovery was also good by all three methods. Single Residue method gave highest per cent recovery followed by QuEChERS method whereas, CDFA was less efficient. Fipronil and its metabolites showed variable results in recovery studies. Single Residue method was the most superior in extracting maximum residues of fipronil and its metabolites whereas, CDFA and QuEChERS methods were least efficient. Good recovery of lambda-cyhalothrin was obtained by all three methods under study at two levels of fortification in arils, whole fruits and peel.

In arils, initial deposit of imidacloprid took 1 day for normal dose (27 g a.i. ha<sup>-1</sup>) and 3 days for double dose (54 g a.i. ha<sup>-1</sup>) to reach below detection limit of 0.05 µg g<sup>-1</sup>. Spinosad residues in arils of pomegranate were observed only in the samples collected at 0 and 1 DAS for normal (56.25 g a.i. ha<sup>-1</sup>) and higher dose (112.5 g a.i. ha<sup>-1</sup>). Fipronil and its metabolites were detected up to 5 days for normal dose (25 g a.i. ha<sup>-1</sup>) and up to 7 days for higher dose (50 g a.i. ha<sup>-1</sup>) in arils of pomegranate fruit. The initial deposit of lambda-cyhalothrin took 5 days for normal dose (12.5 g a.i. ha<sup>-1</sup>) and 7 days for higher dose (25 g a.i. ha<sup>-1</sup>) to reach below detection limit. Thus, the pomegranate fruits harvested on 0 day from the plants treated with imidacloprid 17.8 SL 27 g a.i. ha<sup>-1</sup>, spinosad 45 SC 56.25 g a.i. ha<sup>-1</sup>, fipronil

5 SC 25 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup> were not risk free from the residue point of view and certain waiting periods must be followed before harvesting and consumption. Whole fruits showed higher residues as compared to arils. Imidacloprid persisted up to 5 and 7 days at normal and higher dose. Spinosad residues remained in the fruits up to 3 days at both doses. Fipronil and its metabolites were detected in the fruits collected at 7 and 10 DAS for normal and higher dose. Imidacloprid persisted up to 7 and 10 days, spinosad up to 5 and 7 days, fipronil up to 10 and 14 days and lambda-cyhalothrin up to 7 and 10 days at normal rate of application and at double dose respectively in peel of pomegranate fruits. Residues of these insecticides were not detected in the soil collected 21 days after last spray. Similarly, residues of lindane and chlorpyrifos used in pomegranate stem pasting were also not found in the soil samples collected at 30 days after pasting.

# 1. Introduction

Pomegranate (*Punica granatum* L.) Family: Puniceae is native of Iran and one of the favorite table fruits of tropical and subtropical regions. It is domesticated in 2000 BC and adapted to the Mediterranean region of Central Asia, Africa and Europe. It is a well known arid zone horticultural crop grown all over the world and more extensively cultivated in countries like India, Iran, Turkey, USA, Spain, Afghanistan, and to some extent in China, Japan and Russia. In view of the health benefits and demand in the International market, there is a wide scope for pomegranate production and trade. Pomegranate juice inhibited the progression of atherosclerotic lesions, improved stress-induced ischemia in patients with coronary heart disease and some lipid profile in diabetic patients. A gel containing extract of *P. granatum* was effective in dental diseases. Pomegranate has a wide-spectrum of antibacterial, antiviral, and antihelminthic properties, as well as anticancer properties in the cases of prostate, breast, colon, and skin tumors (Louba 2007). These positive medicinal properties make pomegranate the preferred fruit that should be included in everyday nutrition.

Anticancer effects of pomegranate extracts were found in human breast cancer cells in vitro and also chemo preventive activity of pomegranate fermented juice polyphenols in a mouse mammary organ culture (Mehta and Lansky, 2004). Pomegranate peel extract possessed a relatively high antioxidant activity and might be considered as a rich source of natural antioxidant (Yasoubi *et al.*, 2007). Pomegranate juice is a polyphenol rich with

antioxidant, antihypertensive and anti-inflammatory effects (Basu and Penugonda, 2010).

It is because of these health promoting properties, pomegranate cultivation has become a boon for Indian farmers especially in arid region. Export potential of this crop is also attracting the farmers towards its cultivation. About 50 years ago, India used to import pomegranate from Iran, Muskat and Afghanistan. Presently, India produces ample quantity of superior quality fruits and exports mainly to Middle East, UK, Holland, Germany and other countries. The export trade of this crop from India has increased from 4,773 tons (valued at ₹. 104.14 million) in 2001 to 2002 to 33,415 tone (valued at ₹.1,184 million) in 2007-2008 (Anonymous, 2009). The future demand for export quality pomegranate will certainly show increasing trend. In order to maintain good quality production of pomegranate fruits, proper package of practices in relation to plant protection will play an important role in pomegranate cultivation.

India ranks first in area (120,000 ha) and production (9.0 million tonnes) of pomegranate followed by Iran with an area of 65,000 ha. Other important pomegranate growing countries are Turkey, USA and Spain. The productivity of this crop in India is only 7.4 t ha<sup>-1</sup> which is significantly less than other pomegranate growing countries like Spain (18.5 tons ha<sup>-1</sup>), USA (18.3 tons ha<sup>-1</sup>), Turkey (11.3 tons ha<sup>-1</sup>) and Iran (9.23 tons ha<sup>-1</sup>) (Anonymous, 2008). In India, Maharashtra state ranks first with an area of 96,000 ha constituting 70% of the total area under pomegranate followed by Karnataka (13,000 ha) and Andha Pradesh (5,100 ha). However, average productivity of pomegranate in Maharashtra, is very less *i.e*

only 6.2 tons ha<sup>-1</sup>. In Maharashtra, Nashik District has an area of 35,400 ha followed by Solapur-31,000 ha, Ahmednagar-6,390 ha and Sangli-6,300 ha. Other districts viz., Dhule, Pune, Satara, Osmanabad etc. also have pomegranate cultivation.

The insect pests and diseases play significant role in reducing the production of this crop. In the profit driven agriculture, the market price of a commodity decides the production strategy. The farmers adhere to preventive pest control strategies in case of high-priced commodities such as pomegranate, grape, apple, mango etc. They ignore Good Agricultural Practices and apply pesticides indiscriminately. The disadvantages of insecticide use known as 4Rs (Resistance, Resurgence, Risk and Residue), are well known. Since pomegranate fruit is consumed mostly as a table purpose fresh fruit, insecticide residues in this crop are of much concern. Insecticide residues are also becoming a major obstacle in reducing India's export to international market. The export scenario shows that India contributes only 25.9 % of International market while Iran with 44.8 % share is most dominant. India exports only 3 % out of total production while Spain exports 80 % of its total production (Anonymous, 2008).

The increased use of pesticides for the control of crop pests, more so in horticultural crops due to relatively heavy carry over of pests, has created the problems of contamination of fruits with toxic pesticide residues. The persistence of pesticide residues on or in fruits at harvest is of direct concern of consumer's health as the fruits are consumed fresh. Further, the bioaccumulation of pesticide residues in human body over a period of time can also lead to long term health effects. While there is a necessity to regulate the

pesticide residues in fruits for internal market, there is also an economic need for such regulations in view of quality control of growing export of fruits in global market. These factors suggest to rationalize the use of pesticides on fruit crops by critically evaluating plant protection schedules for the persistence of pesticide residues and manage the resultant toxic pesticide residues through working out pre-harvest waiting periods.

Eighty six species of insect pests infesting pomegranate have been reported from various parts of the world (Zirpe, 1966). Infestation of *Scirtothrips dorsalis* (H.) contribute to major losses in pomegranate cultivation, both qualitatively and quantitatively. Thrips, with their rasping and sucking type of mouth parts, feed on the developing fruits, tender shoots and buds contributing huge losses. Ananthakrishnan (1971) reported that most thrips species are polyphagous and cosmopolitan in distribution infesting cabbage, tea, garlic, chilli, cotton, peas, ornamental and fruits crops. The pest is active throughout the year and found on onion and garlic from November to May. Thereafter, it migrates on to cotton and other *Summer* crops in June and then to cole crops during September-October (Butani and Verma, 1976). Mote and Sonone 1977 reported about 50 per cent losses due to thrips in onion crop.

Due to lack of alternate effective pest control methods, chemical insecticides are widely used by farmers in combating *S. dorsalis* on pomegranate in Maharashtra. This crop has great export potential, therefore, newer molecules reported to be effective against thrips on other crops were tested to see their potential in combating *S. dorsalis* on pomegranate. The selected insecticides were imidacloprid, spinosad, fipronil and lambda-cyhalothrin. These

insecticides are listed as reduced risk or OP alternative pesticides in United States of America. "Reduced risk pesticides" is the term used by Environmental Protection Agency to designate pesticides with one or more of the following properties-low impact on human health, low toxicity to non-target organisms (birds, plants, fish), low potential for water contamination, low use rates, low potential for development of pest resistance and IPM compatible (low toxicity to predators and parasitoids). Keeping in view negligible work on pomegranate, as revealed from the review of literature, the present study was planned with following objectives.

1. To study the bioefficacy and persistence toxicity of reduced risk insecticides against pomegranate thrips *Scirtothrips dorsalis* (H.)
2. To compare different methods of insecticide residue analysis for their efficiency.
3. To study the extent of residues of insecticides in pomegranate fruits and soil.
4. To study the probability of leaching of lindane and chlorpyrifos used in pomegranate stem pasting.

## 2. Review of Literature

The present research work was planned to study the bioefficacy and persistence toxicity of imidacloprid 17.8 SL, spinosad 45 SC, fipronil 5 SC and lambda-cyhalothrin 5 EC against pomegranate thrips *Scirtothrips dorsalis* (H.). The studies were extended to study residues and dissipation of these insecticides in pomegranate fruits. Various methods of residue analysis were also compared for their efficiency. The literature regarding bioefficacy and residues of these insecticides on pomegranate is not available hence references closely related to either pest or pesticides are reviewed in this chapter under following sub-headings.

- 2.1 Studies on the bioefficacy and persistence toxicity of reduced risk insecticides against pomegranate thrips
  - 2.1.1 Imidacloprid
  - 2.1.2 Spinosad
  - 2.1.3 Fipronil
  - 2.1.4 Lambda-cyhalothrin
- 2.2 Comparison of different methods of insecticide residue analysis for their efficiency
- 2.3 Studies on the extent of residues of insecticides in pomegranate fruits and soil
- 2.4 Studies on leaching of lindane and chlorpyrifos used in pomegranate stem pasting.

## **2.1 Studies on the bioefficacy and persistence toxicity of reduced risk insecticides against pomegranate thrips**

Thrips, *Scirtothrips dorsalis* (H.) is one of the most important pests infesting pomegranate crop. It feeds on the foliage as well as fruits deteriorating quality of the fruits. At International level thrips are considered as a potential pest in pomegranate being responsible for deteriorating quality of the fruits (Gilbert, 1986 and Wang, 1994). The reports on the bioefficacy of chemical insecticides against thrips are less. However, the work on thrips found on other field and horticultural crops is presented below.

In an experiment conducted by Bagle (1993) in Gujrat, out of eight insecticides, spraying of 0.05% monocrotophos provided effective control of thrips (*S. dorsalis*) on pomegranate. Spray treatments of insecticides viz., 0.03% imidacloprid (Manjunatha *et al.*, 2000 and Patil *et al.*, 2002) and 0.016% acetamiprid (Jayewar *et al.*, 2003) provided effective control of thrips infesting chilli crop. Duraimurugan and Jagadish (2002) studied the seasonal incidence of *S. dorsalis* on local red rose in Bangalore, India, during September 1999 to August 2000. The investigations revealed that the incidence prevailed throughout the flowering period and reached its peak during the first fortnight of April (42.81 thrips per flower). Severe infestation occurred between April and May. The incidence was significantly and positively correlated with the maximum temperature and sunshine hours but negatively correlated with the mean relative humidity.

Seal *et al.* (2005) evaluated the efficacy of different insecticides (spinosad, imidacloprid, chlorfenapyr, novaluron,

abamectin, spiromesifen, cyfluthrin, methiocarb, and azadirachtin) for the control of chilli thrips, *S. dorsalis* (H.) on 'Scotch Bonnet' pepper at St. Vincent. Irrespective of the number of applications and use of surfactant, chlorfenapyr was the most effective treatment in reducing the densities of *S. dorsalis* adults and nymphs followed by spinosad and imidacloprid. The performance of other insecticides in controlling *S. dorsalis* populations was inconsistent. Nevertheless, all of the above insecticides, if applied repeatedly, were effective in suppressing *S. dorsalis* populations. Addition of the surfactant-sticker, Nu-Film 17TM, improved the performance of all insecticides. Spinosad was slightly harmful and chlorfenapyr was moderately harmful to predator *Cryptolaemus* sp.

The bioefficacy of triazophos (350 and 700 ml ha<sup>-1</sup>), acephate (1000 and 1500 g ha<sup>-1</sup>), cypermethrin (150 and 300 ml ha<sup>-1</sup>) and imidacloprid (50 and 70 g ha<sup>-1</sup>) was studied by Kumar *et al.* (2001) against the major pest complex aphids, *Myzus persicae* (Sulzer); thrips, *Scirtothrips dorsalis* (H.); gram pod borer, *Helicoverpa armigera* (Hubner); tobacco caterpillar, *Spodoptera litura* (Fabricius); and sunhemp hairy caterpillar, *Utetheisa pulchella* (Linnaeus) of chilli (*Capsicum* spp.) in a field experiment conducted at Hyderabad, India during the *Kharif* season of 1997-98. Imidacloprid (70 g ha<sup>-1</sup>) was the best treatment in controlling aphids (99.76 per cent reduction). Acephate (1500 g ha<sup>-1</sup>) was the most effective in controlling thrips (87.22 per cent reduction) and cypermethrin (300 g ha<sup>-1</sup>) was the most effective insecticide against borers. Nderitu *et al.* (2007) conducted a field study to evaluate the effectiveness of four insecticides lambda-cyhalothrin (Karate 1.75 EC), petroleum spray oil (DC Tron 500 ML), spinosad (Tracer 48

SC) and fipronil (Regent 5 SC) for the control of thrips infesting French beans (*Phaseolus vulgaris* L.) at Kabete, Central Kenya. Results showed that Tracer 48 SC and Regent 5 SC sprayed plots had the lowest thrips numbers across all varieties. Individual thrips species infestation differed across the treatments. For example, the mean number of *Frankliniella occidentalis* (Pergande) in Karate 1.75 EC sprayed plots was higher and significant compared to plots sprayed with Tracer 48 SC and Regent 5 SC but mean number of *Megalurothrips sjostedti* Trybom was not significantly different in all plots except those sprayed with DC Tron 500 ML and the control (unsprayed) plots.

Biradar and Navi (2006) determined the efficacy of 10, 20 and 40 g phorate 10, 25, 75 and 100 g carbofuran per plant and 20 g lindane per plant for controlling aphids and pests infesting pomegranate cv. Ganesh in a field experiment conducted in Karnataka, India during 2001-03. Application of 100 g carbofuran per plant resulted in the highest reduction in aphids (98.6 per cent), whereas application of 75 g carbofuran per plant resulted in the highest reduction in thrips population (97.9 per cent). The mean crop yield was highest with the application of 100 g carbofuran per plant (45.69 q ha<sup>-1</sup>) followed by application of 75 g carbofuran per plant (45.56 q ha<sup>-1</sup>). Efficacy of methomyl against chilli thrips *S. dorsalis* (H.) was studied by Satpathy *et al.* (2006) in a field experiment conducted in the farmer's field during 2001 to 2002 and 2002 to 2003. On the basis of post-treatment thrips infestation and yield, application of methomyl @ 300 g a.i. ha<sup>-1</sup> was found to be most effective compared to the check insecticide dimethoate and untreated control. Relative infestation in treatments at different

intervals after spray indicated that persistent effect was noticed upto 10 days after spray.

### **2.1.1 Imidacloprid**

Mote *et al.* (1993) tested imidacloprid 70 WS as seed dresser for okra at 5, 7.5, 10 and 15 g kg<sup>-1</sup> seed for control of sucking pests. They reported that seed treatment with imidacloprid 15 g kg<sup>-1</sup> was found promising against sucking pests *viz.*, aphids, jassids, thrips, mites and whiteflies. They also observed least per cent of Yellow Vein Mosaic attacked plants and obtained higher okra yield in these treatments. Two separate experiments were conducted by Rajendra Kumar *et al.* (2008) during winter season in New Delhi, India, to control the mustard aphid, *Lipaphis erysimi* (Kaltenbach). Imidacloprid was applied as seed treatment (Gaucho 70 WS, 5 and 10 g a.i. kg<sup>-1</sup> seed) and foliar spray (Confidor 200 SL, 20 and 40 g a.i. ha<sup>-1</sup>) at 50% pod formation stage on mustard, *Brassica campestris* (L.). Imidacloprid effectively controlled the aphid population when used as seed and foliar spray treatment. The lower treatment rates (seed treatment at 5 g a.i. kg<sup>-1</sup> and foliar spray at 20 g a.i. ha<sup>-1</sup>) proved sufficient to optimize the yield of mustard crop. Mustard grains and soil at harvest did not contain imidacloprid residues. The results also revealed that there was no build up or leaching of imidacloprid in soil.

Dhandapani *et al.* (2002) conducted two field experiments during September to February 2000-01 and August to February 2001-02 in Tamil Nadu, India and revealed that seed treatment with the new insecticides, clothianidin (Poncho 600FS) at 9 ml kg<sup>-1</sup> seed and imidacloprid (Gaucho 600 FS) at 12 g kg<sup>-1</sup> seed, effectively controlled the sucking pests of cotton, aphids (*Aphis gossypii* G.),

thrips (*Scirtothrips dorsalis* H.) and leaf hoppers (*Amrasca biguttula biguttula* L.), up to 8 weeks after sowing. Seed treatment with imidacloprid 70 WS @ 0.2, 0.3 and 0.5 per cent and thiamethoxam @ 0.2, 0.3 and 0.5 per cent were evaluated for their efficacy against sucking pests of green gram, cv. TARM-18, at Rahuri during *Kharif* season of 1999. Though all the dosages of imidacloprid and thiamethoxam were found effective in controlling sucking pests, the treatments with 0.5 per cent concentration were the most effective. Aphids and jassids were controlled effectively, while there was little effect on thrips and no effect on mites was observed by both of these insecticides; when two chemicals were compared with each other, thiamethoxam (70 WS) was found to be superior to imidacloprid (70 WS) in all respects (Nakat *et al.*, 2002).

Patil *et al.* (2002) evaluated imidacloprid 17.8 SL for its relative efficacy against sucking pest complex of chilli *viz.*, aphids, jassids and thrips in comparison with conventional insecticides during *Kharif* 2002 and reported that imidacloprid @ 125 and 150 ml ha<sup>-1</sup> was highly effective against the sucking pest complex of chilli and proved to be better than monocrotophos and dimethoate. Shitole *et al.* (2002) conducted a field experiment during *Rabi*-2000 to evaluate the performance of certain new chemicals for the management of onion thrips. Cypermethrin 75 g a.i. ha<sup>-1</sup> and imidacloprid 17.8 SL @ 20 g a.i. ha<sup>-1</sup> were found effective. Rathod *et al.* (2003) conducted a field experiment at Cotton Research Station, Nanded (MS), India during 1997-2000 to determine the efficacy of imidacloprid against jassids (*Amrasca biguttula biguttula*), aphids (*Aphis gossypii*), and thrips (*Thrips tabaci* Lindeman) infesting cotton. The treatments comprised imidacloprid

seed treatment at 5, 7.5, and 10 g kg<sup>-1</sup> and foliar spray of difenthiuron 300 and 400 g ha<sup>-1</sup> and dimethoate at 1.25 L ha<sup>-1</sup>. The lowest mean population of jassids (0.99), aphids (4.41), and thrips (1.73) per 3 leaves was observed in the treatments with 10 g imidacloprid kg<sup>-1</sup>, 300 g difenthiuron ha<sup>-1</sup> and 5 g imidacloprid kg<sup>-1</sup>, respectively. The highest cotton yield (826 kg ha<sup>-1</sup>) was obtained with 5 g imidacloprid kg<sup>-1</sup> seed treatment.

Beltran *et al.* (2004) investigated the efficiency and residual effects of systemic insecticides applied on or mixed with cotton seeds to control thrips and aphids in trials in Argentina during 1999-2000 and 2000-01. The insecticides were: aldicarb 10 G at 150 and 300 g a.i. ha<sup>-1</sup>; thiodicarb 35 LF at 700 g a.i. 100 kg<sup>-1</sup> seeds; imidacloprid 60 FS at 282 g a.i. 100 kg<sup>-1</sup> seeds; thiamethoxan 35 FS at 210 g a.i. 100 kg<sup>-1</sup> seeds in both the years. All the treatments were better for thrips and aphids control compared to the untreated. The most efficient treatments with the highest residual effects were aldicarb, thiamethoxam and imidacloprid. Kannan *et al.* (2004) studied the impact of insecticides on sucking pests and natural enemy complex on transgenic *Bt* cotton during *Kharif* 2002 at Tamil Nadu Agricultural University, Coimbatore, India under irrigated conditions. Results of field studies revealed that the seed treatment of transgenic cotton with imidacloprid at 5 g kg<sup>-1</sup> was more effective than other treatments (dimethoate) in controlling the populations of leafhoppers (*Amrasca biguttula biguttula*), aphids (*Aphis gossypii*), thrips (*Scirtothrips dorsalis*) and whitefly (*Bemisia tabaci* Gennadius) and kept them below economic threshold level up to 40 days after sowing. Sreekanth *et al.* (2004) determined the efficacy of imidacloprid,

thiamethoxam, acetamiprid, fipronil, dimethoate, fenvalerate and azadiractin for controlling *Thrips palmi* (Karny), the vector of peanut bud necrosis virus (PBNV) infesting mung bean in a field experiment conducted at Hyderabad, India during the *Kharif* and *Rabi* seasons of 2000. All the insecticides reduced *T. palmi* population and PBNV incidence, with imidacloprid treatment resulting in the highest thrips control (57.47 and 67.41 per cent) and consequently, the lowest PBNV incidence (19.11 and 29.74 per cent) during both the seasons.

Ameta and Sharma (2005) reported that two sprays of commercial formulations of imidacloprid, *i.e.* Confidor 350 SC (60 and 75 ml ha<sup>-1</sup>) and Confidor 200 SL (100 and 125 ml ha<sup>-1</sup>) at 15 days interval were found effective in controlling *Aphis gossypii*, *Amrasca biguttula biguttula*, *Thrips tabaci* on cotton and gave highest cotton yield during the year 2003-2004. Mishra *et al.* (2005) conducted field experiments during *Kharif* 2002 and 2003 in Orissa, India to evaluate the efficacy of some new insecticides in controlling thrips (*S. dorsalis*) on chilli; the insecticides were applied as foliar sprays on the crop twice, *i.e.* at 40 and 70 days after planting. Imidacloprid was the most effective in suppressing the thrips population (average of 1.46 thrips per 10 apical leaves) and also increased the fruit yield of chilli (27.63 q ha<sup>-1</sup>), followed by monocrotophos and acetamiprid. Bhadane *et al.* (2007) conducted a field experiment on bioefficacy of Confidor 200 SL against sucking pests on groundnut at Oilseeds Research Station, Jalgaon, India during *Kharif* 2000 and 2001. The authors concluded that all the three doses of Confidor 200 SL @ 100, 125 and 150 ml ha<sup>-1</sup> found to be significantly effective in reducing the nymphal population of

thrips as compared with conventional insecticides, dimethoate and acephate on 3, 7 and 14 days after spraying.

Sunitha *et al.* (2008) conducted an experiment at Bijapur, Karnataka, India, during 2006-07 to evaluate the efficacy of various insecticides against *Thrips hawaiiensis*, *T. palmi* and *S. dorsalis* on grape (cv. Thompson Seedless) and found that acetamiprid 20 SP, imidacloprid 17.8 SL and thiamethoxam 25 WG were superior in the reduction of thrips population to the extent of 94.4, 96.0 and 95.7 per cent, respectively. Bhede *et al.* (2008) studied the population dynamics and bioefficacy of newer insecticides against chilli thrips, *S. dorsalis* at Vegetable Research Station, MKV, Parbhani, (MS), India, during *Kharif* 2002-03. The incidence of thrips was highest during 40<sup>th</sup> meteorological week when the prevailing maximum and minimum temperatures, morning-evening relative humidity, rainfall and bright sunshine hours were 35.8 °C, 18.0 °C, 76 and 34 per cent, 0.00 mm and 11 h, respectively. Application of phosphamidon 40% + imidacloprid 2% SP at 700 g ha<sup>-1</sup> was the most effective for suppression of thrips population and also increased the yield of green chilli.

### **2.1.2 Spinosad**

Spinosad possesses broad spectrum activity with quite good efficacy against many species of insect pests (Sparks *et al.*1995). Spinosad is a contact, nerve and stomach poison (Salgado, 1997). In case of cotton crop, infestation of thrips was effectively minimized by spraying of spinosad (Hollowy and Forrester, 1998; Herbert *et al.*, 1998).

A overview of the efficiency of insecticides against thrips infesting fruiting vegetables, onion and corn in Hawaii is provided in a paper presented in 'International symposium on Thysanoptera' held in Turkey (Mau *et al.*, 1999). Field experiments on watermelon, egg plant and green pepper showed that chlorfenapyr and abamectin proved very effective in controlling *T. palmi*. Spinosad appeared to be effective against the pest on aubergines. In field tests on onion, lambda-cyhalothrin and fipronil were highly effective on *T. tabaci*. The effect of spinosad on thrips in cotton was studied by Herbert *et al.* (1998). The plants treated with spinosad matured faster and produced an average 180 lb per acre higher lint yield than untreated control. Cloyd and Sadof (2000) reported that spinosad @ 50, 100 and 200  $\mu\text{g g}^{-1}$  and acephate @ 600  $\mu\text{g g}^{-1}$  were effective against western flower thrips (*Frankliniella occidentalis* Pergande) on gerbera. A field trial on efficacy of spinosad against vegetable pests was conducted by Leader and Dutton (2002). They found that the foliar application of spinosad can control thrips in leeks and salad onion as well as caterpillar pests in head and flowering brussels sprouts.

Zeulina and Blazic (2003) investigated the bioefficacy of eight different insecticides based on four active substances (dimethoate, imidacloprid, spinosad and abamectin) in 2002 in Goriska region of Slovenia and found that spinosad and abamectin exhibited the highest efficiency against *T. tabaci*. Seal *et al.* (2005) evaluated modern insecticides against chilli thrips and observed that chlorfenapyr (Alert 2F) 731 ml ha<sup>-1</sup> was the most effective in reducing the densities of *S. dorsalis* adults and larvae followed by spinosad (Spintor TM 2 SC) 511 ml ha<sup>-1</sup> and imidacloprid (Provado

1.6 F) 274 ml ha<sup>-1</sup>. Kadam (2006) evaluated some newer insecticides for control of pomegranate fruit borer at Mahatma Phule Krishi Vidyapeeth, Rahuri (MS), India. He sprayed spinosad 45 SC @ 0.018 and 0.025 per cent, emamectin benzoate 5 SG @ 0.0016 and 0.0022 per cent, thiodicarb 75 WP @ 0.15 and 0.18 per cent, deltamethrin @ 0.002 per cent and NSKE 5 per cent. The results showed that emamectin benzoate 5 SG @ 0.0022 and 0.0016 per cent was the most effective treatment in minimizing fruit borer (79.45 per cent and 75.68 per cent) followed by spinosad 45 SC @ 0.025 and 0.018 per cent which recorded 69.96 per cent and 57.21 per cent reduction in fruit damage, respectively.

Dhanalakshmi and Mallapur (2008) conducted a field experiment at Dharwad, Karnataka, India, during the *Kharif* of 2005 to evaluate the efficacy of different insecticides against sucking pests of okra (hybrid RASI-5) and found that spinosad 45 SC at 0.1 ml L<sup>-1</sup>, imidacloprid 200 SL at 0.5 ml L<sup>-1</sup> and acetamiprid 20 SP at 0.2 g L<sup>-1</sup> were the most effective against thrips. The highest fruit yield was recorded from the plots treated with emamectin benzoate 5 SG at 0.2 g L<sup>-1</sup> (47.02 quintal ha<sup>-1</sup>), followed by spinosad 45 SC at 0.1 ml L<sup>-1</sup> (45.94 quintal ha<sup>-1</sup>) and indoxacarb 14.5 SC at 0.3 ml L<sup>-1</sup> (43.03 quintal ha<sup>-1</sup>). Emamectin benzoate 5 SG at 0.2 g L<sup>-1</sup>, spinosad 45 SC at 0.1 ml L<sup>-1</sup> and acetamiprid 20 SP at 0.2 g L<sup>-1</sup> were comparatively safe to natural enemies (Coccinellid larvae, spiders and *Chrysoperla* larvae).

### **2.1.3 Fipronil**

Ester *et al.* (1997) investigated effectiveness of various insecticides applied as a seed coating to control *Thrips tabaci* in winter leeks (*Allium porrum*); seed coating with fipronil and

imidacloprid gave good control. Garzo *et al.* (2000) conducted experiment on bell pepper (*Capsicum annuum* L.) leaf disks immersed in different concentrations of fipronil, acrinathin and formetanate and compared their toxicities on *Frankliniella occidentalis* under laboratory conditions. The data showed that 13 hrs of exposure was needed to obtain 95 per cent mortality of thrips with fipronil at 50 ml L<sup>-1</sup>; it was more effective than other two insecticides. Two fipronil formulations were evaluated by Kadam and Dethe (2002) against chilli thrips (*S. dorsalis*) at Rahuri (MS), India. Fipronil (0.3 G) granules incorporated in seed-bed at the rate of 40 to 60 g per m<sup>2</sup> suppressed the incidence of thrips on seedlings considerably and four foliar sprays of fipronil 5 SC at fortnightly interval lowered the level of infestation in transplanted crop. Increase in plant height, chlorophyll content and green chilli yield was also reported. Fipronil was found effective at 50 g a.i.ha<sup>-1</sup> against chilli thrips as reported by Jadhav *et al.* 2004. Jadhav (2003) evaluated the efficacy of fipronil 5 SC at different concentrations against sucking pests of chilli in comparison with imidacloprid 17.8 SL @ 20 g a.i. ha<sup>-1</sup>; phosalone 35 EC @ 500 g a.i. ha<sup>-1</sup> and fipronil 5 SC @ 100 g a.i. ha<sup>-1</sup> recorded lowest population of sucking pests and highest yield.

Kale (2003) reported that fipronil provided excellent control of jassids (mortality 85 per cent or more). The order of efficacy of different insecticides against jassids was fipronil > abamectin > spinosad. The author concluded that fipronil emerged as the next effective insecticide against jassids and thiamethoxam and fipronil fit well in controlling leaf hoppers and could also be incorporated in rotational sprays. He also concluded that thiamethoxam, a systemic

insecticide alternated with spinosad and fipronil would be the best IPM tool for managing major pests (aphid, jassid and fruit borer) in okra. Wadnerkar *et al.* (2003) evaluated fipronil 5 SC against insect pests of cotton *viz.*, aphid, jassids and thrips. Fipronil 5 SC @ 50, 75 and 100 g a.i. ha<sup>-1</sup> was found to be effective in lowering the insect pest population. However, fipronil 5 SC @ 100 g a.i. ha<sup>-1</sup> was found to be optimum for reducing the bollworm infestation and 50 to 75 g a.i. ha<sup>-1</sup> dose was found optimum against aphid, jassid and thrips.

Rajkumar *et al.* (2005) conducted field studies at Rose garden, Agricultural Research Institute, Rajendranagar, Hyderabad, India during April to May, 2001 and studied the relative efficacy of six selected insecticides against rose thrips (*Rhipiphorothrips cruentatus* H.). The results revealed that fipronil (0.01%) was the most effective chemical and protected the crop against thrips up to 15 days after treatment. Acephate (0.075%) and imidacloprid (0.1%) were least effective against the thrips. Reddy *et al.* (2005) studied the bioefficacy of certain new insecticides along with traditional insecticides as foliar spray against chilli thrips (*S. dorsalis*) and mites (*P. latus*) in India during 2001 and 2002. Seventeen insecticides were sprayed 3 times at an interval of 10 days. Fipronil 5 SC (0.01%) followed by thiamethoxam 25 WG (0.005%), acetamiprid 20 SP (0.002%) and dimethoate 30 EC (0.06%), were the most effective treatments against thrips, while carbaryl 50 WDP (0.15%), followed by phosalone 50 EC (0.07%) and chlorpyrifos 20 EC (0.05%), were the least effective.

### 2.1.4 Lambda-cyhalothrin

Asokan and Venugopal (1992) evaluated lambda-cyhalothrin (Karate), a new synthetic pyrethroid in laboratory for its efficacy against *Scirtothrips dorsalis* H. alongwith cypermethrin 75  $\mu\text{g g}^{-1}$ , deltamethrin 15  $\mu\text{g g}^{-1}$  and methyl demeton 250  $\mu\text{g g}^{-1}$  etc. Cyclothrin 62.5 and 50  $\mu\text{g g}^{-1}$  and cypermethrin 75  $\mu\text{g g}^{-1}$  registered cent per cent mortality. Bocak (1995) tested eleven insecticides against *T. tabaci* in onion, of which alpha-cypermethrin (25 g a.i.  $\text{ha}^{-1}$ ) and lambda-cyhalothrin (12.5 g a.i.  $\text{ha}^{-1}$ ) reduced the pest population significantly. Further, he stated that pyrethroids had very good and relatively long lasting efficacy against thrips. A field experiment on onion was conducted by Khan *et al.* (1995), they found that monocrotophos 36 WSC (60 ml per 100 lit. of water) and cypermethrin 5 EC (50 ml per 100 lit. of water) were the most effective insecticides for controlling the infestation of *T. tabaci*, followed by lambda-cyhalothrin 2.5 EC (25 ml), triazophos 40 EC (80 ml) and fenvalerate 20 EC (30 ml) 100  $\text{L}^{-1}$  of water. Branco (1996) reported that lambda-cyhalothrin was the most effective treatment for suppression of tomato thrips followed by permethrin and deltamethrin.

Goncalves (1996) tested different dosages of insecticides *viz.*, deltamethrin + triazophos (EC) at 3.0 + 105.0, 4.5 + 157.5 and 6.0 + 210.0 g a.i.  $\text{ha}^{-1}$ , cypermethrin (EC) at 50, 120 and 150 g a.i.  $\text{ha}^{-1}$  and lambda-cyhalothrin (WP) at 15 g a.i.  $\text{ha}^{-1}$  against *T. tabaci*. The treatments with lambda-cyhalothrin and cypermethrin were effective, but only cypermethrin at 150.0 g a.i.  $\text{ha}^{-1}$  increased the yield of onion bulbs. A field experiment was carried out by Seaton *et al.* (1996) for the evaluation of insecticides against thrips

(*F. occidentalis*) on cut flowers. The results revealed that methamidophos, diclorvos and lambda-cyhalothrin were effective in lowering population of thrips in descending order. Shelton *et al.* (1998) studied efficacy of 17 insecticides including acephate 75 SP, dimethoate 4 EC, imidacloprid 2 F, lambda-cyhalothrin 1 EC, methyl parathion 2 EC, etc. against onion thrips. They concluded that these insecticides reduced the thrips population significantly when applied alone and in split season programme with methamidophos. An experiment was conducted to evaluate the efficacy of four newer insecticides *viz.*, difenthiuron (Pegasus 50 WP), thiamethoxam (Actara 25 WG), acetamiprid (Pride 20 SP) and lambda-cyhalothrin (Karate 5 EC) against onion thrips during *Rabi* 2003 at NRCOG Rajagurunagar, Pune, India. The results showed that lambda-cyhalothrin @ 80 g a.i. ha<sup>-1</sup> was very effective, followed by lambda-cyhalothrin @ 40 g a.i. ha<sup>-1</sup> and monocrotophos 0.05 per cent against onion thrips (Anonymous, 2003).

In another field experiment, four new insecticides were tested during *Rabi* season each at two doses against *T. tabaci* on onion. It was observed that lambda-cyhalothrin (Karate @ 50 g a.i. ha<sup>-1</sup>) was significantly effective in reducing the thrips population in all the four sprays, followed by its lower dose 25 g a.i. ha<sup>-1</sup> (Anonymous, 2005). Sule *et al.* (2008) evaluated the efficacy of fipronil 5 SC (0.01%), acetamiprid 20 SP (0.004%), difenthiuron 50 WP (0.05%), lambda-cyhalothrin 5 EC (0.005%), bifenthrin 10 EC (0.016%) and endosulfan 35 EC (0.035%) against *T. tabaci* on onion (cv. N 2-4-1) in Pune, (MS), India, during the winter season of 2005. The insecticides were sprayed on foliage at the initial occurrence of thrips. Subsequent three sprays at 15 days interval (E1) or two at

21 days interval (E2) were given. All the insecticides were effective against the pest. In E1 and E2, lambda-cyhalothrin was the most effective, as it recorded the lowest cumulative thrips count (2.63 and 3.62, respectively) and highest yields (23.99 and 22.55 t ha<sup>-1</sup>). E1 was more effective than E2.

## **2.2 Comparison of different methods of insecticide residue analysis for their efficiency**

The analytical results depend upon the efficiency of the method of insecticide residue analysis. Recovery percentage is the measure of efficiency of analytical methods. California Department of Food Adulteration (CDFA), QuEChERS and Environmental Protection Agency (EPA) are the most common multiresidue methods used in insecticide residue analysis. Moreover, the manufacturers also provide Single Residue Method (SRM) for the analysis of a particular compound. In order to validate the method of analysis for each compound on pomegranate fruits different methods were compared for their efficiency.

The work done on the residues of various insecticides in India has been reviewed up to 1971 by Bindra and Kalra (1973) and from 1971 to 1977 by Agnihothrudu and Mithyantha (1978). The literature on residues of imidacloprid 17.8 SL, spinosad 45 SC, fipronil 5 SC and lambda-cyhalothrin 5 EC on pomegranate fruits is not available. Hence, the review of residues of test insecticides on other crops is presented. Anderson and Palsheden (1991) compared the efficiency of acetone and ethyl acetate extraction methods for multi-residue determination by GLC in fruit and vegetables. Ethyl acetate gave higher recovery of polar insecticides and was easier, quicker and cheaper to perform. However, some

co-extractives were observed in the GLC analysis. Both the methods were acceptable and had similar insecticide recovery. Pang *et al.* (1994) developed packed column gas chromatographic method for simultaneous determination of ten pyrethroid insecticides including cyhalothrin and cyfluthrin in fruits and vegetables. The multiresidues were extracted with acetone, petroleum ether and cleaned up on Florisil column prior to determination by gas chromatograph equipped with electron capture detector (GC-ECD).

The simple residue method for synthetic pyrethroids including cyhalothrin in vegetables was described by Wan *et al.* (1994). Insecticides were extracted with ethanol (100 ml), partitioned into toluene (6 ml), cleaned up on mini column with Florisil (0.5 g) prior to gas chromatographic determination. The detection limits were 0.02 to 0.05  $\mu\text{g g}^{-1}$  without concentrating the extract, which were below MRLs specified by Singapore Government. An analytical method developed by West (1996) for detection of spinosad from cotton seed and cotton seed processed commodities had a limit of quantification (LOQ) of 0.01  $\mu\text{g g}^{-1}$  and limit of detection (LOD) of 0.003  $\mu\text{g g}^{-1}$ . The residues were cleaned up on SPE cartridge and determined by reverse phase HPLC with ultra violet (UV) detection at 250 nm. Yeh *et al.* (1997) observed average recovery of spinosad in the range between 77 and 97 per cent at LOD of 0.003  $\mu\text{g g}^{-1}$  in leafy vegetables, pepper and tomatoes. Tan *et al.* (1998) compared three well established methods for insecticide clean up (using Alumina, silica and Florisil) and contrasted with a view of obtaining improved recovery for a wider range of 30 insecticides (including dieldrin, DDT, endrin, lindane, aldrin, clorothalonil, folpet,

captan and iprodione), as well as improving the clean up efficiency of the sample extract from lettuce. The method using neutral Alumina as the clean up adsorbent was the most efficient in removing contaminants from the sample. However, it allowed only 70 per cent recovery of only 23 from 30 insecticides studied. The method using Florisil was not efficient in removing contaminants from sample extracts, but gave >70 per cent recovery for all insecticides, except dichlofluanid. The average recovery of spinosad ranged from 69 to 96 per cent from wheat straw, sorghum fodder and corn stover when estimated by liquid chromatograph mass spectrophotometry (Schwedler *et al.*, 2000).

Colume *et al.* (2001) determined the organochlorine and pyrethroid residues in fruits using gas chromatograph equipped with electron capture detector and a mass spectrometric detector (GC-MS) was used for confirmation. Among the pyrethroid insecticides lambda-cyhalothrin, beta-cyfluthrin and alpha-cypermethrin provided average recovery of  $89 \pm 8$  per cent. Kale (2003) showed 91 per cent average recovery of spinosad from the fortified samples of okra fruits. Fan-ZhiXian *et al.* (2003) determined the residual dynamics of imidacloprid in tomato and soil with high performance liquid chromatography, using a Spherisorb 5 micro-C18 column and acetonitrile and water (30:70) as the mobile phase. The results showed that the recovery of imidacloprid in soil and tomato varied from 80 to 120 per cent; the half-life of imidacloprid was 8.2 to 21 days. A gas chromatography (GC) method was developed by Luo GongShu *et al.* (2005) to analyse the residues of fipronil in soil planted with vegetables. Fipronil was extracted with acetonitrile, cleaned up with chromatography column,

and then determined by GC. The fortified average recovery varied from 87.79 to 98.45 per cent. Results indicated that the half-life of fipronil in soil was 9.52 and 9.96 days, the residue of fipronil was  $0.045 \text{ mg kg}^{-1}$  two weeks after application, and the final residue amount was less than  $0.01 \text{ mg kg}^{-1}$ . Kamble and Saran (2005) conducted an experiment in Nebraska, USA, to study the effect of imidacloprid ( $500$  and  $750 \text{ } \mu\text{g g}^{-1}$ ), fipronil ( $600$ ,  $950$  and  $1250 \text{ } \mu\text{g g}^{-1}$ ) and bifenthrin ( $600$ ,  $900$  and  $1200 \text{ } \mu\text{g g}^{-1}$ ) concentrations on their adsorption behaviour in the soil. The fipronil adsorption isotherm was L-type and there was a decrease in adsorption site availability as the solution concentration increased. Fipronil soil partition coefficient and organic carbon partition coefficient values clearly indicated a concentration dependent adsorption trend. The slope of adsorption for bifenthrin was L-type. The adsorption isotherm showed similar concentration dependent trend as indicated for imidacloprid and fipronil.

Ueno, *et al.* (2006) developed a simple and reliable method for the determination of spinosyns A and D, the active ingredients of spinosad, in vegetables and fruits by high-performance liquid chromatography with UV detection (HPLC-UV) and confirmation by mass spectrometry (MS); the method uses selected gel permeation chromatography (GPC) and a 2-layered column for solid-phase extraction system. An aliquot of the crude sample extract obtained by acetonitrile extraction was loaded onto the GPC system. The fraction containing spinosyns A and D was selectively collected and loaded directly onto a 2-layered column consisting of graphitized carbon (upper layer) and cyclohexyl-bonded silica gel (lower layer). The column was rinsed with the GPC mobile phase

acetone-cyclohexane (3+7), the column was eluted with acetonitrile containing 2% triethylamine. The eluate was used for HPLC-UV/MS analysis. Average recovery from fortified cabbage, green perilla, fig, and strawberry at analyte concentrations of 0.05 and 0.25  $\mu\text{g g}^{-1}$  was > 85 per cent, and the relative standard deviations were < 9 per cent. The detection limits for spinosyns A and D in green perilla were 0.005  $\mu\text{g g}^{-1}$  by UV detection and 0.001  $\mu\text{g g}^{-1}$  by MS detection.

Esteve-Turrillas *et al.* (2006) carried out a comparative study for the simultaneous determination of 11 pyrethroid insecticides in soil by gas chromatography (GC)-ion trap (IT)-mass spectrometry (MS), by means of two different ionization modes; electron impact and negative chemical ionization and three data acquisition procedures; full scan, selected ion monitoring and MS/MS. Pyrethroids investigated were tetramethrin, bifenthrin, phenothrin, lambda-cyhalothrin, permethrin, cyfluthrin, cypermethrin, fenvalerate, fluvalinate and deltamethrin. Soil samples were treated with toluene or water by microwave-assisted extraction for 9 min at 700 W and a cleaning up with Florisil was performed. Clean soil samples were spiked with pyrethroids at a spiking level of 10, 25 and 50  $\text{ng g}^{-1}$ . The ionization gas employed in the negative chemical ionization mode was methane. The use of MS/MS acquisition, in electron impact ionization, provided the best results, due to its high selectivity and sensitivity, giving very low limits of detection from 0.08 to 0.54  $\text{ng g}^{-1}$ . In negative chemical ionization full scan and selected ion monitoring methods detection limits from 0.12 to 1.40  $\text{ng g}^{-1}$  were found. The proposed methods were applied to several levels from 10 to 50  $\text{ng g}^{-1}$  of spiked soils, electron impact

MS/MS method which minimizes matrix spectrum interferences provided average recovery values from 84 to 120 per cent with relative standard deviations varying from 3.2 to 7.2 per cent. Diao-ChuanYun *et al.* (2007) analysed imidacloprid residues in pear by a modified HPLC method. When a mobile phase with acetonitrile:water in a ratio of 40:60 (v:v) was used and the wavelength for detection was set at 268 nm, the recovery rate of imidacloprid residue in pear varied from 83.3 to 116.6 per cent, with a low relative standard deviation of less than 5.06 per cent. This approach was optimum in the rapid and accurate detection of imidacloprid.

### **2.3 Studies on the extent of residues of insecticides in pomegranate fruits and soil**

Research estimate shows that not more than 1 per cent of the insecticide, applied on the crop reaches to the target pest and about 99 per cent degrades in the atmosphere including soil.

Davies and Kuhr (1976) stated that furrow application of emulsion concentrate and granular formulation of chlorpyrifos at the rates of 1 and 2 lb toxicant per acre on onion crop persisted in muck soil in New York State at concentrations above  $1 \mu\text{g g}^{-1}$  for 16 weeks and most of this was confined to the outer wrapper leaves. Talekar *et al.* (1977) studied the persistence of some insecticides in subtropical soil in Taiwan and found that residues of DDT and dieldrin declined 20 and 25 per cent in the winter and autumn months, respectively. Two organophosphates (fonofos and phorate) and one carbamate (carbofuran) degraded rapidly, resulting in only 8, 0.4 and 32 per cent recovery. Rai *et al.* (1980) studied residues of cyhalothrin (0.005%) in cauliflower head. Initial residue of 0.23

$\mu\text{g g}^{-1}$  declined to  $0.03 \mu\text{g g}^{-1}$  in 11 days and reached BDL after 15 days of application. Further they concluded that the problem of residues remaining on crop is much less with synthetic pyrethroids than quinalphos and trichlorfos. The residues of lambda-cyhalothrin in cotton lint were studied by Agnihotri *et al.* (1990) and they found that residues were 0.16 to 0.8 and 0.27 to  $1.0 \mu\text{g g}^{-1}$  at lower ( $50 \text{ g a.i.ha}^{-1}$ ) and higher ( $100 \text{ g a.i.ha}^{-1}$ ) doses, respectively.

Mukharjee and Gopal (1992) estimated 0.003 to 0.09  $\mu\text{g}$  residues of lambda-cyhalothrin from brinjal. Fenvalrate was the most persistent insecticide followed by monocrotophos and lambda-cyhalothrin. At an application rate of  $12.5 \text{ g a.i. ha}^{-1}$ , fipronil residue levels in the water column in small rice plots under glasshouse condition declined from  $2.1 \mu\text{g L}^{-1}$  after transplanting to  $0.01 \mu\text{g L}^{-1}$  at 14 days after treatment (Stevens *et al.*, 1998). Segura and Abakerli (1999) conducted studies on use of insecticides in irrigated tomato crop for quantifying residue levels in the fruits by multiresidue method. The residues of lambda-cyhalothrin were detected ( $0.03 \mu\text{g g}^{-1}$ ) during fruit formation and maturation stages of the crop. Dixit *et al.* (2001) studied residues of lambda-cyhalothrin ( $35 \text{ g a.i.ha}^{-1}$ ) on brinjal fruits. Residues were below detectable limit after seven days and the half-life of lambda-cyhalothrin on brinjal was 1.45 to 2.54 days. Indumathi *et al.* (2001) studied the uptake and dissipation of imidacloprid in okra by treating the seeds with Gaucho at  $9 \text{ g a.i. kg}^{-1}$  seed and spraying okra crop at the fruiting stage with Confidor 200 SL at 0.3 and  $0.6 \text{ ml L}^{-1}$ . They found that residues persisted in plant for more than 30 days after germination. However, residues could not be detected in fruits harvested at 50, 55 and 60 days after germination.

Imidacloprid residues dissipated exponentially with time following foliar application with a half-life of 2 to 4 days in two consecutive seasons. The residues, however, became non-detectable 10 days after treatment at lower concentration and 15 days after treatment at higher concentration.

Debi Sharma *et al.* (2002) conducted periodic dissipation studies of lambda-cyhalothrin in cauliflower cv. F1 hybrid NS-60N at Bangalore, India. Treatments comprised of 2.5 and 5 EC formulations of lambda-cyhalothrin at 15 and 30 g a.i. ha<sup>-1</sup>, treated cauliflower heads were sampled at periodic intervals at 0, 1, 3, 5, 7, 10 and 15 days after treatment. Although the initial deposits of lambda-cyhalothrin were high from all the treatments (0.81 to 1.59 mg kg<sup>-1</sup>), these dissipated quickly to reach below detectable limit within 10 to 15 days. The half-lives RL<sub>50</sub> of lambda-cyhalothrin in cauliflower were 2.0 to 2.2 days for the 2.5 EC formulation and 2.2 to 2.4 days for the 5.0 EC formulation, while the waiting periods (Ttol) were between 4.2 to 4.5 and 5.0 to 5.2 days for the 2.5 and 5.0 EC formulations, respectively. Mathirajan (2002) studied dissipation of lambda-cyhalothrin (Karate 5 EC) in/on tomato fruits at application rates of 7.5, 15 and 30 g a.i. ha<sup>-1</sup>. The lowest dose persisted to detectable level for 5 days while at the medium and highest dose, it persisted for 7 days and reached below detectable level 10 days after of application.

Rajabaskar *et al.* (2002) conducted two supervised trials during 1999-2000 and 2000-2001, respectively. Three applications of lambda-cyhalothrin @ 10, 15, 20, 30, and 40 g a.i. ha<sup>-1</sup> were given. Samples were collected on 0, 1, 3, 5, 7 and 15 days after treatment. Residues in 50 g samples were extracted with acetone,

cleaned up with dichloromethane and final determination was done by GC-ECD. The initial deposits of 0.67 and 1.1  $\mu\text{g g}^{-1}$  were detected on immature cashew apples at the lowest concentration of 10 g a.i.  $\text{ha}^{-1}$  during 2000 and 2001 respectively. The deposit was as high as 2.8 and 3.7  $\mu\text{g g}^{-1}$  at the highest concentration of 40 g a.i.  $\text{ha}^{-1}$ . The residues dissipated to BDL irrespective of the concentrations on day 15 of application. The estimated half-life was 0.9 to 1.0 day at the lowest dose and 1.4 to 1.5 days at the highest dose. The tentative waiting period arrived was 4.4 to 5.7 days at the recommended concentration of 10 g a.i.  $\text{ha}^{-1}$ , considering the MRL of 0.02  $\mu\text{g g}^{-1}$ .

Regupathy *et al.* (2002) conducted two trials in Tamil Nadu, India, in 1999-2000 and 2000-2001 to investigate the persistence and dissipation of lambda-cyhalothrin (Karate 5 EC) residues in cardamom cv. Malabar. Three insecticidal sprays were applied at 21 days interval at concentrations of 20, 30, 40, 60 and 80 g a.i.  $\text{ha}^{-1}$ . Matured and uniform sized capsules were collected at 0 (1 h), 1, 3, 5, 7 and 15 days after the third application of the insecticide. The residues were extracted with acetone and cleaned up with dichloromethane. The final determination of residues in the samples was done using GC-ECD. The initial residue deposit on green capsules at the lowest (20 g a.i.  $\text{ha}^{-1}$ ) and highest (80 g a.i.  $\text{ha}^{-1}$ ) concentrations was in the range 1.10 to 1.86 and 4.21 to 4.23  $\mu\text{g g}^{-1}$  with an estimated half-life of 0.58 to 0.6 days and 1.2 to 1.35 days, respectively. The waiting period was 3.5 to 3.9 days at the lowest rate, and 8.8 to 10.9 days at the highest application rate, considering the MRL of 0.02  $\mu\text{g g}^{-1}$ .

Sivaveerapandian *et al.* (2002) conducted an experiment at Tamil Nadu, India to study the persistence of imidacloprid on bhendi (*A. esculentus*) fruits at the time of harvest and its dissipation behaviour. No residue of imidacloprid was detected in the fruits harvested from the plots where seed treatments and foliar applications were given. In dissipation studies where 20, 40 and 80 g imidacloprid ha<sup>-1</sup> were given, the residue of imidacloprid persisted up to the third day in 20 and 40 g a.i. ha<sup>-1</sup>, while in the highest rate (80 g a.i. ha<sup>-1</sup>) residue persisted up to 5 days in the fruits. The safe waiting period was 0.89, 2.34 and 3.52 days in the first experiment and 1.40, 2.24 and 3.47 days in the second field experiment at 20, 40 and 80 g a.i. ha<sup>-1</sup> of foliar sprays, respectively.

Sureshkumar *et al.* (2002) reported that residues of lambda-cyhalothrin (12.5 and 25 g a.i. ha<sup>-1</sup>) were below detectable levels in rice, bran, husk and straw at harvest. Kale (2003) studied dissipation of abamectin, spinosad and fipronil at 15 and 30 g a.i. ha<sup>-1</sup> levels on okra fruits and reported that the higher application rate resulted in higher initial residues. Initial residues in okra fruits of abamectin were 0.13 and 0.22 µg g<sup>-1</sup> for 15 and 30 g a.i. ha<sup>-1</sup>. The initial residues of spinosad were 0.18 and 0.30 µg g<sup>-1</sup> at 15 and 30 g a.i. ha<sup>-1</sup>, while for fipronil; the initial deposits were 0.17 and 0.30 µg g<sup>-1</sup> at 15 and 30 g a.i. ha<sup>-1</sup>. Singh and Singh (2003) studied the dissipation of lambda-cyhalothrin residues on chickpea (*cv.C-235*) at Rajendra Agricultural University, Pusa, India during the *Rabi* season of 1999 and 2000. The two applications of lambda-cyhalothrin at 25 and 50 g a.i. ha<sup>-1</sup> to chickpea at pod initiation stage and 15 days thereafter resulted in initial residues of 0.335 and 0.462 mg kg<sup>-1</sup> on green pods. These residues dissipated

with half-life values of 4.9 and 5.0 days. At harvest, the residues in grains were below the detectable level ( $<0.05 \text{ mg kg}^{-1}$ ).

The persistence of imidacloprid (Confidor 200 SL) sprayed at 20 and 40 g a.i.  $\text{ha}^{-1}$  on cabbage cv. Golden Acre and cauliflower cv. *Ketki* curds and leaves in 2000 and 2001 was studied by Gajbhiye *et al.* (2004). Cabbage and cauliflower samples were collected at different time intervals. In general, cauliflower retained more spray material than cabbage due to differences in surface texture and morphology. Lower deposits were obtained on leaves compared to curds. The residue dissipated with time and 54 to 78% dissipation was recorded within 2 days. The half-life values were in the range 0.6 to 1.5 days based on first order kinetics. Xu-ZhiChun *et al.* (2004) studied the residual amount of imidacloprid in poplar (*Populus* sp.). Imidacloprid was injected into the bottom part of poplar tree trunks and the acetonitrile extracts of the injected trees were analyzed using HPLC. The results showed that the detectable levels of imidacloprid in poplar remained longer than 40 days after application, the highest in leaves, moderate in twigs, and lowest in tree trunks. Zhou *et al.* (2004) studied fipronil residues in vegetable field ecosystem in China and reported that degradation of fipronil was faster in Pakchoi (half- life 2.6 days) than in soil (half-life 7.3 days). They reported faster degradation of fipronil metabolites in soil.

Gupta *et al.* (2005) conducted experiments to study the persistence of imidacloprid, acetamiprid and thiamethoxam in chickpea following seed dressing (3 and 6 g a.i.  $\text{kg}^{-1}$  seed) and foliar application (imidacloprid @ 20 and 40 g a.i.  $\text{ha}^{-1}$ , acetamiprid and thiamethoxam @ 25 and 50 g a.i.  $\text{ha}^{-1}$ ). The residues in green plant

persisted beyond 30 days after sowing following seed dressing of thiamethoxam and acetamiprid. However, no residues were detected in green plants 45 days after foliar spray; the persistence of all the insecticides was short. The residues of imidacloprid persisted beyond 3 days but no residues were detected on 5<sup>th</sup> day. Similarly, the residues of thiamethoxam and acetamiprid persisted beyond 5 days but no residues were detected on 10<sup>th</sup> day except for high dose of thiamethoxam. Similar trend was observed in combined treatment (seed dressing + foliar spray) of thiamethoxam. No residues of any insecticide were detected in harvested seed and straw samples. Sable (2005) evaluated the dissipation of 10 insecticides on cauliflower and reported that in case of endosulfan 35 EC @ 350 g a.i. ha<sup>-1</sup> initial deposit on 0 day was 0.206 µg g<sup>-1</sup> and on day 1, it was 0.137 µg g<sup>-1</sup>. The half-life and T<sub>BDL</sub> was 1.71 and 13.13 days. However, initial deposit on 0 and 1 day was 0.08 and 0.05 µg g<sup>-1</sup> at spinosad 45 SC @ 96.4 g a.i. ha<sup>-1</sup>. The calculated half-life (RL<sub>50</sub>) and T<sub>BDL</sub> was 1.47 and 9.81 days.

Deshmukh and Bhamare (2006) evaluated residues of different insecticides on aubergine fruits harvested at 3 days after the last spray during 2002-03 at Akola, (MS), India. Residues of cypermethrin 25 EC at 0.006% and spinosad 45 SC at 0.1% were found below the detection limit. Endosulfan 35 EC at 0.05%, monocrotophos 36 WSC at 0.05% and thiodicarb 75 WP at 0.1% had residue deposits of 0.092, 0.061 and 0.178 µg g<sup>-1</sup>, respectively. However, they were within the prescribed MRLs. Translocation and persistence of imidacloprid in apple fruits was studied by Dubey *et al.* (2006). Imidacloprid (Confidor 200 SL) was drenched in apple tree basin at 890 g a.i. ha<sup>-1</sup> (20 ml per 4 L<sup>-1</sup>) and at 1780 g a.i. ha<sup>-1</sup>

(40 ml per 4 L<sup>-1</sup>) at fruit development stage in Himachal Pradesh (Solan, Mashobra and Thanedhar), India. After drenching apple tree basins, imidacloprid was translocated to the fruits. Imidacloprid residues in the range of 2.34 to 5.49 and 3.62 to 6.08 mg kg<sup>-1</sup> were detected in fruit samples collected after 10 and 20 days after drenching, respectively, whereas residues were not detected on 30 and 40 days. However, soil samples analysed 40 days after drenching contained 0.14-3.61 mg kg<sup>-1</sup> imidacloprid residues.

Kaushik Banerjee *et al.* (2006) reported degradation rate of lambda-cyhalothrin and methomyl residues in grape and found that residues of lambda-cyhalothrin were lost with pre-harvest intervals (PHI) of 12.0 to 12.5 and 15.0 to 15.5 days, corresponding to the applications at 25 and 50 g a.i. ha<sup>-1</sup>, respectively. Battu *et al.* (2007) conducted a field experiment at Ludhiana, India and found that acephate and imidacloprid when applied on cotton using ready-mix acephate 50% + imidacloprid 1.8% formulation (Lancer Gold), at 500 + 18 and 1000 + 36 g a.i. ha<sup>-1</sup> (acephate+imidacloprid), imidacloprid residues reached below detectable level of 0.02 mg kg<sup>-1</sup> after 5 and 7 days. The half-life values for imidacloprid were observed to be 1.70 and 2.26 days, corresponding to lower and higher dose of application, respectively. Iqbal *et al.* (2007) conducted a study during 2006 at Faisalabad, Pakistan to evaluate the insecticide residues on aubergine fruits by HPTLC. Chlorpyrifos, acephate, imidacloprid, dichlorvos and carbofuran were sprayed on plants and analysis was done at 0, 3 and 7 days after treatment. Fruit samples were extracted with ethyl acetate and cleaned up with activated charcoal. Samples contained all insecticide residues, except residues of imidacloprid. Residue levels

were negligible after 7 days. Results indicated that fruits were suitable for consumption at 3 days after treatment.

Reddy *et al.* (2007) conducted studies to estimate the residues of selected insecticides in/on sweet pepper and tomato grown in greenhouse as well as open field. On 5<sup>th</sup> day, residues of imidacloprid, acephate and abamectin in sweet pepper as well as in tomato were higher in greenhouse as compared to open field. However, 15 days after treatment, residues of all the insecticides except imidacloprid reached below detectable level in greenhouse as well as in open field. An approximate waiting period of 10 days was found to be adequate for safe harvest of the vegetable crops.

Arora *et al.* (2008) estimated residues of imidacloprid in the pulp and rind of Kinnow mandarin fruits separately on high performance liquid chromatograph. Following the application of imidacloprid at 0.008 and 0.016 % on Kinnow mandarin plants, the average initial deposits at both these dosages on the rind of fruits were 2.40 and 3.90 mg kg<sup>-1</sup>. The corresponding values in the pulp were 0.03 and 0.04 mg kg<sup>-1</sup>. A sudden decline in the residue levels in the rind and a corresponding increase in the pulp was observed on the fifth day. Thereafter, the residue levels steadily decreased both in the rind and pulp. Residues of imidacloprid were below its maximum residue limit of 1.0 mg kg<sup>-1</sup> in whole citrus fruits at zero day sampling.

Debashis Dutta *et al.* (2008) standardized a method for the extraction and estimation of residues of fipronil and three of its metabolites from cabbage and soil. Mobile phase consisting of methanol:water (70:30) was found optimum for resolution of the parent compound and the metabolites. Recovery of fipronil along with three of its metabolites from cabbage as well as from soil

ranged from 80 to 88 per cent. The limit of quantification of fipronil was  $0.06 \mu\text{g g}^{-1}$  in both matrices. Desulfinyl and sulfone derivatives of fipronil were the major metabolites, found in the 1 day samples of cabbage and soil, which reached their maximum level on 3<sup>rd</sup> day after application. The half-life of fipronil in cabbage varied from 7.5 to 7.6 days. Kumar *et al.* (2008) determined the harvest time residues of imidacloprid 70 WS (Gaucho) and 200 SL (Confidor) formulations in cotton lint, seed and oil and found that the level of imidacloprid residues in lint, seed and oil samples from treated plots was below detectable limit (BDL) in all samples of first as well as third picking. Liang Jun *et al.* (2008) monitored degradation behaviour of cyhalothrin in apple fruit on gas chromatograph equipped with electronic capture detector. The results showed that cyhalothrin residues in apple fruit were more in higher doses. The spraying volume was the major factor affecting cyhalothrin residues in apple fruit. Cyhalothrin mainly remained in peel and was 9 to 40 fold more than in pulp. The degradation behaviour of cyhalothrin in apple fruit occurred in the first-order kinetic model with half-life of 17.6 days. The degradation rate of cyhalothrin in peel was faster than in pulp.

## **2.4 Studies on leaching of lindane and chlorpyrifos used in pomegranate stem pasting**

Sarode and Lal (1981) studied the persistence of lindane applied on cauliflower in Delhi, India in 1977-78 by spraying at 1.1 and 2.2 kg a.i.  $\text{ha}^{-1}$  at the stage of head formation, using 1100 litres emulsion  $\text{ha}^{-1}$ . The initial residue in the leaves was 10.89 and 16.82  $\mu\text{g g}^{-1}$  for the lower and higher concentrations and 9.50 and 13.75  $\mu\text{g g}^{-1}$  in the head. These residues fell below detectable level after

21 days. A waiting period of 6 to 7 days was necessary after spraying for safe consumption. Chinniah *et al.* (1997) determined initial residues ( $4.5 \mu\text{g g}^{-1}$ ) of lindane 20 EC ( $300 \text{ g a.i. ha}^{-1}$ ) in chillies which dissipated to  $0.6 \mu\text{g g}^{-1}$  on 5<sup>th</sup> day and reached BDL on 30<sup>th</sup> day. Chinniah and Kuttalam (2001) studied the persistence of chlorpyrifos and lindane in cotton cv. MCU 5 in a field experiment conducted during *Kharif* 1997 and 1998 at Coimbatore, India. The crop was sprayed 4 times at an interval of 20 days, starting from the 25<sup>th</sup> day after sowing. Insecticide residues were extracted from different matrices, *i.e.* lint, seed and oil. Chlorpyrifos when applied at 400 and 800 g a.i.  $\text{ha}^{-1}$  left residues of 0.045 and 0.063  $\mu\text{g g}^{-1}$  in lint. In the seed sample, the terminal residue was 0.014 and 0.016  $\mu\text{g g}^{-1}$  for recommended doses of chlorpyrifos and lindane, respectively. The residues of both insecticides were slightly higher in cotton oil compared to the other matrices. The harvest-time residues of lindane, when applied at 500 and 1000 g a.i.  $\text{ha}^{-1}$  were 0.015 and 0.017  $\mu\text{g g}^{-1}$  in lint, whereas in seed the residue levels were 0.016 and 0.025  $\mu\text{g g}^{-1}$ . Considering the MRL of  $1.0 \mu\text{g g}^{-1}$  of lindane in cotton, the residue was well below the tolerance limit and safe to the users and environment.

### 3. Material and Methods

Pomegranate (*Punica granatum* Linn.) crop suffers heavily due to infestation of various pests. Application of insecticides in vegetative and reproductive stages of crop is a common practice followed by the cultivators. Keeping in view the economic importance of thrips, *Scirtothrips dorsalis* (H.) on pomegranate, studies were undertaken to evaluate reduced risk insecticides viz., imidacloprid, spinosad, fipronil and lambda-cyhalothrin, for their bioefficacy and residues.

The field experiments were carried out at Research Project on Arid Zone Fruits, Department of Horticulture, Mahatma Phule Krishi Vidyapeeth, Rahuri Dist. Ahmednagar (MS), India during *Ambia* bahar (*Summer* 2010) and *Mrig* bahar (*Kharif* 2010) and the laboratory research was conducted at All India Network Project on Pesticide Residues, Department of Agril. Entomology, Mahatma Phule Krishi Vidyapeeth, Rahuri, Dist. Ahmednagar (MS), India. The material used and methods adopted during the present investigation are presented in this chapter.

#### **3.1 Studies on the bioefficacy and persistence toxicity of reduced risk insecticides against pomegranate thrips**

Experimental trial was conducted to evaluate the bioefficacy of newer insecticides against thrips, *S. dorsalis* (H.) on pomegranate. The experimental details are as under.

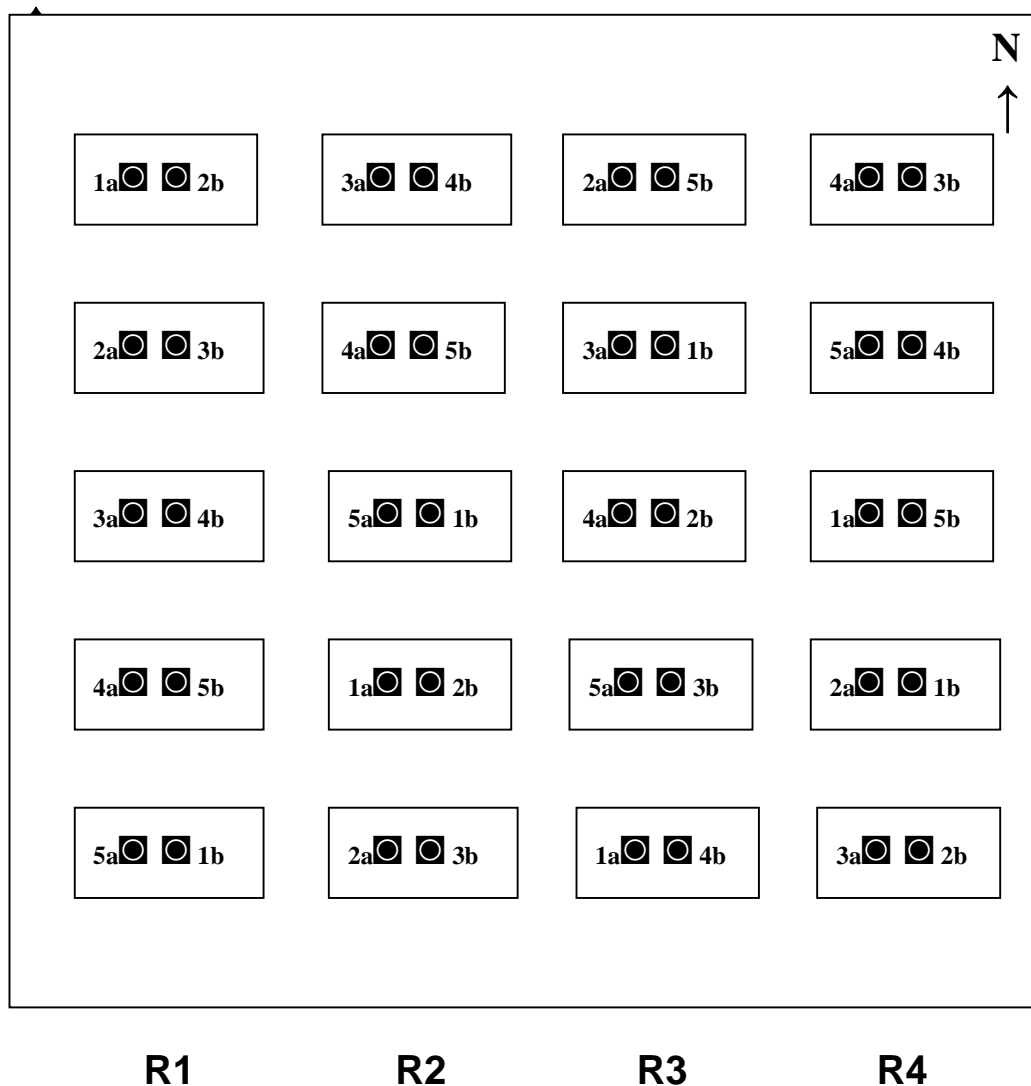
The field experiments were conducted during the *Ambia* bahar (*Summer*) and *Mrig* bahar (*Kharif*) seasons of 2010 on a five-year-old orchard at the Research Project on Arid Zone Fruits,

Horticulture Farm, Department of Horticulture, Mahatma Phule Krishi Vidyapeeth, Rahuri Dist. Ahmednagar (MS), India. The orchard site was uniform with medium black cotton soil, having high fertility and fairly good drainage. The intercultural operations were completed as per the recommended agronomic practices.

### **3.1.1 Design of experiment**

Design	: Randomized Block Design
Replications	: Four
Treatments	: Five
Crop	: Pomegranate
Variety	: <i>Bhagva</i>
Spacing	: Row to row: 4.5 and Plant to plant: 3.0 m.

Experiments were conducted on orchard of '*Bhagva*' variety of pomegranate pruned for the production of fruits of *Ambia* Bahar (*Summer* 2010) and *Mrig* Bahar (*Kharif* 2010). The pomegranate orchard was 5-year-old. Two adjacent trees were considered as a treatment for evaluation of each spray treatment. Each treatment was replicated four times and the tree between two treatments and replication was left untreated through out the experimental period. This helped in maintaining the pest pressure and also in avoiding insecticide drift. The plan of layout is presented in Fig. 3.1. The detailed meteorological data for weather conditions during *Summer* 2010 and *Kharif* 2010 are presented in Appendix-I.



Bold numbers represent Sr. No. of treatments specified in Table 3.2

a : Summer season b : Kharif season ● : Treatment plants

R : Replication

**Fig. 3.1 Plan of layout for experiment on pomegranate thrips**

### 3.1.2 Administration of treatments

With the beginning of thrips infestation at fruit setting stage, the first spray of insecticidal treatment was applied followed by two sprays at an interval of 15 days. The spray volume for treatment application was calibrated by spraying control plants with plain water. Spraying was taken up early in the morning hours. The required quantity of insecticide was mixed in small quantity of water in a beaker and then added to the bucket containing required volume of water. Spraying was done using high volume knapsack sprayer with hollow cone nozzle. The dates of the spraying for both the trials are given below.

<b><i>Bahar</i> and period of season</b>	<b>Dates of spraying</b>		
	First	Second	Third
<i>Ambia Bahar</i> (Jan. to July)	10/03/2010	24/03/2010	07/04/2010
<i>Mrig Bahar</i> (July to Dec.)	07/06/2010	21/06/2010	05/07/2010

### 3.1.3 Technical details of insecticides

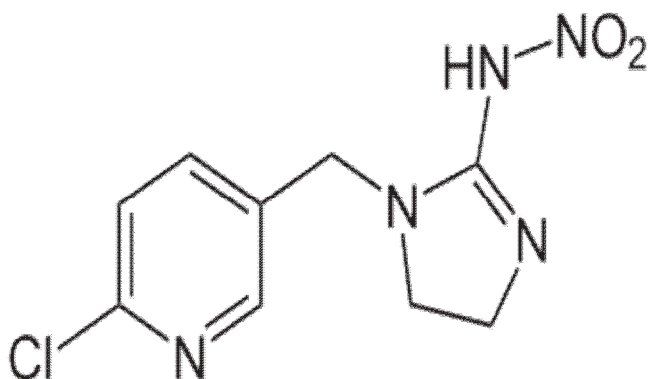
In the present investigation following four insecticides were evaluated.

#### 3.1.3.1 Imidacloprid

It is the first generation neonicotinoid insecticide introduced by Bayer in 1991. It is a neurotoxin and acts by binding the nicotinic acetylcholine receptor (Abbink, 1991). This chemical possesses plant systemic properties and is effective at low concentrations against a spectrum of sucking insects and at higher concentrations against various chewing insects.

Common Name : Imidacloprid  
 Chemical Name : 1-[(6-Chloro-3 pyridinyl) methyl]-4-5-dihydro-N-nitro-1-H-imidazol-2-amine

Empirical formula :  $C_9H_{10}ClN_5O_2$



**Fig. 3.2 Structural formula of imidacloprid**

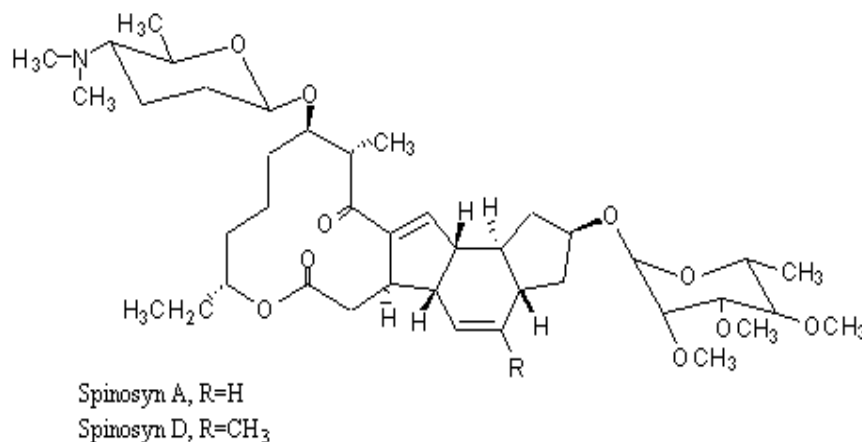
Trade name : Confidor 17.8 SL, Admire 70 WG.  
 Chemical class : Neonicotinoid  
 Chemical subclass : Chloronicotinyl compound (first generation)  
 Source : Bayer Crop Science India Ltd.

### 3.1.3.2 Spinosad

The spinosyns are a new family of macrolide compounds that are active against several classes of insects, especially lepidopterous pests. A total of 23 spinosyns have been isolated so far (Mertz and Yao, 1990). Spinosad is a name given to a mixture of spinosyn A (65-95 per cent) and spinosyn D (5-35 per cent), the active metabolites produced during fermentation by naturally occurring soil actinomycete bacterium *Saccharopolyspora spinosa*. Spinosad is selective, environmentally safer due to low persistence and spares the key beneficials and pollinators (Miles and Dutton, 2000). It acts as both contact and stomach poison. Available information indicates that spinosad acts on the insect nervous

system with the action on the nicotinic acetylcholine receptor and GABA receptor.

Common Name	:	Spinosad
Chemical Name	:	2-[(6-deoxy-2,3,4-tri-o-methyl- $\alpha$ -L-manno-pyranosyl)oxy]-13-(15-(dimethylamino) tetrahydro-6-methyl-2H-pyran-2-yl)oxy]- $\alpha$ -ethyl.2,3,3a,5a,5b,6,9,10,11,12,13,14,16a,16b-tetradecahydro-14-methyl-1H-as-indacerno (3,2d) oxacyclododecin-7,15-dion
Chemical formula	:	$C_{41}H_{65}NO_{16}$ (spinosyn A) $C_{42}H_{67}NO_{16}$ (spinosyn D)



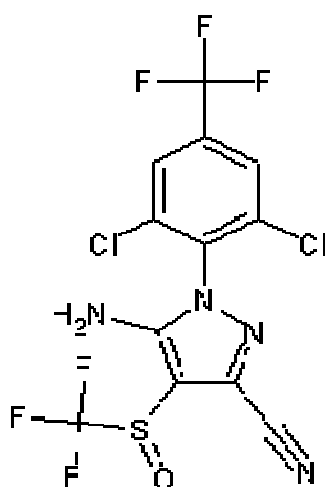
**Fig. 3.3 Structural formula of spinosad**

Chemical class	:	Naturalyte- macrocyclic lactone
Trade name	:	Tracer 45 SC, Success 2.5 SC
Manufacturer	:	DowAgro Sciences India Ltd.

### 3.1.3.3 Fipronil

Fipronil is a phenylpyrazole insecticide which was discovered in 1987 by Rhone-Poulenc Scientists. It has excellent activity against piercing-sucking and chewing insects. It has been shown to be effective when applied as a seed treatment and foliar spray. It enhances the formation of roots, vegetative growth and yield. In the target organism fipronil interferes with the Gamma-aminobutyric acid (GABA) regulated chloride channel, disrupting activity of the central nervous system and causing death (Cole *et al.*, 1993).

Common Name	:	Fipronil
Chemical Name	:	(+)-5-amino-1-(2, 6,-dichloro-a, a, a-trifluoro-p-tolyl)-4-trifluoromethylsulphonyl pyrazole-3-carbonitrile
Emperical formula	:	C <sub>10</sub> H <sub>4</sub> Cl <sub>2</sub> F <sub>6</sub> N <sub>4</sub> OS



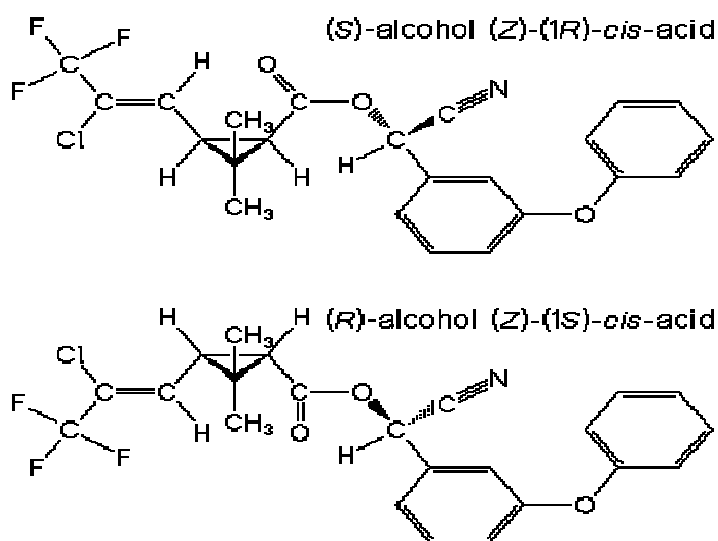
**Fig. 3.4 Structural formula of fipronil**

Trade name	:	Regent 5 SC, Jump 80 WDG
Manufacturers	:	Bayer Crop Science India Ltd.

### 3.1.3.4 Lambda-cyhalothrin

Lambda-cyhalothrin is one of the active molecules available for control of aphids, jassids, thrips, beetles and lepidopteran larvae in vegetables and cotton. It rapidly penetrates insect cuticle, disrupts nerve conduction within a minute leading to cessation of feeding, loss of muscular control, paralysis and eventually death. Besides, contact and stomach action, it is a good repellent too. It provides rapid knock down and long residual action.

Common Name : Lambda-cyhalothrin  
 Chemical Name : [(1 $\infty$ ,3 $\infty$  (Z)) - [ $\pm$  - cyano (3-Phenoxy- enyl) methyl 3- (2-chloro-3,3,3-trifluoro-1-progenyl)-2,2-dimethyl cyclopropanecarboxylate)]



**Fig. 3.5 Structural formula of lambda-cyhalothrin**

Chemical class : Synthetic pyrethroid  
 Trade name : Karate 5 EC, Kungfu 2.5 EC  
 Manufacturer : Syngenta, India Ltd.

### **3.1.4 Method of recording observations**

Thrips with their rasping and sucking type of mouth parts feed on the developing buds, fruits and shoots and deteriorate quality of fruits. Such fruits show corky appearance and other deformities. The live population of thrips (nymphs and adults) was recorded on randomly selected four fruits on each tree. Two plants were selected as a treatment and overall eight fruits from each direction East, West, South and North were observed. Shoot infestation was observed on one developing shoot from each direction on only one plant per treatment. The count of thrips on both fruits and shoots was recorded one day prior to first spray and subsequently at 3, 7, 10 and 14 days after each spray.

### **3.1.5 Statistical analysis**

The data obtained on population counts of thrips (mean no. per fruit and shoot) were transformed to Poisson value ( $\sqrt{n + 0.5}$ ) and statistically analyzed in RBD where  $n$  = count of live population of thrips. The analysis of pooled data of two *bahars* (*Ambia* and *Mrig*) 2010 was carried out to ascertain the relative efficacy of the insecticide treatments against pomegranate thrips. Appropriate statistical methods were employed to work out standard error (SE) and critical difference (CD) for deciding the significance of treatments (Gomez and Gomez, 1984).

### **3.1.6 Laboratory experiment for persistence toxicity of insecticides against pomegranate thrips**

The healthy one-year-old pomegranate plants were maintained in a glasshouse for persistence toxicity studies. Three plants comprised one treatment. The plants were sprayed separately with the solution of imidacloprid, spinosad, fipronil and

lambda-cyhalothrin at recommended doses. Thrips were collected from the untreated control plants from the field by cutting the infested branches of pomegranate shoot. Such shoots were carried to the laboratory and known number of thrips (30 per plant) were released on each plant at 1, 3, 5, 7, 10 and 14 days after treatment. The observations on mortality were taken after 24 hrs of release. Mortality counts were transferred into per cent mortality. Persistence toxicity value was calculated as per the method elaborated by Pradhan (1967). The product (PT) of the average residual toxicity (T) and the period (P) for which the residual toxicity was studied, served as an index of persistence toxicity.

$$\text{Persistence toxicity (PT)} = \text{Product of P} \times \text{T}$$

Where, P = Period (days) to which mortality observed  
T = Average toxicity

### **3.2 Comparison of different methods of insecticide residue analysis for their efficiency**

California Department of Food and Agriculture (CDFA), Quick, Easy, Cheap, Effective, Rugged, Safe (QuEChERS) and Single Residue Method (SRM) are the most common methods used in insecticide residue analysis. The analytical results depend upon the efficiency of the method in extracting maximum residues from a particular sample. To generate reliable residue data the insecticide residues must be detected at MRL levels or below. Recovery is the best measure to study the efficiency of all residue analysis methods. Higher the recovery more reliable is the method of insecticide residue analysis. The insecticides used in the present study; imidacloprid, spinosad, fipronil and lambda-cyhalothrin were analyzed by each method by fortifying fruits of pomegranate with known quantities of each chemical and extracting fruit samples by

each method. The recovery obtained from each method was compared and the best method was re-validated for the analysis of pomegranate fruits. Moreover, the edible portions (arils) as well as whole fruits (along with the peel) were analyzed separately since many of the importing countries are demanding residue data on whole fruit as well as in edible portion. The details of the recovery studies are as follows.

**Table.3.1. Methods of analysis and levels of fortification for recovery study**

Method of analysis	Commodity	Level of fortification ( $\mu\text{g g}^{-1}$ )
California Department of Food and Agriculture (CDFA)	Arils Whole fruit Peel	0.05 and 0.1
Quick Easy Cheap Effective Rugged Simple (QuEChERS)	Arils Whole fruit Peel	0.05 and 0.1
Single Residue Method (SRM)	Arils Whole fruit Peel	0.05 and 0.1

### 3.3 Studies on the extent of residues of insecticides in pomegranate fruits and soil

Studies on residues of imidacloprid, spinosad, fipronil and lambda-cyhalothrin on pomegranate fruits were carried out in the field experiment conducted in *Ambia* bahar (*Summer* season) of 2010.

Insecticide residues were analyzed in peel, arils and whole fruits separately, on fruits collected periodically after the third spray to decide the safety of treatments to consumers. It was also expected to find insecticide residues in soil below the canopy as a result of foliar sprays, therefore, the present study was extended

and soil samples from the orchard were collected and analyzed for determining the insecticide residues in soil 21 days after last spray. According to residue studies protocol prescribed by Central Insecticides Board (CIB) two doses-recommended and double the recommended dose, need to be evaluated for residues. Hence, each insecticide was evaluated at two doses as given in Table 3.2.

**Table 3.2. Details of treatments**

Name of treatment	Dose (g a.i.ha <sup>-1</sup> )	Product quantity (ml/g L <sup>-1</sup> )	Spray concentration (% a.i.)
T <sub>1</sub> Imidacloprid 17.8 SL	27	0.3	0.0055
T <sub>2</sub> Imidacloprid 17.8 SL	54	0.6	0.011
T <sub>3</sub> Spinosad 45 SC	56.25	0.25	0.0112
T <sub>4</sub> Spinosad 45 SC	112.5	0.5	0.0224
T <sub>5</sub> Fipronil 5 SC	25	1.0	0.005
T <sub>6</sub> Fipronil 5 SC	50	2.0	0.001
T <sub>7</sub> Lambda-cyhalothrin 5EC	12.5	0.5	0.0025
T <sub>8</sub> Lambda-cyhalothrin 5EC	25	1.0	0.005
Control	--	--	--

\* Note: Spray treatments at T<sub>2</sub>, T<sub>4</sub>, T<sub>6</sub> and T<sub>8</sub> based on double the recommended dose of insecticide were included for studies on residues and not considered for comparison of bioefficacy.

The marketable quality pomegranate fruits weighing about 1 kg were collected separately from each replication plot, stored in labeled polythene bags and shifted to laboratory. Samples were collected at an interval of 0 ( $\approx$  2 hr), 1, 3, 5, 7, 10, 14 and 21 days after last spray for residue analysis. From composite sample, by

quartering method after cutting, 50 g representative sample was taken for extraction, cleanup and estimation as described under each compound. Such procedure was separately followed for arils, whole fruit and peel. Further, soil samples were also collected from the periphery of the treated plants at 21 days after last spray and analyzed for insecticide residues. Soil samples (1 kg) were collected in labeled polythene bags and 25 g representative sample was taken for analysis.

### **3.3.1 Imidacloprid**

#### **1. Extraction**

The fruit sample was cut and arils were separated. The peel, arils and peel with arils (whole fruit) were weighed separately. The 100 g sample was accurately weighed in a 500 ml glass bottle. Two hundred and fifty ml acetonitrile was added and sample was homogenized with the high speed blender for 3 minutes. The extract was filtered through Buchner funnel overlaid with 10 to 15 g Celite 545 filter aid. Blender jar and funnel were washed with 100 ml acetonitrile, filtered and combined the acetonitrile extract in 1000 ml round bottom flask. The acetonitrile extract was concentrated in a rotary vacuum evaporator. A 50 ml saturated sodium chloride solution was added to aqueous remainder and extract was transferred into a 500 ml separatory funnel. The flask was rinsed with 100 ml n-hexane and n-hexane was added to separatory funnel. After vigorous shaking, the lower aqueous phase of extract was drained into another 500 ml separatory funnel and 100 ml n-Hexane was added. The funnel was shaken vigorously and after phase separation n-hexane was discarded. The extract was taken into a 500 ml separatory funnel. The container was washed with

100 ml of hexane/ethyl acetate mixture (98:2) and shaken. The aqueous phase was drained into a 250 ml separatory funnel and the organic phase was discarded. The aqueous phase was shaken with 3 x 100 ml dichloromethane and collected in a 500 ml separatory funnel, washed with 50 ml of 0.01 molar aqueous potassium carbonate solution. The aqueous phase was drained and discarded. Dichloromethane was dried over anhydrous sodium sulfate and sodium sulfate was washed with 50 ml of dichloromethane. The combined dichloromethane was evaporated just to dryness.

## **2. Cleanup**

The sintered glass column was rinsed with 10 ml ethyl acetate. The column was slurry-packed by taking 4.5 g Florisil deactivated with 5% water in 20 ml ethyl acetate and applied quantitatively into the column. It was then covered with a 0.5 cm layer of anhydrous sodium sulfate. The solvent was allowed to drain down to the sodium sulfate layer. The residue was dissolved in a small amount of ethyl acetate. The solution was applied on top of the column by means of a pipette and allowed to percolate. The column was rinsed with 20 ml acetonitrile. The eluate was concentrated just to dryness and the residue was dissolved in 1.0 ml acetonitrile (analytical grade).

## **3. Estimation**

### **HPLC parameters:**

Name of the instrument: Liquid chromatograph (Model LC-20 AT, Shimadzu, Japan) equipped with PDA detector SPD-M20A and LC solution data software.

**Liquid chromatographic conditions:**

Mobile phase	: Acetonitrile
Wavelength	: 272 nm
Flow rate	: 0.6 ml/min
Column	: RP-18e, Chromolith 100x4.6 mm i.d.
Injection volume	: 20 µl
Retention time	: 2.7 min

**3.3.2 Spinosad****1. Extraction**

The analytical procedure outlined by Utting *et al.* (1998) and West and Turner (2000) was used for analysis of spinosad residues. The fruits were cut with a knife and arils were separated. Fifty g arils, peel and arils with peel (whole fruit) were blended separately with 100 ml acetonitrile:water (8:2). The sample was shaken at 500 rpm for 5 min and centrifuged at 3000 rpm for 5 min. Portion of the supernatant (75 ml) was then transferred to a bottle. After adding 40 ml water and 75 ml dichloromethane, the extract was shaken at 500 rpm for 5 min and centrifuged at 300 rpm for 5 min. Immediately, the upper aqueous layer was completely pipetted out and discarded. The lower organic layer was transferred to a 250 ml boiling flask and dried under vacuum at 40 °C on rotary vacuum evaporator. The residue was taken in 20 ml hexane for cleanup.

**2. Cleanup**

Silica gel column was wet packed with 10 ml of dichloromethane: methanol (75:25) followed by 10 ml of acetonitrile and 10 ml of hexane. The hexane extract (20 ml) was loaded on to the column and discarded eluate. Spinosad was eluted with 10 ml

of dichloromethane: methanol (75:25) and transferred to 250 ml boiling flask. The sample eluent was immediately evaporated and evaporation process was closely monitored so that the sample could be removed from the evaporator immediately to prevent loss of residue. The residues were dissolved in 1 ml of acetonitrile, methanol and 2% aqueous ammonium acetate (1:1:1). The sample vial containing residue was sonicated for 2 min and briefly centrifuged at 3000 rpm. Spinosad residue was transferred to another vial for estimation.

### **3. Estimation**

The determinations were made on the dual pump HPLC system. The mobile phase comprised of 30 % reservoir A and 70 % reservoir B (isocratic). Reservoir A contained methanol: water: acetonitrile: 2 % aqueous ammonium acetate (50:10:30:10) and reservoir B contained methanol: water: 2 % aqueous ammonium acetate (80:10:10). The flow rate was  $1.2 \text{ ml min}^{-1}$ .

#### **HPLC parameters:**

Name of the instrument: Liquid chromatograph (Model LC-20 AT, Shimadzu, Japan) equipped with PDA detector SPD-M20A and LC solution data software

#### **Liquid chromatographic conditions:**

The chromatograms were generated on LC-MS and the parameters of LC are as under.

Mobile phase : Acetonitrile (42%) : Methanol (42%):  
2% Ammonium acetate (16%)  
Wavelength : 250 nm  
Flow rate : 0.4 ml/min  
Column : RP C-18, Grace Vydac 150x3.2 mm i.d.

Injection volume : 10  $\mu$ l

Retention time : Spinosyn A : 9.34 min

Spinosyn D : 9.64 min

### **3.3.3 Fipronil**

#### **1. Extraction**

The residues were extracted in acetonitrile and vacuum filtered. The co-extractives were partitioned into 100 ml hexane in 500 ml separatory funnel by vigorous shaking for 1 minute and the hexane layer was discarded after phase separation. The solvent extract was drained into a 500 ml round bottomed flask and concentrated to aqueous remainder on rotary vacuum evaporator at 40°C. The supernatant was decanted in a 50 ml volumetric flask and the volume was adjusted to 50 ml with water after adding 2 ml isopropyl alcohol.

#### **2. Cleanup**

Silica gel glass column was prewashed with 3 ml methanol and 5 ml of water. Sample extract (5 ml) was applied on to the column and discarded the eluate. The column was again rinsed with 5 ml of water followed by 5 ml of water: methanol (9:1). Fipronil residues were eluted with a 5 ml collection volume of methanol. Methanol was removed on Turbo Vap LV concentrator and residues were dissolved in 3 ml of toluene for estimation.

#### **3. Estimation**

##### **GC parameters:**

Name of the instrument: Shimadzu Gas Chromatograph Model GC-2010 equipped with AOC-20 Auto injector and GC solution data software.

**Gas chromatographic conditions:**

Detector used	: Electron Capture Detector (ECD)
Column used	: DB-1, 30 m x 0.25 mm x 0.25 $\mu$ m
Temperature parameters	: Injector : 250 °c Detector : 300 °c
Oven Temperature	: 180°c, 1 min hold, @ 1.5°c/min 200°c, 18°c/min 270°c
Carrier gas	: Nitrogen
Gas flow rate	: 2.70 ml/min
Purge rate	: 3.0 ml/min
Make up	: 30 ml/min
Volume injected	: 1 $\mu$ l
Retention time	: Fipronil : 9.862 min. MBO 6513 : 6.313 min. MBO 46163 : 13.691min. MBO 45950 : 9.480 min.

**3.3.4 Lambda-cyhalothrin****1. Extraction**

Accurately weighed 50 g sample was blended in a high speed blender for extraction. Added 150 ml acetone and extracted for 30 minutes using a mechanical shaker. The extract was vacuum-filtered on Buchner funnel and the cake re-extracted with 2 x 75 ml of acetone. Acetone solvent in the combined extract was evaporated and added 50 ml saturated sodium chloride solution to the remaining aqueous layer. The aqueous extract was further cleaned up by partitioning.

## 2. Cleanup

The aqueous extract was transferred quantitatively to a 1 litre separating funnel with 50 ml distilled water and 100 ml hexane. The layers were partitioned by shaking vigorously and the aqueous layer was drained into another separating funnel. The aqueous layer was re-extracted by partitioning again with 2 x 50 ml hexane. The hexane phase was collected, combined and concentrated on RVE to approximately 10 ml.

A sintered disc glass column of 400 x 18 mm diameter was filled up with 10 g de-activated Florisil overlaid with 15 mm layer of anhydrous sodium sulfate. The column was conditioned with 50 ml hexane and the concentrated sample extract was loaded onto the column. The sample flask was rinsed with 5 ml hexane and added to the column. The column was washed with 10 ml of the same solvent. The lambda-cyhalothrin residue was eluted with 150 ml ethyl acetate + hexane (5:95). The collected eluate was evaporated to near dryness and reconstituted in 10 ml ethyl acetate for GC-ECD analysis.

## 3. Estimation

### GC parameters:

Name of the instrument: Shimadzu Gas Chromatograph Model GC-2010 equipped with AOC-20 Auto injector and GC solution data software

### Gas chromatographic conditions:

Detector used : Electron Capture Detector (ECD)

Column used : DB-1, 30 m x 0.25 mm x 0.25 µm

Temperature parameters	: Injector : 250 °c
	Detector : 300 °c
Oven Temperature	: 205°C, 2 min hold, @ 2 <sup>0</sup> c/min 230 <sup>0</sup> c, 5 <sup>0</sup> c/min 245 <sup>0</sup> c 2 min hold.
Carrier gas	: Nitrogen
Gas flow rate	: 2.50 ml/min
Purge rate	: 3.0 ml/min
Make up	: 30 ml/min
Volume injected	: 1 µl
Retention time	: 15.71 min.

### 3.3.5 Calculations

The concentration ( $\mu\text{g g}^{-1}$ ) of the analyte in the sample was calculated from the following formula.

$$\text{Residue } (\mu\text{g g}^{-1}) = \frac{\text{FA} \times \text{Vend} \times \text{Wst}}{\text{Fst} \times \text{Vi} \times \text{G}} \times \text{Rf}$$

Where,

- G = Mass of sample (g) taken for analysis
- Vend = Final volume of the sample solution (ml)
- Vi = Aliquot volume of Vend injected in to GLC/HPLC ( $\mu\text{l}$ )
- FA = Peak area/height of analytical sample solution obtained from Vi
- Fst = Peak area/height of standard sample solution corresponding to insecticide at it's retention time obtained from Wst
- Wst = Amount of the reference standard substance injected (ng)
- Rf = Recovery factor

### 3.3.6 Calculation of limits of detection and quantitation

The limits of detection (LOD) and quantitation (LOQ) for the residue method were calculated from the standard deviation (SD) of

the results of the test insecticide concentrations ( $\mu\text{g g}^{-1}$ ) in the fortified recovery samples. For each sample matrix, the LOD was calculated 3 times the standard deviation ( $3 \times \text{SD}$ ) and the LOQ was calculated as 10 times the standard deviation ( $10 \times \text{SD}$ ).

### **3.3.7 Statistical method for data on pesticide residues**

In order to work out dissipation of insecticide residues on pomegranate fruits a statistical procedure suggested by Hoskins (1960) was employed. For this purpose the corresponding levels of residues obtained in ppm were converted in log of residues (Y). The regression equation was worked out and the values of the following parameters were calculated.

- a. **RL<sub>50</sub>**: Half-life of the initial residues on fruit in days (also called  $T_{1/2}$  which indicates the time required for initial residues to dissipate by 50 per cent)
- b. **T<sub>MRL</sub>**: Time required for initial residues to reach below the maximum residue limit (MRL) specified by the authorities.
- c. **T<sub>BDL</sub>**: Time required for the residues to reach below the detectable limit (BDL) stated for the specified method of analysis.
- d. **PHI**: Pre-harvest interval, is a gap allowed between applications of pesticide and harvesting of fruits taking into account the safety of consumers. In fact it is a safe period to be followed in between harvesting and pesticide treatment.

## **3.4 Studies on the leaching of lindane and chlorpyrifos used in pomegranate stem pasting**

Pasting of tree trunk with insecticides is an age old practice to avoid pest incidence. In pomegranate orchard farmers are commonly pasting the tree trunk with a mixture of lindane or

chlorpyrifos and Bordeaux mixture (Copper oxychloride). There is a likelihood of leaching these chemicals into the soil. It was therefore, felt necessary to undertake studies on translocation of these insecticides in soil. In this study the tree trunks were pasted after pruning for *bahar* treatment and the samples were collected at 30 days after pasting. These samples were analyzed in the laboratory for their residues.

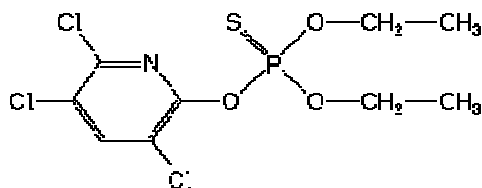
### 3.4.1 Details of insecticides

In the present investigations two insecticides, most commonly used by the cultivators for pomegranate stem pasting were tested for their residues in the soil. The details of the insecticides are as follows.

#### 3.4.1.1 Chlorpyrifos

Chlorpyrifos is an organophosphorus insecticide, having broad range of insecticidal activity. It is effective by contact, stomach and fumigant action. It is used against various soil insect pests, foliar crop pests and household pests. It is nonphytotoxic at recommended concentrations and persists in soil for 60 to 120 days.

Common Name : Chlorpyrifos  
 Chemical Name : O,O- Diethyl -O-3,5,6 - trichloro -2-  
 pyridyl phosphorothioate  
 Chemical formula :  $C_9H_{11}Cl_3NO_3PS$



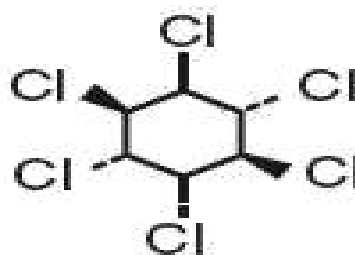
**Fig. 3.6 Structural formula of chlorpyrifos**

Chemical class	:	Organophosphate
Trade name	:	Dursban 20 EC
Manufacturer	:	DeNocil Crop Protection, India Ltd.

### 3.4.1.2 Lindane

Lindane, also known as gamma-hexachlorocyclohexane, ( $\gamma$ -HCH), Gammaxene, Gammallin and erroneously known as hexachloro cyclohexachloride (HCH), is an organochlorine chemical variant of hexachlorocyclohexane that has been used as an agricultural insecticide. Lindane is a neurotoxin that interferes with GABA neurotransmitter function by interacting with the GABA receptor-chloride channel complex at the picrotoxin binding site. In humans, lindane affects the nervous system, liver and kidneys, and may be a carcinogen.

Common Name	:	Lindane
Chemical Name	:	1 $\alpha$ ,2 $\alpha$ ,3 $\beta$ ,4 $\alpha$ ,5 $\alpha$ ,6 $\beta$ - hexachlorocyclohexane
Chemical formula	:	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>
Chemical class	:	Organochlorine



**Fig. 3.7. Structural formula of lindane**

Trade name	:	Lindane 20 EC, Lintox 20 EC
Manufacturer	:	Devidayal Pesticides, India Ltd.

### **3.4.2 Analytical method**

Soil samples were analysed for detection of residues of lindane and chlorpyrifos by following the method specified for lambda-cyhalothrin. The detection was done on gas chromatograph equipped with electron capture detector ( $\text{Ni}^{63}$ ) at the sensitivity of  $0.01 \mu\text{g g}^{-1}$ .

## 4. Experimental Results

The present research work was planned to evaluate the bioefficacy of four insecticides *viz.*, imidacloprid 17.8 SL, spinosad 45 SC, fipronil 5 SC and lambda-cyhalothrin 5 EC against pomegranate thrips (*Scirtothrips dorsalis* H.) under field condition during *Summer* and *Kharif* seasons of 2010. These insecticides were also studied for their residues and dissipation pattern in pomegranate fruits (arils, peel and whole fruit). Furthermore, most common methods of insecticide residue analysis were compared to investigate appropriate method of residue analysis for this fruit crop particularly for evaluated insecticides. The data obtained from the present study were statistically processed and results based on the same are presented in this chapter.

### 4.1 Bioefficacy and persistence toxicity of reduced risk insecticides against pomegranate thrips

#### 4.1.1. Bioefficacy of insecticides against thrips on pomegranate fruits

The four insecticides *viz.*, imidacloprid, spinosad, fipronil and lambda-cyhalothrin were evaluated for bioefficacy against thrips (*S. dorsalis* H.) infesting developing fruits of pomegranate. Field trial was conducted on the orchard pruned for *Ambia* bahar and *Mrig* bahar 2010. Each insecticide treatment was consisting of three sprays applied at fortnightly interval, initiating first spray at the time of fruit setting. Effectiveness of the insecticide spray treatments was judged on the basis of level of thrips incidence on randomly selected fruits from treatment plants. The count of thrips was recorded one day prior to first spray. However, the post-counts were

recorded at 3, 7, 10 and 14 days after each spray (DAS). Randomly selected eight fruits from each treatment representing all four directions were observed for the incidence of thrips after each insecticide application.

### **a. Summer season 2010**

The data on the infestation of thrips (No./fruit) presented in Table 4.1 was recorded from the field trial conducted in *Summer* season 2010. The graphical comparison of the bioefficacy of treatments in a span of about 45 days after pest initiation is depicted in Fig. 4.1.

#### **i. First spray**

Before initiation of insecticidal spray treatments the mean pre-count of thrips on pomegranate fruits ranged from 14.66 to 15.03 thrips per fruit. Thrips population on untreated plants (control) showed an increasing trend from 14.75 to 17.72 thrips per fruit during a span of 14 days covering the first spray.

All insecticide treatments were significantly superior over untreated control in minimizing the incidence of thrips on fruits. Overall mean thrips count observed in insecticide spray treatments during post-spray period of 10 days was in the range of 4.16 (spinosad @ 56.25 g a.i.ha<sup>-1</sup>) and 5.44 thrips per fruit (imidacloprid @ 27 g a.i.ha<sup>-1</sup>). On 14 DAS, incidence of thrips in all spray treatment was increased. Spinosad @ 56.25 g a.i.ha<sup>-1</sup> (7.00 thrips/fruit) was the most superior treatment followed by fipronil @ 25 g a.i.ha<sup>-1</sup> (7.03 thrips/fruit) and both the treatments were at par with each other. Plants treated with lambda-cyhalothrin @ 12.5 g a.i.ha<sup>-1</sup> (9.47 thrips/fruit) and imidacloprid @ 27 g a.i.ha<sup>-1</sup> (9.97 thrips/fruit) showed higher incidence.



## ii. Second spray

After second spray, the thrips population recorded on untreated control plants was in between 22.47 (14 DAS) and 19.02 (3 DAS) thrips/fruit. All insecticide treatments were significantly superior over untreated control in minimizing the incidence of thrips. At 14 DAS, fipronil @ 25 g a.i.ha<sup>-1</sup>(4.06 thrips/fruit) and spinosad @ 56.25 g a.i.ha<sup>-1</sup>(4.19 thrips/fruit) were found to be the most superior treatments and were at par with each other, whereas plants treated with lambda-cyhalothrin @ 12.5 g a.i.ha<sup>-1</sup>(5.65 thrips/fruit) and imidacloprid @ 27 g a.i.ha<sup>-1</sup>(5.56 thrips/fruit) showed relatively more counts of thrips compared to former insecticides.

## iii. Third spray

The gradual increase in thrips population on untreated plants continued during the third spray and it increased to 25.25 thrips per fruit in a span of 14 days. However, thrips count up to 10 DAS on the plants of insecticide treatments were between 2.53 (spinosad @ 56.25 g a.i.ha<sup>-1</sup>) and 3.53 (imidacloprid @ 27 g a.i.ha<sup>-1</sup>) which clearly indicated that the spray treatments were significantly superior over untreated control. Thrips count on 14 DAS showed that spinosad @ 56.25 g a.i.ha<sup>-1</sup>(3.00 thrips/fruit) was the most superior chemical treatment followed by fipronil @ 25 g a.i.ha<sup>-1</sup> (3.62 thrips/fruit) and were more effective as compared to lambda-cyhalothrin @ 12.5 g a.i.ha<sup>-1</sup>(4.90 thrips/fruit) and imidacloprid @ 27 g a.i.ha<sup>-1</sup>(5.16 thrips/fruit).

## b. *Kharif* season 2010

The data on thrips counts recorded on the experimental pomegranate orchard for the *Kharif* season 2010 are given in Table

4.2. Graphical comparison of insecticide treatments is depicted in Fig. 4.2.

### **i. First spray**

Before initiation of insecticide spray treatments on the experimental plants, thrips incidence on pomegranate fruit was in the range of 10.87 to 11.50 thrips/fruit. During post-spray period of 14 days, the incidence of thrips on untreated control plants showed steady increase and reached to 14.00 thrips per fruit. All spray treatments showed significantly less counts of thrips at 3 DAS. On 7, 10 and 14 DAS thrips population increased from 3.44 to 7.65 (imidacloprid @ 27 g a.i.ha<sup>-1</sup>), 3.54 to 7.59 (lambda-cyhalothrin @ 12.5 g a.i.ha<sup>-1</sup>), 2.63 to 5.50 (fipronil @ 25 g a.i.ha<sup>-1</sup>) 2.41 to 4.81 (spinosad @ 56.25 g a.i.ha<sup>-1</sup>). Minimum increase was noticed in plants treated with spinosad indicating that the chemical treatment with spinosad @ 56.25 g a.i.ha<sup>-1</sup> was the most effective.

### **ii. Second spray**

Thrips counts on untreated control fruits rose up to 18.06 from 15.37 during a span of 14 days. As against this, the thrips counts in all spray treatments were significantly low. Among various insecticide treatments, the count of thrips was below 3 upto 7 DAS except in lambda-cyhalothrin @ 12.5 g a.i. ha<sup>-1</sup> (3.19 thrips/fruit). As on 14 DAS plants treated with spinosad @ 56.25 g a.i.ha<sup>-1</sup> recorded the lowest population of thrips (3.37 thrips/fruit). Next superior treatment was fipronil @ 25 g a.i.ha<sup>-1</sup> (3.97 thrips/fruit), while imidacloprid @ 27 g a.i.ha<sup>-1</sup> (5.37 thrips/fruit) and lambda-cyhalothrin @ 12.5 g a.i.ha<sup>-1</sup> (5.62 thrips/fruit) recorded higher counts of thrips.



### iii. Third spray

Untreated control plots showed moderate increase in thrips population and had 21.58 thrips/fruit. All insecticides were significantly effective. The overall efficacy was similar for all the three sprays indicating superiority of spinosad @ 56.25 g a.i.ha<sup>-1</sup> as the most effective treatment.

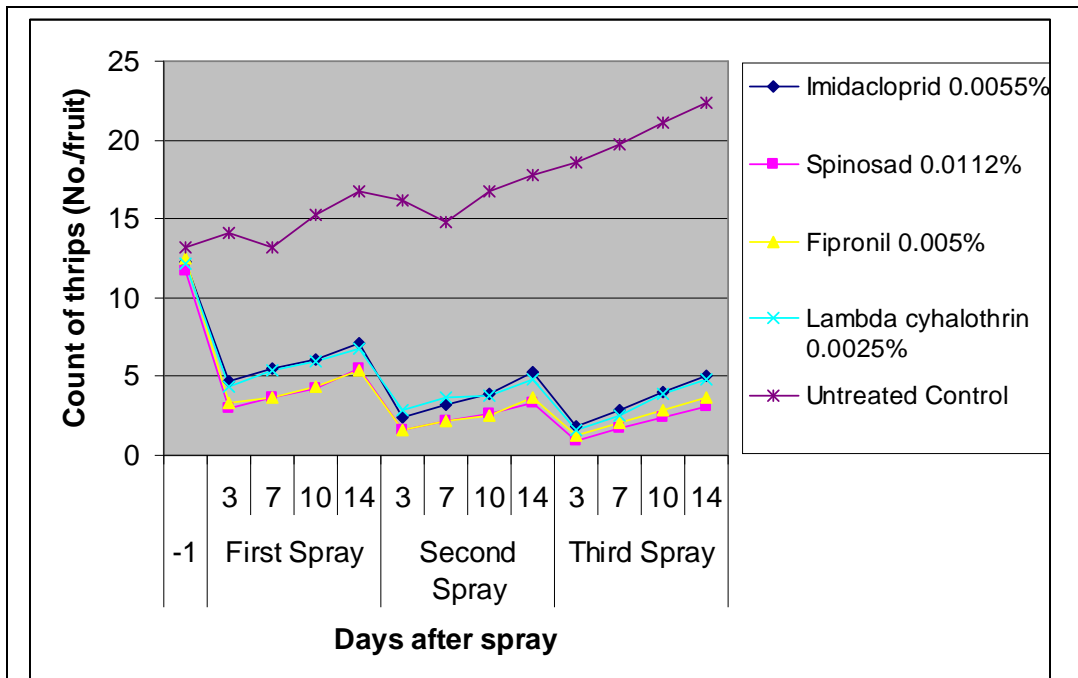
### c. Overall efficacy based on pooled data - *Summer* and *Kharif* 2010

Pooled data on incidence of thrips (No./fruit) of two seasons *viz.*, *Summer* and *Kharif* 2010 are presented in Table 4.3. The pre-treatment count of thrips before initiation of the spray treatments was in the range of 12.77 to 13.20 thrips/fruit. Based on the mean of three sprays, the post-treatment counts of thrips population on untreated control plants were 15.35, 15.67, 17.00 and 18.07 thrips on 3, 7, 10 and 14 days after spray (DAS), respectively. The thrips incidence in all insecticide treatments was significantly low indicating that all the insecticides were significantly effective against thrips. The treatments comprised of spinosad @ 56.25 g a.i. ha<sup>-1</sup> was the most effective treatment (4.26 thrips/fruit) at 14 DAS followed by fipronil @ 25 g a.i. ha<sup>-1</sup> (4.42 thrips/fruit) and were at par with each other. The graphical comparison of spray treatments based on the incidence of thrips is depicted in Fig. 4.3.

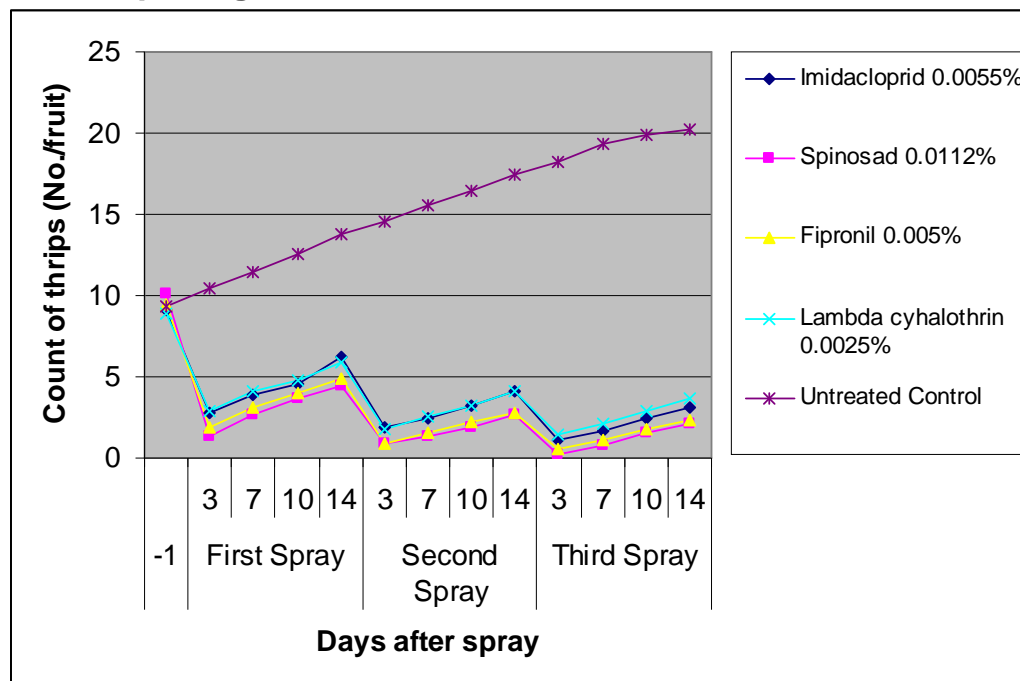
**Tab.4.3 Bioefficacy of insecticides against thrips on pomegranate fruits based on pooled data- Summer and Kharif 2010**

Treatment	Spray conc <sup>n</sup> (% a.i.)	Average number of thrips				
		Pre count (First spray)	Post count (mean of 3 sprays)			
			3 DAS	7 DAS	10 DAS	14 DAS
Imidacloprid	0.0055	13.20 (3.69)	2.71 (1.78)	3.50 (1.99)	4.22 (2.16)	6.37 (2.60)
Spinosad	0.0112	13.00 (3.67)	1.77 (1.49)	2.34 (1.67)	3.06 (1.87)	4.26 (2.15)
Fipronil	0.005	12.77 (3.68)	2.05 (1.58)	2.65 (1.76)	3.29 (1.93)	4.42 (2.20)
Lambda-cyhalothrin	0.0025	13.22 (3.70)	2.59 (1.75)	3.43 (1.98)	4.28 (2.18)	6.35 (2.60)
Untreated Control	---	12.85 (3.64)	17.37 (4.20)	17.56 (4.23)	18.74 (4.37)	19.84 (4.49)
S.E.±		0.05	0.05	0.05	0.04	0.04
C.D. at 5%		NS	0.14	0.14	0.13	0.12

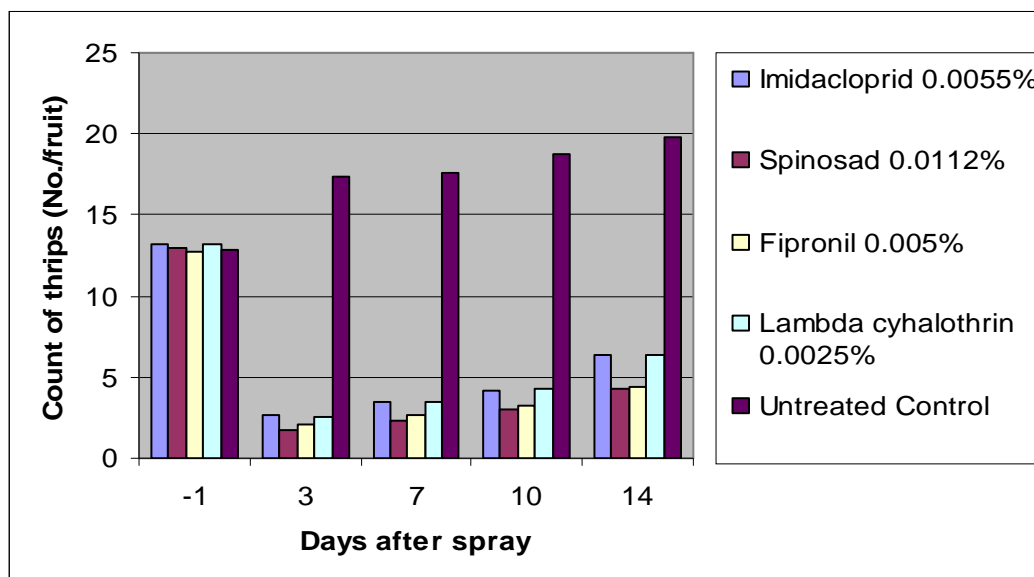
Figures in parentheses are  $\sqrt{n+0.5}$  transformed values  
DAS = Days after spray



**Fig. 4.1 Bioefficacy of insecticides against thrips on pomegranate fruits-Summer 2010**



**Fig. 4.2 Bioefficacy of insecticides against thrips on pomegranate fruits-Kharif 2010**



**Fig. 4.3 Bioefficacy of insecticides against thrips on pomegranate fruits based on pooled data- *Summer* and *Kharif* 2010**

#### **4.1.2 Bioefficacy of insecticides against thrips on pomegranate shoots**

Randomly selected four shoots from the treatment plants representing all four directions were observed for the incidence of thrips after each insecticide application.

##### **a. Summer season 2010**

In *Summer* season, the experimental pomegranate shoots showed infestation of thrips throughout the season. Level of infestation recorded prior to insecticide application in all treatments was homogenous as the differences in the data recorded on different treatment plants were statistically non-significant. The data regarding infestation of thrips (No./shoot) are presented in Table 4.4 and graphically depicted in Fig.4.4.

##### **i. First spray**

The initial mean number of thrips one day before first spray ranged from 11.75 to 13.19 thrips/shoot and did not differ significantly between the spray treatments and untreated control indicating normal distribution of the pest. At 3 DAS, treatment spinosad @ 56.25 g a.i. ha<sup>-1</sup> showed the lowest number of thrips with a mean abundance of 2.94 thrips/shoot; however, it was at par with fipronil @ 25 g a.i. ha<sup>-1</sup> recording 3.38 thrips/shoot.

On 7 and 10 DAS, similar trend of results was obtained. The thrips counts on 14 DAS clearly indicated that all spray treatments had increased levels of thrips infestation, to the extent of 5.44 (fipronil), 5.56 (spinosad), 6.81 (lambda-cyhalothrin) and 7.06 (imidacloprid) thrips/shoot. The significant differences were noticed on all sampling dates in between treated and untreated plants.



## **ii. Second spray**

The data on mean thrips count after second spray revealed that the counts varied in the range of 14.81 to 17.81 during 14 days and there was significant difference in between treated and untreated plants. The data recorded from treatment plants clearly indicated that fipronil @ 25 g a.i. ha<sup>-1</sup> and spinosad @ 56.25 g a.i. ha<sup>-1</sup> were equally effective in controlling thrips at 3, 7, 10 and 14 DAS. Imidacloprid @ 27 g a.i. ha<sup>-1</sup> was the least effective treatment with 5.25 thrips/shoot (14 DAS).

## **iii. Third spray**

During a post-spray span of 14 days the thrips count increased from 17.81 to 22.38 thrips/shoot in untreated control plants. The data obtained from treatment plants revealed that all four test insecticides were significantly effective against thrips. On third day minimum thrips count (0.88 thrips/shoot) was observed from the plants treated with spinosad @ 56.25 g a.i. ha<sup>-1</sup> followed by fipronil @ 25 g a.i. ha<sup>-1</sup> (1.25 thrips/shoot) which were found at par with each other.

The data on thrip counts on 7, 10 and 14 DAS showed a slight increase in the thrip counts and there was no variation in the order of effectiveness of insecticides. The data clearly indicated that spinosad and fipronil were the most effective chemicals as compared to lambda-cyhalothrin and imidacloprid. The untreated plants had significantly more number of thrips than the insecticide treated plants.

## **b. Kharif season 2010**

The data on pre-count pest infestation revealed that all the treatments were statistically non-significant indicating natural

distribution of pest. The data on thrips infestation (No./ shoot) are shown in Table 4.5 and depicted graphically in Fig. 4.5.

### **i. First spray**

The mean pre-count on thrip population in all experimental plants one day prior to first spray ranged from 8.94 to 10.06 thrips/shoot. It reached to 13.81 thrips during a span of 14 days. Lowest counts were observed in plants treated with spinosad @ 56.25 g a.i. ha<sup>-1</sup> followed by fipronil 25 g a.i. ha<sup>-1</sup>. On 14 DAS imidacloprid @ 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin @ 12.5 g a.i. ha<sup>-1</sup> recorded 6.25 and 5.88 thrips/shoot respectively, which was above ETL of 5 thrips/shoot.

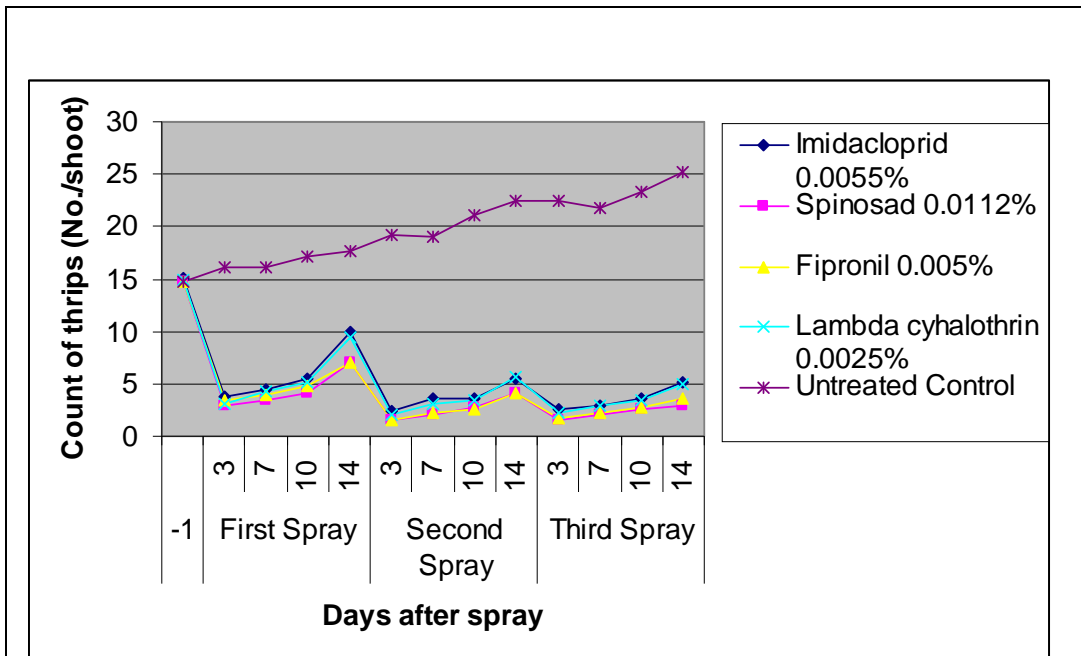
### **ii. Second spray**

Data on thrips counts after second spray showed that natural infestation was slowly increasing in untreated (control) plants. All insecticidal spray treatments were significantly effective in reducing thrips population. Moreover, spinosad @ 56.25 g a.i. ha<sup>-1</sup> and fipronil @ 25 g a.i. ha<sup>-1</sup> were the most consistent chemical treatments as compared to imidacloprid @ 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin @ 12.5 g a.i. ha<sup>-1</sup>.

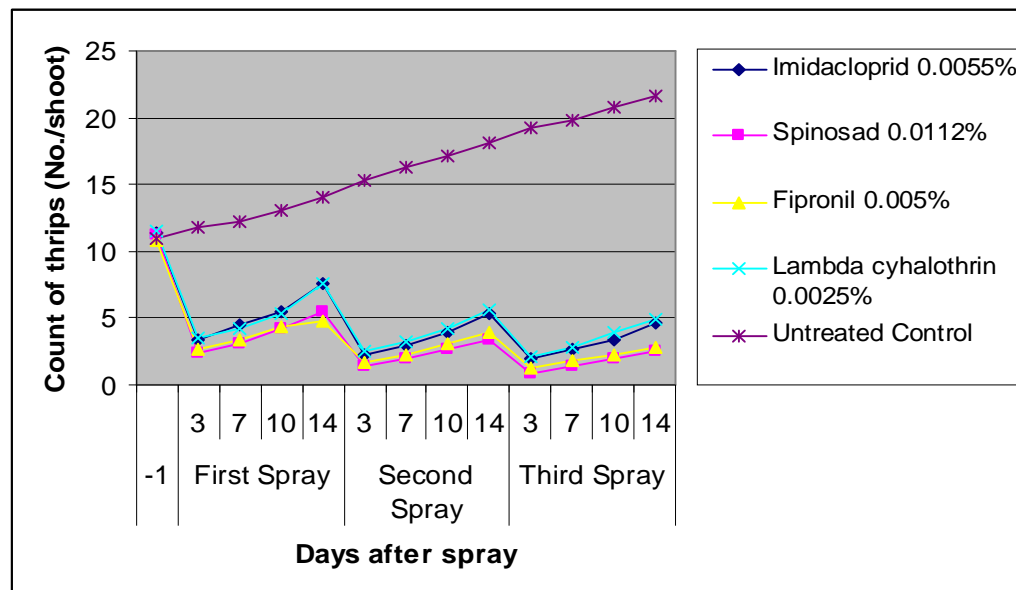
### **iii. Third spray**

After third spray it was observed that all the insecticidal treatments were significantly effective over untreated control. Amongst the various chemical treatment spinosad @ 56.25 g a.i. ha<sup>-1</sup> (2.06 thrips/shoot) was the most superior treatment followed by fipronil @ 25 g a.i. ha<sup>-1</sup> (2.38 thrips/shoot) at 14 DAS. Lambda-cyhalothrin @ 12.5 g a.i. ha<sup>-1</sup> (3.69 thrips/shoot) was the least effective treatment after imidacloprid @ 27 g a.i. ha<sup>-1</sup> (3.13 thrips/shoot).





**Fig. 4.4 Bioefficacy of insecticides against thrips on pomegranate shoots-Summer 2010**



**Fig. 4.5 Bioefficacy of insecticides against thrips on pomegranate shoots-Kharif 2010**

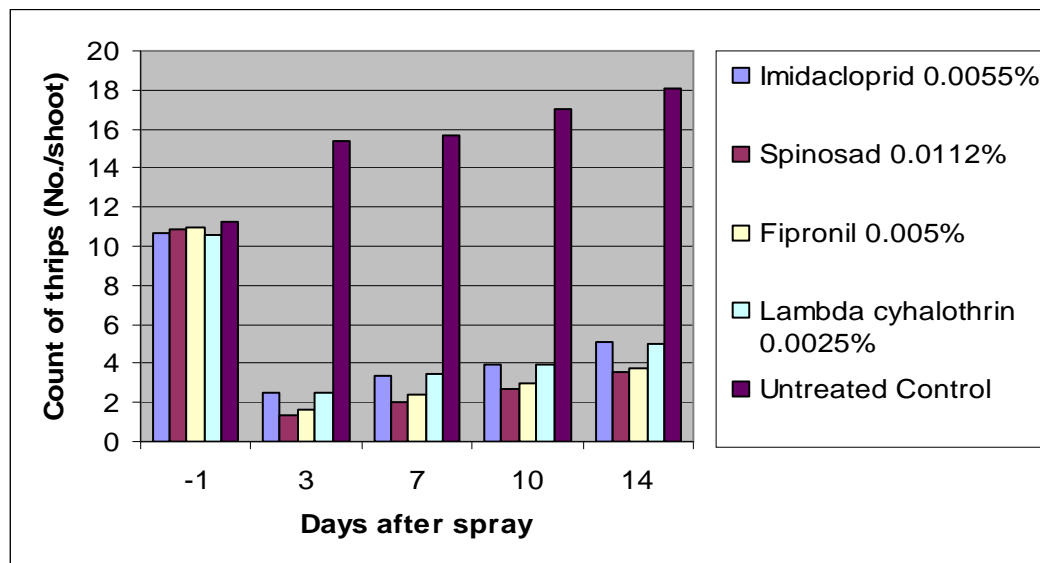
### c. Overall efficacy based on pooled data - *Summer and Kharif 2010*

Pooled data on thrip counts (No./shoot) are presented in Table 4.6. The graphical comparison of sprays treatment based on the incidence of thrips is depicted in Fig. 4.6. The untreated (control) plants showed thrips in the range of 11.29 to 18.07 indicating natural abundance. All chemical treatments were significantly superior over untreated control in minimizing pest population during both the seasons. Spinosad @ 56.25 g a.i. ha<sup>-1</sup> and fipronil @ 25 g a.i. ha<sup>-1</sup> were the most persistent and provided better protection to pomegranate against thrips. Both the treatments were at par with each other and the plants showed thrips counts below ETL of 5 thrips per shoot upto 14 DAS. Though the thrips population in imidacloprid @ 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin @ 12.5 g a.i. ha<sup>-1</sup> was above ETL at 14 DAS the insecticides were fairly effective in reducing the thrips.

**Tab.4.6 Bioefficacy of insecticides against thrips on shoots of pomegranate based on pooled data -*Summer and Kharif 2010***

Treatment	Spray conc <sup>n</sup> (% a.i.)	Average number of thrips				
		Precount (First spray)	Post count (means of 3 sprays)			
			3 DAS	7 DAS	10 DAS	14 DAS
Imidacloprid	0.0055	10.72 (3.34)	2.47 (1.69)	3.37 (1.93)	3.94 (2.09)	5.14 (2.36)
Spinosad	0.0112	10.91 (3.38)	1.31 (1.30)	2.05 (1.57)	2.66 (1.76)	3.54 (1.99)
Fipronil	0.005	10.97 (3.38)	1.61 (1.42)	2.37 (1.66)	2.97 (1.85)	3.79 (2.05)
Lambda cyhalothrin	0.0025	10.57 (3.32)	2.50 (1.71)	3.49 (1.97)	3.97 (2.10)	5.01 (2.34)
Untreated Control	---	11.29 (3.42)	15.35 (3.96)	15.67 (4.00)	17.00 (4.21)	18.07 (4.30)
S.E.±		0.06	0.07	0.06	0.05	0.04
C.D. at 5%		NS	0.20	0.19	0.15	0.13

Figures in parentheses are  $\sqrt{n+0.5}$  transformed values DAS = Days after spray



**Fig. 4.6 Bioefficacy of insecticides against thrips on pomegranate shoots based on pooled data- Summer and Kharif 2010**

### 4.1.3 Persistence toxicity of insecticides to thrips on pomegranate shoots

The reduced risk insecticides were also evaluated on the basis of persistence toxicity (PT) indices (Table 4.7 and 4.8). Higher the PT value, greater would be the persistence. Among the evaluated insecticides, spinosad 56.25 g a.i. ha<sup>-1</sup> proved to be extremely persistent *i.e* PT = 819.94 while imidacloprid 27 g a.i. ha<sup>-1</sup> was the least persistent insecticide (PT = 452.76). Fipronil 25 g a.i. ha<sup>-1</sup> was less persistent than spinosad 56.25 g a.i. ha<sup>-1</sup> showing PT=786.62. Lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup> also showed comparatively more persistence than imidacloprid 27 g a.i. ha<sup>-1</sup> PT= 497.20.

**Tab. 4.7 Persistence toxicity of insecticides to thrips on pomegranate shoots**

Treatment	Per cent mortality of thrips after treatment in days									
	0	1	3	5	7	10	14	P	T	PT
Imidacloprid 17.8 SL 27 g a.i. ha <sup>-1</sup>	75.00 (5.0)	65.00 (5.0)	53.33 (3.0)	40.00 (5.0)	35.00 (9.0)	3.33 (1.0)	0.00	10	45.27	452.76
Spinosad 45 SC 56.25 g a.i. ha <sup>-1</sup>	91.66 (8.0)	83.33 (3.0)	78.33 (3.0)	71.66 (3.0)	55.00 (5.0)	21.6 6 (3.0)	8.33 (2.0)	14	58.57	819.94
Fipronil 5 SC 25 g a.i. ha <sup>-1</sup>	88.33 (3.0)	81.66 (8.0)	75.00 (5.0)	68.33 (3.0)	58.33 (3.0)	16.6 6 (3.0)	5.00 (1.0)	14	56.19	786.62
Lambda- cyhalothrin 5 EC 12.5 g a.i. ha <sup>-1</sup>	78.33 (3.0)	71.66 (3.0)	60.00 (5.0)	45.00 (5.0)	38.33 (3.0)	5.00 (1.0)	0.00	10	49.72	497.20

Figures in parentheses are SD values.

## 4.2 Comparison of different methods of insecticide residue analysis for their efficiency

Three analytical methods of insecticide residue analysis *viz.*, California Department of Food and Agriculture (CDFA), QuEChERS and Single Residue Method (SRM) provided by manufacturer of insecticide were compared for their efficiency on the basis of recovery percentage from fortified samples of pomegranate. The fruit matrices (arils, whole fruit and peel) were fortified at the level of 0.05 and 0.1  $\mu\text{g g}^{-1}$  for each insecticide molecule under test separately and analysed by adopting the procedure specified in each method. The results based on the recovery data are presented in Table 4.9 and graphically depicted in Fig. 4.7 to 4.10.

### 4.2.1. Imidacloprid

Imidacloprid, a neonecotinoid used commonly to manage sucking pests on different crops was analysed by HPLC. The CDFA method showed highest recovery (100.16%) followed by SRM (97.16%) in arils at 0.05  $\mu\text{g g}^{-1}$  level of fortification, however, QuEChERS method gave only 75.85 per cent recovery. In whole fruit Single Residue Method was the most competent with 96.89 per cent recovery followed by CDFA (93.77%). QuEChERS method also gave better recovery (85.58%). Similar trend of recoveries was obtained from the peel of pomegranate at 0.05  $\mu\text{g g}^{-1}$  fortification level. The recoveries obtained were CDFA (90.37%), SRM (93.58%) and QuEChERS (90.37%).

The SRM showed highest recovery in arils (100.69%) at 0.1  $\mu\text{g g}^{-1}$  level of fortification followed by CDFA method (95.30%) and QuEChERS method (85.12%). In whole fruit CDFA method was the most effective method (95.08%) followed by SRM (94.88%) and

QuEChERS method (87.20%). The highest recovery in peel was obtained by SRM (96.25%). The next efficient methods were CDFA (88.91%) and QuEChERS (87.42%). The data regarding recovery of imidacloprid in pomegranate fruits showed that this compound gave acceptable recovery by all three methods compared in present studies.

#### **4.2.2. Spinosad**

Spinosad was analysed by LC-MS following validated analytical method. At both levels of fortification *viz.*, 0.05 and 0.1  $\mu\text{g g}^{-1}$ , SRM gave highest recovery of 97.92 and 86.28 per cent in arils, 88.89 and 85.59 per cent in whole fruits and 93.59 and 84.35 per cent in peel of pomegranate fruits, respectively. The next competent method was QuEChERS giving recovery of 82.29 and 82.64 per cent in arils, 81.08 and 81.42 per cent in whole fruits and 82.64 and 84.08 per cent in peel at 0.05 and 0.1  $\mu\text{g g}^{-1}$  fortification levels, respectively. The CDFA method provided acceptable recovery in the range of 75 to 80 per cent in pomegranate fruits. The recovery of spinosad at corresponding levels of fortification was 75.56 and 75.52 per cent, 77.08 and 76.48 per cent and 78.13 and 78.87 per cent in arils, whole fruits and peel, respectively.

#### **4.2.3. Fipronil and metabolites**

Fipronil, a phenyl pyrazole insecticide and its three metabolites showed variable results in recovery percentage in pomegranate fruits.

The highest recovery of fipronil was found by SRM (102.12%). Whereas, QuEChERS (76.28%) and CDFA (75.45%) methods gave less recovery in arils of pomegranate at 0.05  $\mu\text{g g}^{-1}$  level of

fortification. Similarly at  $0.1 \mu\text{g g}^{-1}$  level of fortification SRM was the most competent method. The CDFA method provided 78.27 per cent recovery whereas QuEChERS was less efficient. In whole fruits recovery of fipronil at both the levels of fortification ranged between 79 to 99 per cent by all three methods under study. In peel of pomegranate at  $0.05 \mu\text{g g}^{-1}$  level of fortification SRM was the most efficient method (114.51%) followed by QuEChERS (81.52%) and CDFA (79.35%). At  $0.1 \mu\text{g g}^{-1}$  level of fortification the order of recovery percentage was SRM (96.12%) > CDFA (85.32%) > QuEChERS (61.50%).

In arils of pomegranate at  $0.05 \mu\text{g g}^{-1}$  level of fortification recovery of metabolite MBO 6513 by SRM was 111.65 per cent and 104.07 per cent followed by 85.33 per cent and 83.45 per cent in CDFA, and 84.45 per cent and 74.06 per cent in QuEChERS method, respectively. Similar trend of recoveries was obtained from whole fruit and peel of pomegranate fruit. Metabolite MBO 45950 showed the highest recovery by SRM (90.77%) & (81.52%) whereas, QuEChERS (65.68%) & (55.30%) & CDFA (62.52%) & (68.50%) methods were less efficient as the recovery was below 75 per cent in arils at both the levels of fortification. In whole fruit and peel acceptable recoveries were obtained only from SRM. QuEChERS and CDFA methods could not prove their efficiency in recovering this metabolite.

Metabolite MBO 46136 gave better recovery by all three methods *viz.*, SRM (111.19%), QuEChERS (82.35%) and CDFA (80.60%) at  $0.05 \mu\text{g g}^{-1}$  level of fortification. Similar recovery trend was observed at  $0.1 \mu\text{g g}^{-1}$  level of fortification with highest recovery by SRM (110.41%) followed by CDFA (90.85 %) and QuEChERS

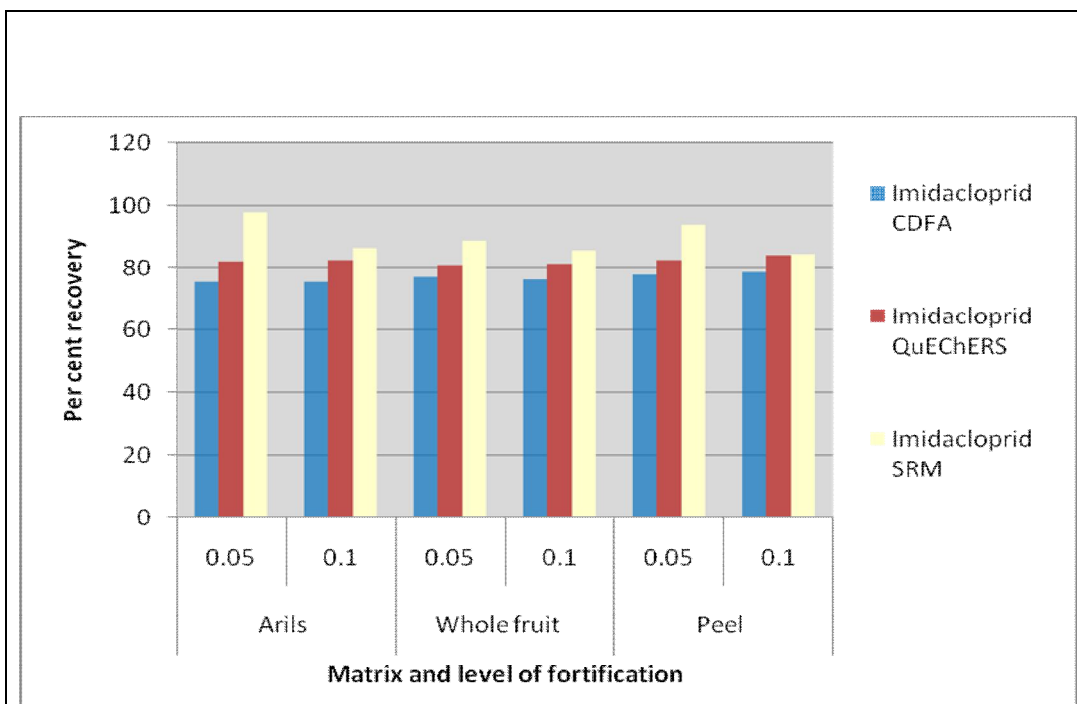
(74.32%). In whole fruit at  $0.05 \mu\text{g g}^{-1}$  SRM was the most competent method (105.74%) followed by QuEChERS (89.93%) and CDFA (82.96%). In general, at  $0.1 \mu\text{g g}^{-1}$  fortification level the order of efficiency of the methods was SRM (107.07%) followed by CDFA (82.58%) and QuEChERS (69.38%). Highest recovery in peel at both the levels of fortification was obtained by SRM.

#### **4.2.4. Lambda-cyhalothrin**

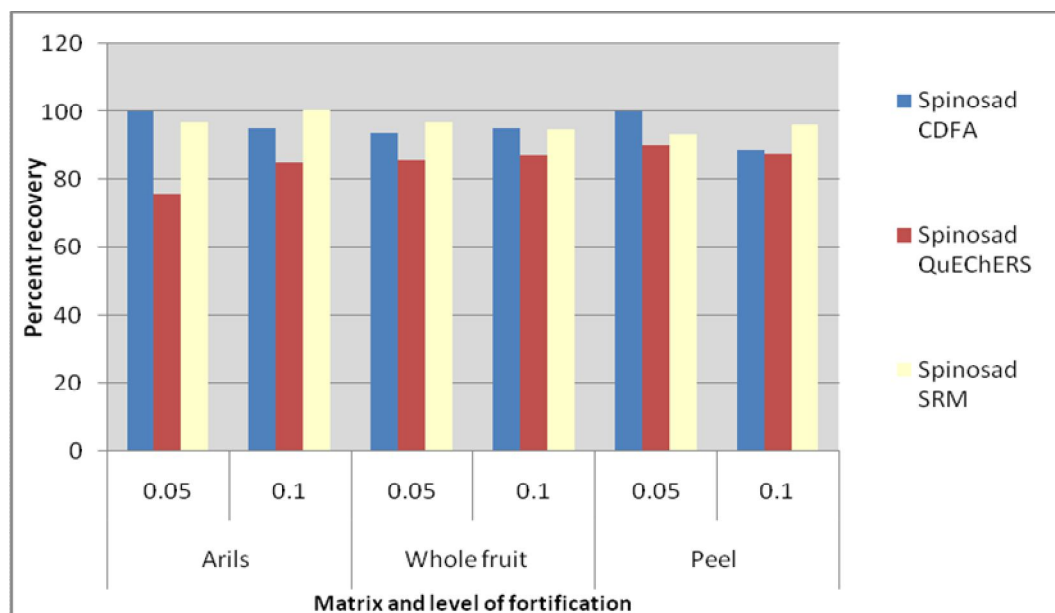
Lambda-cyhalothrin, a synthetic pyrethroid used against many Lepidopteran and Homopteran pests, was studied for its recovery in pomegranate fruit. At both the levels of fortification ( $0.05$  and  $0.1 \mu\text{g g}^{-1}$ ) CDFA method provided the highest recovery of 91.47 and 87.64 per cent, 88.81 and 86.97 per cent and 89.69 and 86.55 per cent in arils, whole fruit and peel, respectively. Other methods also yielded good recovery. SRM gave 82.73, 86.31 and 87.79 per cent recovery in arils, whole fruit and peel, respectively at  $0.05 \mu\text{g g}^{-1}$  level of fortification and 84.55, 84.44 and 86.30 per cent at  $0.1 \mu\text{g g}^{-1}$  level of fortification. The QuEChERS method also showed good recovery of 87.28, 85.06 and 88.33 per cent at  $0.05 \mu\text{g g}^{-1}$  level of fortification and 83.23, 85.13 and 87.21 per cent at  $0.1 \mu\text{g g}^{-1}$  level of fortification in arils, whole fruit and peel, respectively.

**Tab.4.8 Recovery of insecticides by different methods of residue analysis at 0.05 and 0.1  $\mu\text{g g}^{-1}$  fortification level**

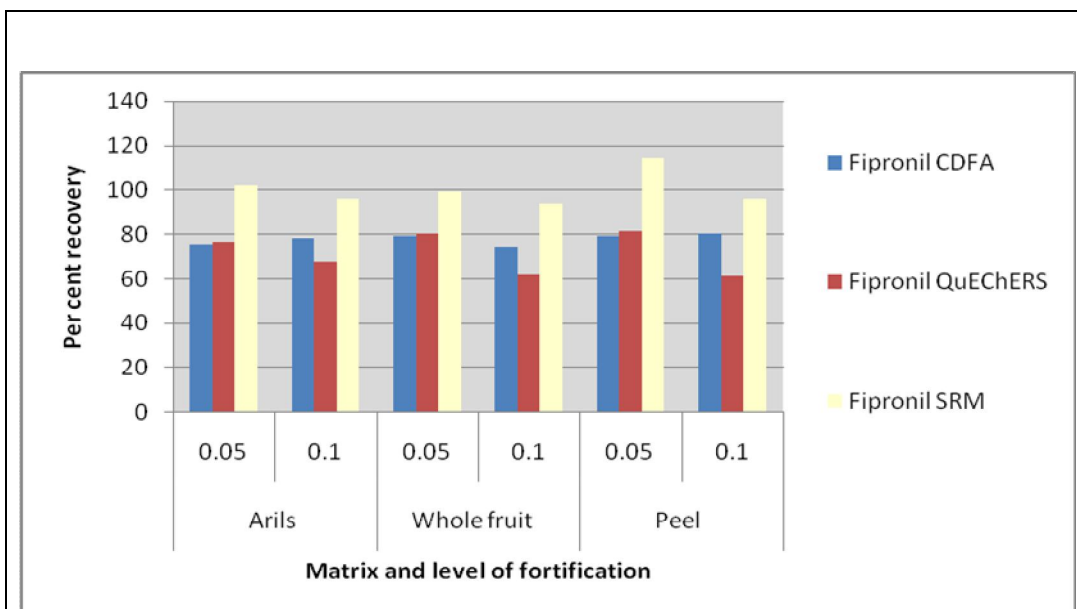
Insecticide	Method of residue analysis	Per cent recovery					
		Arils		Whole fruit		Peel	
		Level of fortification ( $\mu\text{g g}^{-1}$ )		Level of fortification ( $\mu\text{g g}^{-1}$ )		Level of fortification ( $\mu\text{g g}^{-1}$ )	
		0.05	0.1	0.05	0.1	0.05	0.1
Imidacloprid	CDFA	75.56	75.52	77.08	76.48	78.13	78.87
	QuEChERS	82.29	82.64	81.08	81.42	82.64	84.08
	SRM	97.92	86.28	88.89	85.59	93.75	84.35
Spinosad	CDFA	100.16	95.30	93.77	95.08	100.27	88.91
	QuEChERS	75.85	85.12	85.58	87.20	90.37	87.42
	SRM	97.16	100.69	96.89	94.88	93.58	96.25
Fipronil	CDFA	75.45	78.27	79.46	74.24	79.35	80.19
	QuEChERS	76.28	67.74	80.39	61.80	81.52	61.50
	SRM	102.12	96.12	99.06	93.61	114.51	96.12
MBO 6513	CDFA	85.33	83.45	90.61	81.05	90.42	85.32
	QuEChERS	84.45	74.06	86.57	67.30	86.40	67.39
	SRM	111.65	104.07	110.70	101.83	125.26	103.97
MBO 45950	CDFA	62.52	68.50	64.63	61.45	65.13	70.30
	QuEChERS	65.68	55.30	73.01	52.26	76.31	52.41
	SRM	90.77	81.52	83.06	78.85	95.99	80.25
MBO 46136	CDFA	80.60	90.85	82.96	82.58	84.44	93.49
	QuEChERS	82.35	74.32	89.93	69.38	92.51	69.68
	SRM	111.19	110.41	105.74	107.07	122.41	109.25
Lambda-cyhalothrin	CDFA	91.47	87.64	88.81	86.97	89.69	86.55
	QuEChERS	87.28	83.33	85.06	85.13	88.33	87.21
	SRM	82.73	84.55	86.31	84.44	87.79	86.90



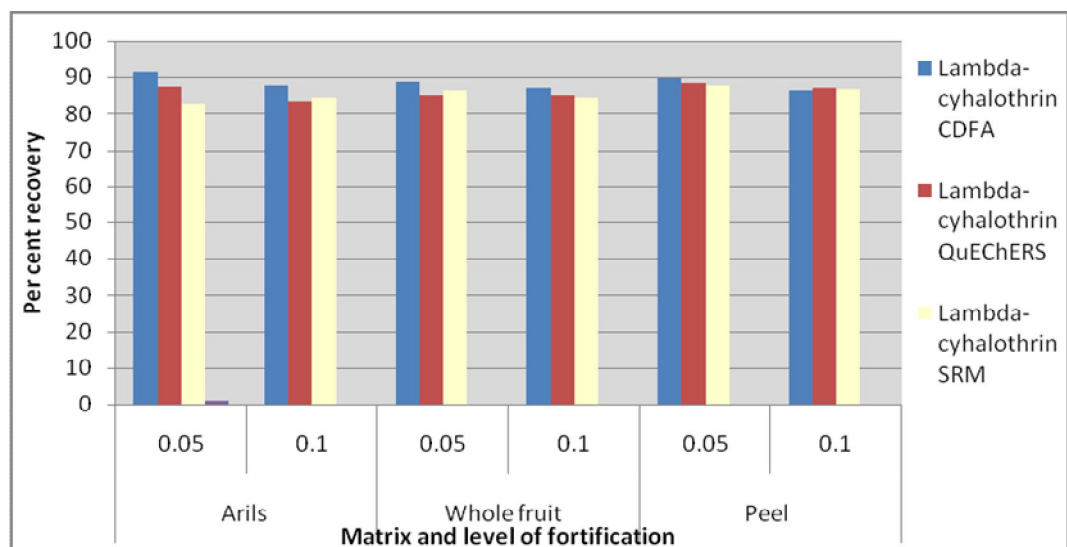
**Fig. 4.7. Recovery of imidacloprid in pomegranate fruits**



**Fig. 4.8. Recovery of spinosad in pomegranate fruits**



**Fig. 4.9. Recovery of fipronil in pomegranate fruits**



**Fig. 4.10. Recovery of lambda-cyhalothrin in pomegranate Fruits**

### **4.3. Residues of insecticides in pomegranate fruits and soil**

The data pertaining to residues of treatment insecticides in pomegranate fruits, half-life ( $RL_{50}$ ), time required to reach the residue below detection limit ( $T_{BDL}$ ) and time required to reach below maximum residue limit ( $T_{MRL}$ ) are presented in Table 4.10 to 4.13 and graphically depicted in Fig. 4.11 to 4.22.

#### **4.3.1 Imidacloprid**

##### **a. Arils**

The fruit samples collected at zero day after third spray indicated that the higher application rate resulted in higher initial deposit (Table 4.8). The initial deposits were 0.097 and 0.167  $\text{mg kg}^{-1}$  at 27 and 54  $\text{g a.i.ha}^{-1}$  doses of imidacloprid. At recommended dose of 27  $\text{g a.i.ha}^{-1}$  the initial deposit dissipated from 0.097 to 0.050  $\text{mg kg}^{-1}$  at 1 DAS and indicated the half-life of 1.05 days. The imidacloprid residues at higher rate (54  $\text{g a.i.ha}^{-1}$ ) fell with time from 0.197 to 0.051  $\text{mg kg}^{-1}$  within 3 days with an estimated half-life of 1.76 days. No detectable residues were found in the samples brought after 3 and 5 DAS at recommended and higher doses considering the 0.05 ppm BDL.

##### **b. Whole fruit**

The mean initial deposits of imidacloprid applied at 27 and 54  $\text{g a.i.ha}^{-1}$  at zero time interval were 0.156 and 0.284  $\text{mg kg}^{-1}$ . (Table 4.8). The residues dissipated gradually within 5 and 7 days for 27 and 54  $\text{g a.i.ha}^{-1}$  doses. The residue half-life under field condition was 3.16 days for recommended dose and 2.65 days for double dose. No residues were detected beyond 5 days in the fruits treated with recommended dose of 27  $\text{g a.i.ha}^{-1}$ .

### c. Peel

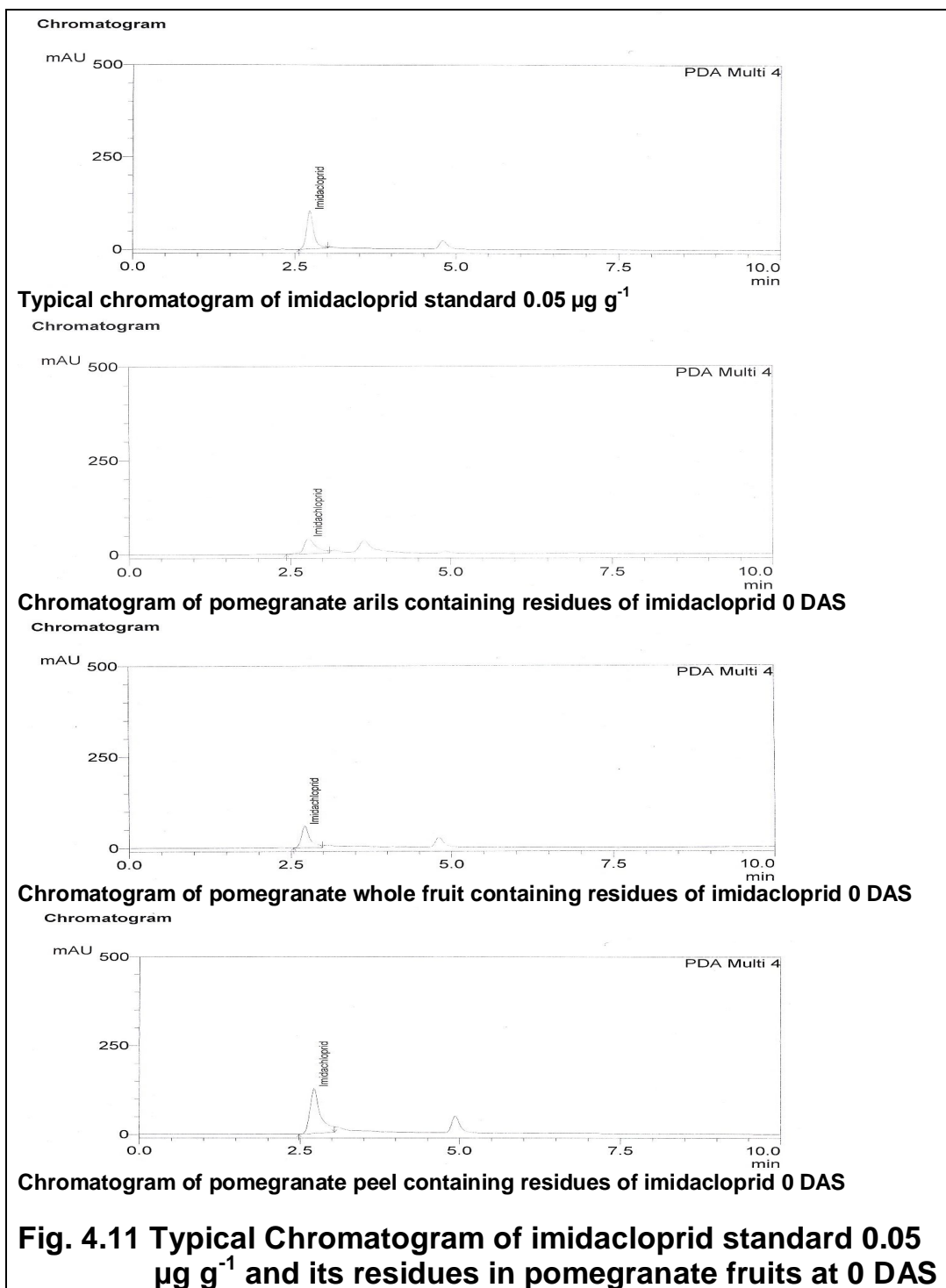
The post application (2 hr) initial deposits of imidacloprid on pomegranate peel were 0.286 and 0.429 mg kg<sup>-1</sup> at 27 and 54 g a.i. ha<sup>-1</sup> (Table 4.8). The initial deposit of 0.286 mg kg<sup>-1</sup> at recommended dose dissipated to 0.235 mg kg<sup>-1</sup> (1 DAS), 0.166 mg kg<sup>-1</sup> (3 DAS), 0.102 mg kg<sup>-1</sup> (5 DAS) and 0.073 mg kg<sup>-1</sup> (7 DAS). These residue levels at different sampling dates were exceeding the MRL of 0.05 ppm which is specified for this crop. However, at higher dose of 54 g a.i. ha<sup>-1</sup> imidacloprid residues dissipated from 0.429 to 0.051 mg kg<sup>-1</sup> within a period of 10 days. The residues of imidacloprid were not detected after 10 days in both the doses.

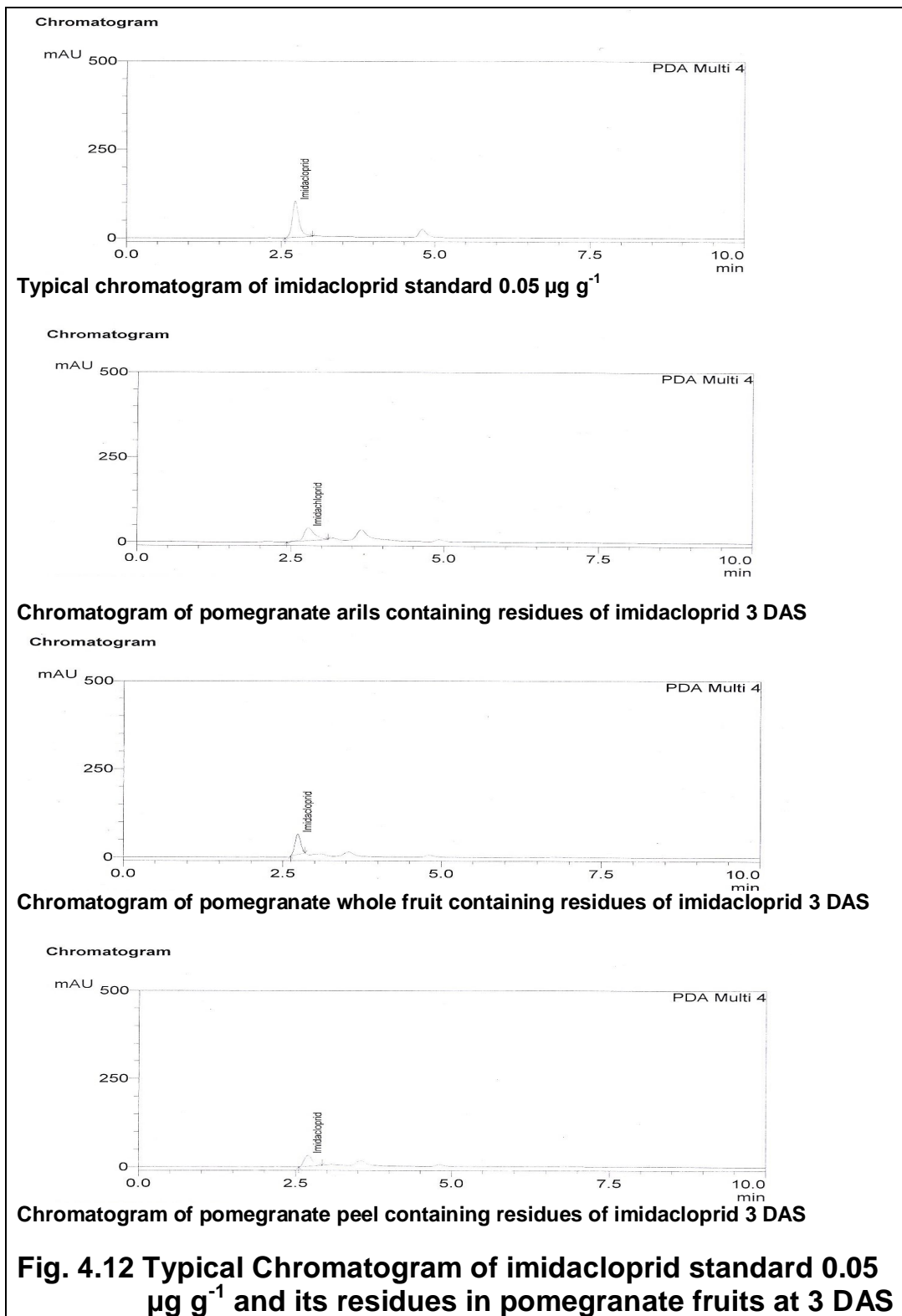
The residue half-lives under field condition ranged in between 3.35 and 3.50 days. The time required for initial deposit to degrade below the detection limit of 0.05 ppm was 8.83 to 10.76 days for both the doses.

**Tab.4.9 Residues of imidacloprid in pomegranate fruits**

Days after spray	Imidacloprid residues (mg kg <sup>-1</sup> )					
	27 g a.i. ha <sup>-1</sup>	54 g a.i. ha <sup>-1</sup>	27 g a.i. ha <sup>-1</sup>	54 g a.i. ha <sup>-1</sup>	27 g a.i. ha <sup>-1</sup>	54 g a.i. ha <sup>-1</sup>
	Arils		Whole fruit		Peel	
0	0.097	0.167	0.156	0.284	0.286	0.429
1	0.050	0.110	0.116	0.246	0.235	0.334
3	BDL	0.051	0.083	0.156	0.166	0.278
5	BDL	BDL	0.050	0.071	0.102	0.199
7	BDL	BDL	BDL	0.051	0.073	0.112
10	BDL	BDL	BDL	BDL	BDL	0.051
14	BDL	BDL	BDL	BDL	BDL	BDL
RL <sub>50</sub> (Days)	1.05	1.76	3.16	2.65	3.50	3.35
T <sub>MRL</sub> (Days)	1.00	3.04	5.09	6.90	8.83	10.76
T <sub>BDL</sub> (Days)	1.00	3.04	5.09	6.90	8.83	10.76

LOQ : 0.05 µg g<sup>-1</sup> BDL : Below detection limit





### **4.3.2 Spinosad**

#### **a. Arils**

Spinosad was estimated by reverse phase liquid chromatography at 250 nm wavelength with analytical parameters outlined in chapter 3. At recommended dose of spinosad 56.25 g a.i. ha<sup>-1</sup> initial average deposit was 0.030 mg kg<sup>-1</sup> which dropped down to below detection limit of 0.02 ppm on 1 DAS. The initial deposit of 0.037 mg kg<sup>-1</sup> observed in the samples collected at 0 DAS (2 hrs) at double dose that fell to 0.027 mg kg<sup>-1</sup>(1 DAS) and no residues were observed in the samples collected on 3 DAS.

#### **b. Whole fruit**

Estimated residues on whole fruit samples at 0 day (2 hrs) interval indicated that higher application rate (112.5 g a.i. ha<sup>-1</sup>) resulted in higher initial residues (Tab. 4.9 and Fig. 4.16). The initial residues of spinosad were 0.075 and 0.036 mg kg<sup>-1</sup> at 56.25 and 112.5 g a.i. ha<sup>-1</sup>. The spinosad residue levels at higher application rate fell with time from 0.075 to 0.036 mg kg<sup>-1</sup> within 3 days with an estimated half-life of 3 days. No detectable residues were found in the samples brought 5 days after spray application. At recommended dose (56.25 g a.i. ha<sup>-1</sup>) no residues were detected in the samples collected at 3 DAS.

#### **c. Peel**

The concentration of spinosad at zero day in pomegranate peel was 0.099 mg kg<sup>-1</sup> for higher dose and 0.045 mg kg<sup>-1</sup> for

normal dose. The initial deposit of 0.099 mg kg<sup>-1</sup> dissipated to 0.024 mg kg<sup>-1</sup> in 5 days with an estimated half-life of 2.47 days at 112.5 g a.i ha<sup>-1</sup>. No residues were detected in the samples collected at 7 DAS. At recommended dose the initial deposit of 0.045 mg kg<sup>-1</sup> took 5 days to reach below detection limit of 0.02 ppm. The estimated half-lives for both the doses were 2.89 and 2.50 days.

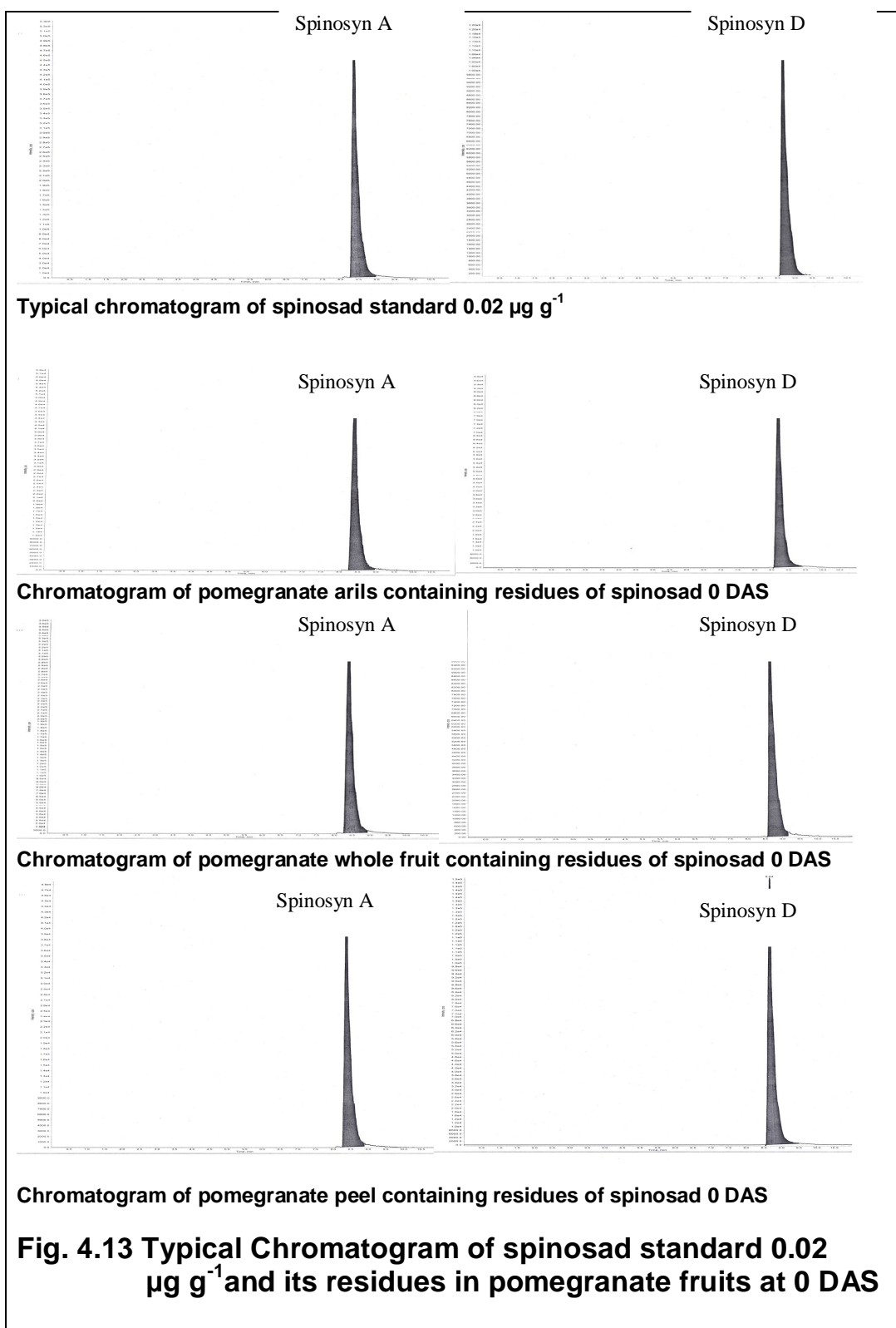
**Tab.4.10 Residues of spinosad in pomegranate fruits**

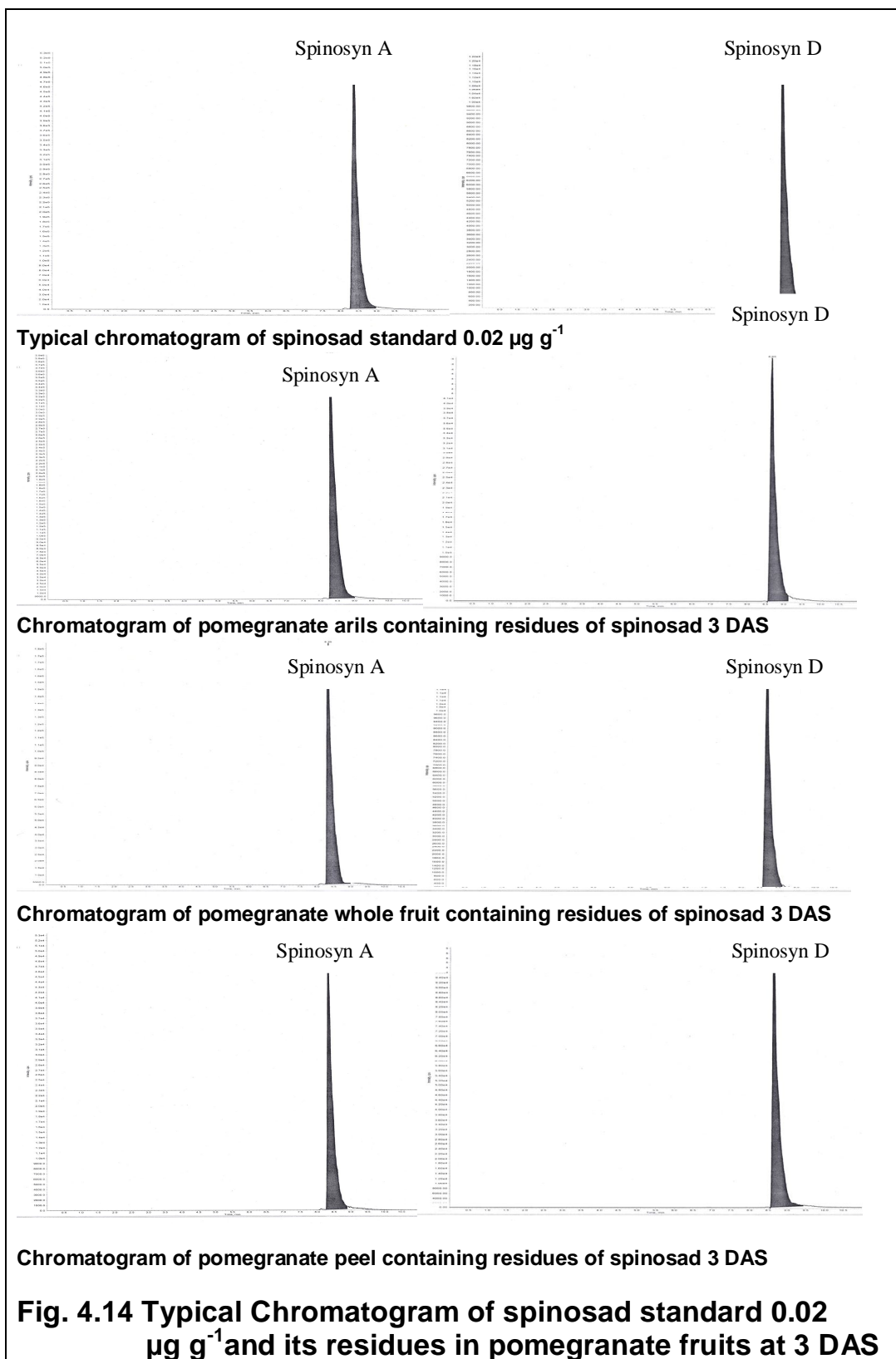
Days after spray	Spinosad residues (mg kg <sup>-1</sup> )					
	56.25 g a.i. ha <sup>-1</sup>	112.5 g a.i. ha <sup>-1</sup>	56.25 g a.i. ha <sup>-1</sup>	112.5 g a.i. ha <sup>-1</sup>	56.25 g a.i. ha <sup>-1</sup>	112.5 g a.i. ha <sup>-1</sup>
	Arils		Whole fruit		Peel	
0	0.030	0.037	0.036	0.062	0.045	0.099
1	BDL	0.027	0.027	0.047	0.036	0.076
3	BDL	BDL	0.023	0.029	0.022	0.049
5	BDL	BDL	BDL	BDL	BDL	0.024
7	BDL	BDL	BDL	BDL	BDL	BDL
10	BDL	BDL	BDL	BDL	BDL	BDL
14	BDL	BDL	BDL	BDL	BDL	BDL
RL <sub>50</sub> (Days)		2.20	3.66	2.75	2.89	2.50
T <sub>MRL</sub> (Days)		1.95	2.90	4.46	3.41	5.86
T <sub>BDL</sub> (Days)		1.95	2.90	4.46	3.41	5.86

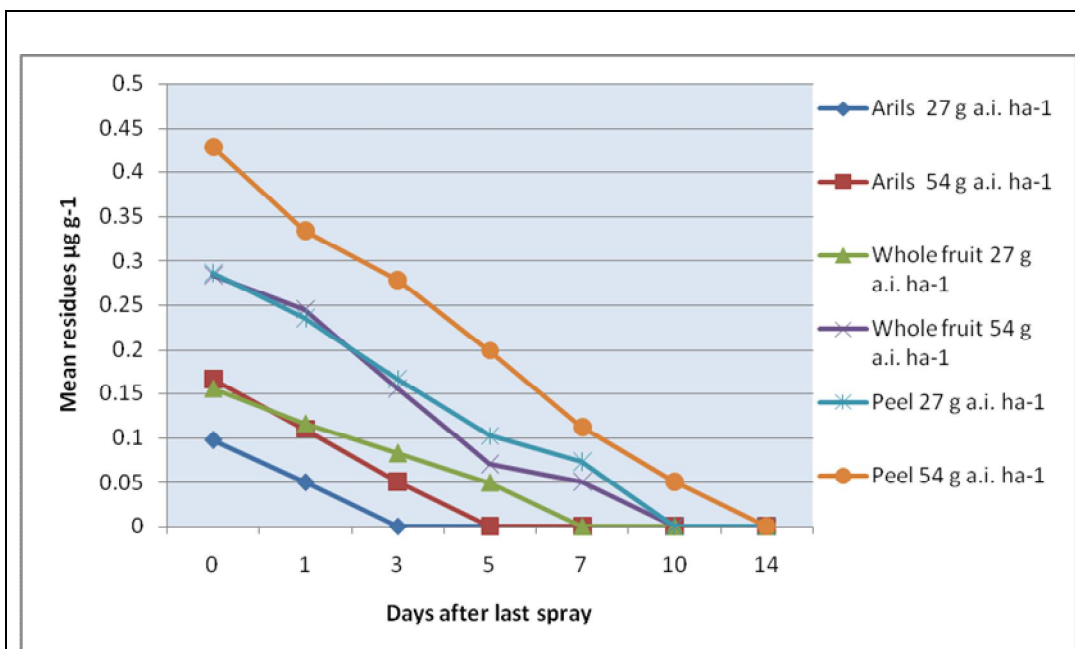
LOQ : 0.02 µg g<sup>-1</sup>

BDL : Below detection limit

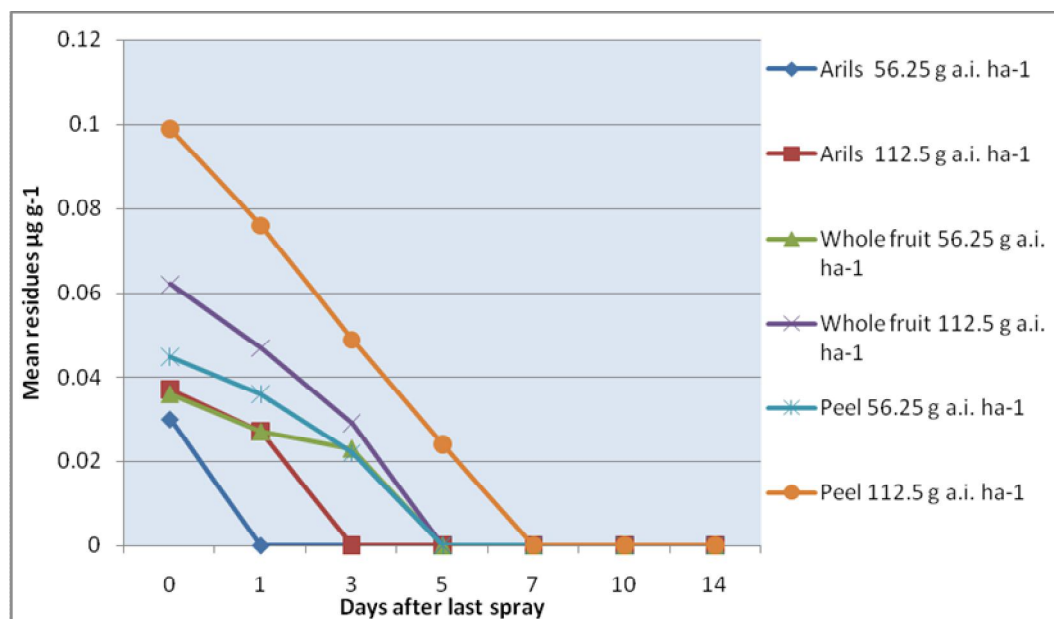
MRL : Maximum residue limit







**Fig. 4.15 Residues of imidacloprid 17.8 SL (27 and 54 g a.i. ha<sup>-1</sup>) in pomegranate fruits**



**Fig. 4.16 Residues of spinosad 45 SC (56.25 and 112.5 g a.i. ha<sup>-1</sup>) in pomegranate fruits**

### 4.3.3 Fipronil and metabolites

#### a. Arils

The GC-ECD analysis of fipronil and metabolites involved extraction in acetonitrile and cleanup by silica gel column chromatography. At normal dose (25 g a.i. ha<sup>-1</sup>) initial average residue of fipronil was 0.034 mg kg<sup>-1</sup> on 0 DAS (Table 4.11). However, residues were not detected from 5<sup>th</sup> day onwards. The half-life (RL<sub>50</sub>) value of 4.45 days indicated that the initial residue decreased to its half within 4.45 days. The time required for initial residues to reach below the detection limit was 3.22 days. The metabolites, MBO 6513, MBO 45950 and MBO 46136 were detected at 1 DAS only and the residue levels were 0.032, 0.022 and 0.028 mg kg<sup>-1</sup>, respectively.

The immediate post-application (zero time) initial deposit of fipronil in pomegranate arils was 0.064 mg kg<sup>-1</sup> at 50 g a.i. ha<sup>-1</sup>. Residues of fipronil were not detected in arils of pomegranate beyond 7 days. The residue half-life under field condition was 3.72 days. The time required for initial residue to reach below detection limit of 0.02 ppm was 6.38 days. The metabolites were detected only up to 5 DAS and were in the range of 0.021 to 0.031 mg kg<sup>-1</sup>.

#### b. Whole fruit

Fipronil and its metabolites residues were found in higher amounts in whole fruit as compared to arils (Table 4.10). The initial deposit of fipronil at normal dose (25 g a.i. ha<sup>-1</sup>) was found to be 0.064 mg kg<sup>-1</sup> at 0 DAS. Fipronil residues were found below

detection limit at 10 DAS. The estimated half-life was of 4.88 days, whereas, residues reached below detection limit of 0.02 ppm in 8.11 days. The metabolite MBO 6513 was observed at a level of 0.043, 0.056 and 0.044 mg kg<sup>-1</sup> at 0, 1 and 3 DAS, respectively. It was not detected in the samples collected at 5 DAS. The other metabolites MBO 45950 and MBO 46136 were found only in the samples collected on 1 and 3 DAS and the levels were 0.045 to 0.039 and 0.054 to 0.047 mg kg<sup>-1</sup>, respectively.

At double dose (50 g a.i. ha<sup>-1</sup>) the initial deposit of fipronil was 0.104 µg g<sup>-1</sup> in whole fruit which dissipated to 0.089, 0.068, 0.054, 0.033 and 0.022 mg kg<sup>-1</sup> at 1, 3, 5, 7 and 10 DAS, respectively. The metabolites detected in the samples collected at 5 DAS were in the range of 0.059 mg kg<sup>-1</sup> (MBO 6513), 0.046 (MBO 45950) and 0.058 (MBO 46136).

### **c. Peel**

The samples collected from the plants treated with recommended dose of fipronil (25 g a.i. ha<sup>-1</sup>) showed initial deposit of 0.110 mg kg<sup>-1</sup> in peel (Table 4.11). The residues dissipated to the levels of 0.104 mg kg<sup>-1</sup> (1 DAS), 0.082 mg kg<sup>-1</sup> (3 DAS), 0.066 mg kg<sup>-1</sup> (5 DAS), 0.049 mg kg<sup>-1</sup> (7 DAS) and 0.034 mg kg<sup>-1</sup> (10 DAS). The fipronil residues in peel of pomegranate took more than 10 days to reach below detection limit of 0.02 ppm with an estimated half-life of 5.77 days. The metabolite MBO 6513 was found in the range of 0.086 mg kg<sup>-1</sup> (3 DAS), 0.073 mg kg<sup>-1</sup> (5 DAS) and 0.054 mg kg<sup>-1</sup> (7 DAS). The metabolite MBO 45950 was also found in the samples collected at 3, 5 and 7 DAS at the level of 0.075 mg kg<sup>-1</sup>, 0.054 mg kg<sup>-1</sup> and 0.041 mg kg<sup>-1</sup>, respectively. The other metabolite MBO 46136 estimated from the samples collected

at 3, 5 and 7 DAS showed residues of 0.098, 0.073 and 0.053 mg kg<sup>-1</sup> respectively.

Fipronil at double the recommended dose (50 g a.i. ha<sup>-1</sup>) showed higher residues, initial residue at 0 DAS was observed to be 0.197 mg kg<sup>-1</sup>. The residues dissipated in pomegranate peel from 0.179 mg to 0.021 mg kg<sup>-1</sup> within 14 days. The estimated half-life was 4.75 days and time required to reach the residues below detection limit was 15.20 days. The metabolites showed a variable dissipation pattern in pomegranate peel. The metabolite MBO 6513 was detected in the samples collected at 3, 5, 7 and 10 DAS at the levels of 0.183, 0.147, 0.097 and 0.023 mg kg<sup>-1</sup>, respectively. The metabolite MBO 45950 was found in the samples collected at 3, 5 and 7 DAS at the levels of 0.025, 0.020 and 0.076 mg kg<sup>-1</sup>, respectively. The metabolites MBO 6513 and MBO 45950 were not detected in the samples collected on 0 and 1 DAS. However, the third metabolite MBO 46136 was detected on (0.022 mg kg<sup>-1</sup>) at 0 DAS. Interestingly, it was not detected in 1 day sample. Thereafter, the samples collected on subsequent days showed residue levels of 0.077 (3 DAS), 0.051 (5 DAS), 0.103 (7 DAS) and 0.033 (10 DAS) mg kg<sup>-1</sup> respectively.

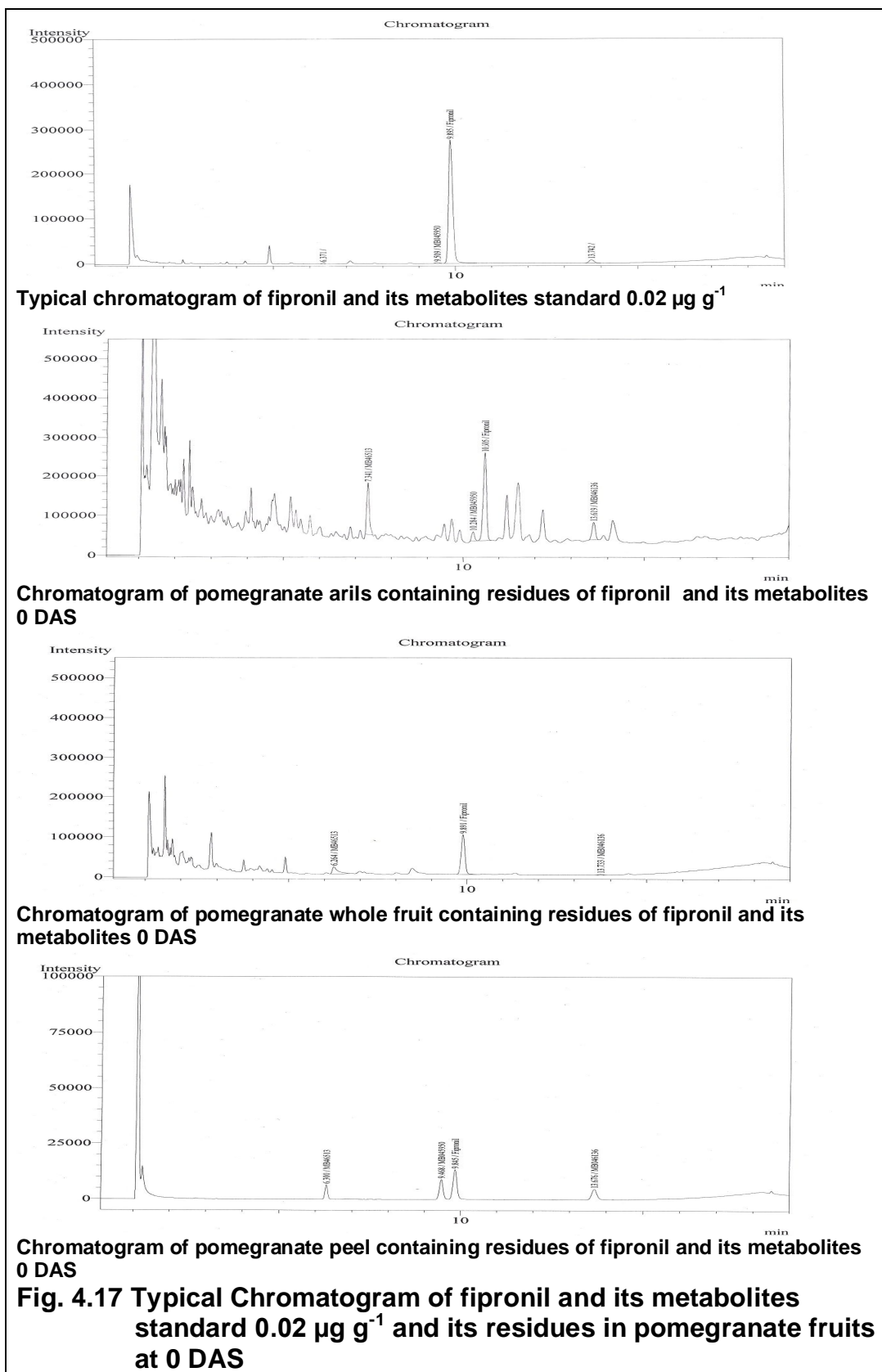
**Tab. 4.11 Residues of fipronil and metabolites in pomegranate fruits**

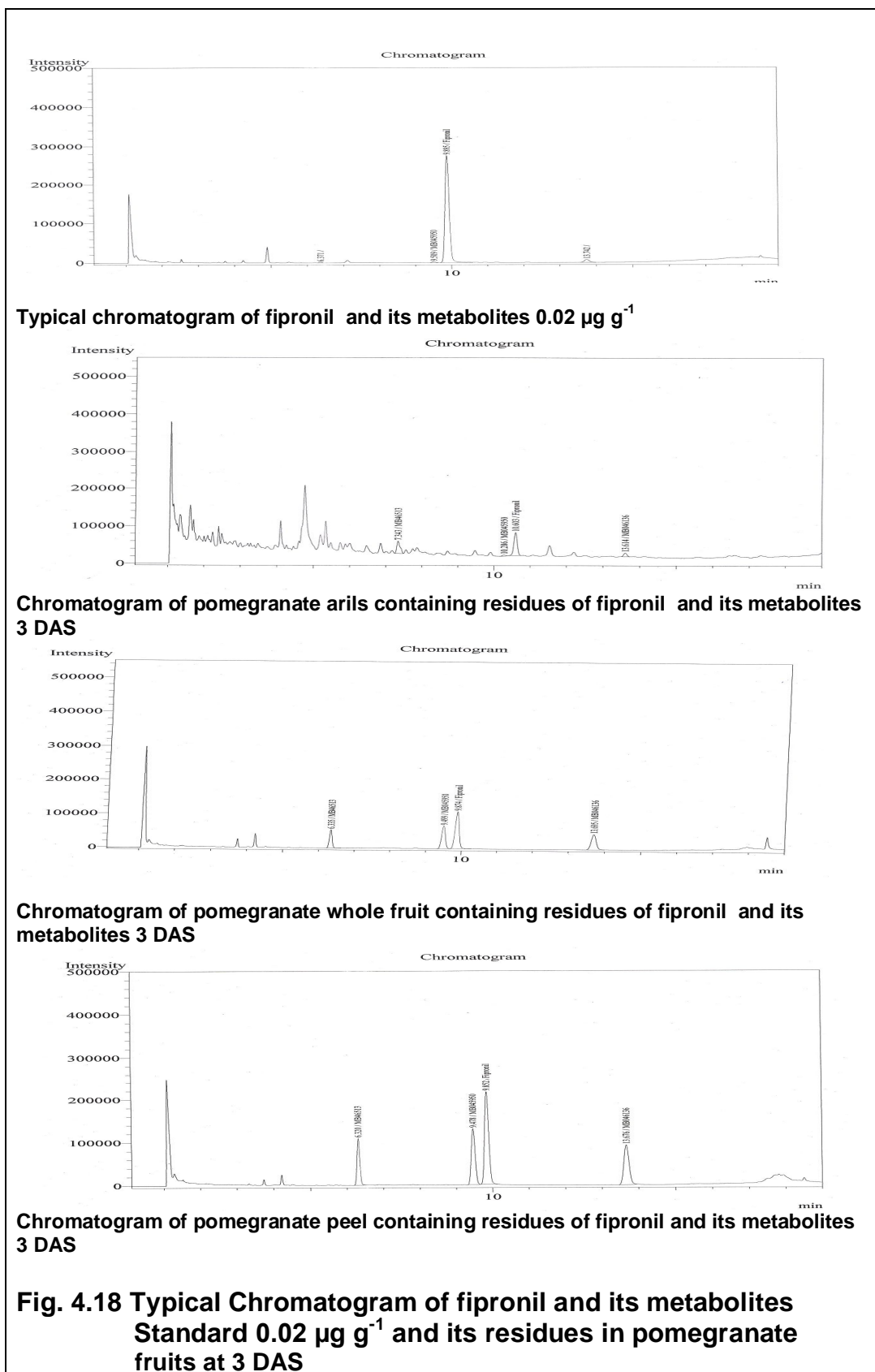
Days after sprays	Fipronil and metabolites	Fipronil residues (mg kg <sup>-1</sup> )					
		25 g a.i. ha <sup>-1</sup>	50 g a.i. ha <sup>-1</sup>	25 g a.i. ha <sup>-1</sup>	50 g a.i. ha <sup>-1</sup>	25 g a.i. ha <sup>-1</sup>	50 g a.i. ha <sup>-1</sup>
		Arils		Whole fruit		Peel	
<b>0</b>	Fipronil	0.034	0.064	0.064	0.104	0.110	0.197
	MBO6513	BDL	BDL	0.043	BDL	BDL	BDL
	MBO45950	BDL	BDL	BDL	BDL	BDL	BDL
	MBO46136	BDL	BDL	BDL	BDL	BDL	0.022
<b>1</b>	Fipronil	0.027	0.059	0.052	0.089	0.104	0.179
	MBO6513	0.032	BDL	0.056	BDL	BDL	BDL
	MBO45950	0.022	BDL	0.045	BDL	BDL	BDL
	MBO46136	0.028	BDL	0.054	BDL	BDL	BDL
<b>3</b>	Fipronil	0.021	0.034	0.042	0.068	0.082	0.140
	MBO6513	BDL	BDL	0.044	BDL	0.086	0.183
	MBO45950	BDL	BDL	0.039	BDL	0.075	0.025
	MBO46136	BDL	BDL	0.047	0.026	0.098	0.077
<b>5</b>	Fipronil	BDL	0.027	0.034	0.054	0.066	0.113
	MBO6513	BDL	0.031	BDL	0.059	0.073	0.147
	MBO45950	BDL	0.021	BDL	0.046	0.054	0.020
	MBO46136	BDL	0.027	BDL	0.058	0.073	0.051
<b>7</b>	Fipronil	BDL	BDL	0.022	0.033	0.049	0.089
	MBO6513	BDL	BDL	BDL	BDL	0.054	0.097
	MBO45950	BDL	BDL	BDL	BDL	0.041	0.076
	MBO46136	BDL	BDL	BDL	BDL	0.053	0.103
<b>10</b>	Fipronil	BDL	BDL	BDL	0.022	0.034	0.046
	MBO6513	BDL	BDL	BDL	BDL	BDL	0.023
	MBO45950	BDL	BDL	BDL	BDL	BDL	BDL
	MBO46136	BDL	BDL	BDL	BDL	BDL	0.033
<b>14</b>	Fipronil	BDL	BDL	BDL	BDL	BDL	0.021
	MBO6513	BDL	BDL	BDL	BDL	BDL	BDL
	MBO45950	BDL	BDL	BDL	BDL	BDL	BDL
	MBO46136	BDL	BDL	BDL	BDL	BDL	BDL
<b>RL<sub>50</sub></b> <b>(Days)</b>		<b>4.45</b>	<b>3.72</b>	<b>4.88</b>	<b>4.41</b>	<b>5.77</b>	<b>4.75</b>
<b>T<sub>MRL</sub></b> <b>(Days)</b>		<b>3.22</b>	<b>6.38</b>	<b>8.11</b>	<b>10.65</b>	<b>14.58</b>	<b>15.20</b>
<b>T<sub>BDL</sub></b> <b>(Days)</b>		<b>12.12</b>	<b>13.82</b>	<b>17.88</b>	<b>19.46</b>	<b>26.11</b>	<b>23.93</b>

LOQ : 0.02 µg g<sup>-1</sup>

BDL : Below detection limit

MRL : Maximum residue limit : 0.005 µg g<sup>-1</sup>





#### **4.3.4. Lambda-cyhalothrin**

##### **a. Arils**

Residues of lambda-cyhalothrin were detected by GC-ECD with the detectability level of 0.01 ppm. The initial deposit of 0.029 mg kg<sup>-1</sup> in case of recommended dose of lambda-cyhalothrin (12.5 g a.i. ha<sup>-1</sup>) reached below detection limit in 5 DAS in arils of pomegranate. The dissipation of lambda-cyhalothrin in arils was in first order kinetics and the initial deposit of 0.029 mg kg<sup>-1</sup> dissipated to 0.012 mg kg<sup>-1</sup> at 3 DAS. The estimated half-life value was 2.47 days and time taken to reach residue below detection limit of 0.01 ppm was 3.51 days at normal dose of 12.5 g a.i. ha<sup>-1</sup>. At higher dose the initial deposit was 0.058 mg kg<sup>-1</sup> at 0 DAS that dissipated to 0.035 (1 DAS), 0.020 (3 DAS) and 0.014 (5 DAS) mg kg<sup>-1</sup> respectively. The estimated half-life was 2.51 days and time required to reach below detection limit was 5.91 days.

##### **b. Whole fruit**

The whole fruit of pomegranate showed initial residue of 0.120 mg kg<sup>-1</sup> (0 DAS) at 12.5 g a.i. ha<sup>-1</sup>. At double dose of 25 g a.i. ha<sup>-1</sup> the residues of lambda-cyhalothrin were 0.170 mg kg<sup>-1</sup> at 0 DAS, 0.122 mg kg<sup>-1</sup> at 1 DAS, 0.088 mg kg<sup>-1</sup> at 3 DAS, 0.061 mg kg<sup>-1</sup> 5 DAS, 0.032 mg kg<sup>-1</sup> 7 DAS and 0.018 mg kg<sup>-1</sup> at 10 DAS. The calculated half-lives for recommended and double the recommended dose were 2.59 to 3.11 days.

##### **c. Peel**

The peel of pomegranate showed higher levels of residues at both the doses. At normal dose of lambda-cyhalothrin (12.5 g a.i. ha<sup>-1</sup>) initial residues of 0.152 mg kg<sup>-1</sup> degraded to 0.097

(1 DAS), 0.058 (3 DAS), 0.035 (5 DAS) and 0.023 (7 DAS) mg kg<sup>-1</sup> within 7 days. At double dose of 25 g a.i. ha<sup>-1</sup> the initial residues of lambda-cyhalothrin were 0.256 mg kg<sup>-1</sup> that dissipated to 0.014 mg kg<sup>-1</sup> in 10 days. The half-life was found in the range of 2.63 days at normal dose and 2.60 days for double dose.

**Tab.4.12 Residues of lambda-cyhalothrin in pomegranate fruits**

Days after sprays	Lambda-cyhalothrin residue (mg kg <sup>-1</sup> )					
	12.5 g a.i. ha <sup>-1</sup>	25 g a.i. ha <sup>-1</sup>	12.5 g a.i. ha <sup>-1</sup>	25 g a.i. ha <sup>-1</sup>	12.5 g a.i. ha <sup>-1</sup>	25 g a.i. ha <sup>-1</sup>
	Arils		Whole fruit		Peel	
0	0.029	0.058	0.120	0.170	0.152	0.256
1	0.018	0.035	0.076	0.122	0.097	0.153
3	0.012	0.020	0.052	0.088	0.058	0.108
5	BDL	0.014	0.026	0.061	0.035	0.082
7	BDL	BDL	0.018	0.032	0.023	0.045
10	BDL	BDL	BDL	0.018	BDL	0.014
14	BDL	BDL	BDL	BDL	BDL	BDL
RL <sub>50</sub> (Days)	2.47	2.51	2.59	3.11	2.63	2.60
T <sub>MRL</sub> (Days)	1.04	3.40	6.36	9.51	7.28	9.43
T <sub>BDL</sub> (Days)	3.51	5.91	8.95	12.62	9.91	12.03

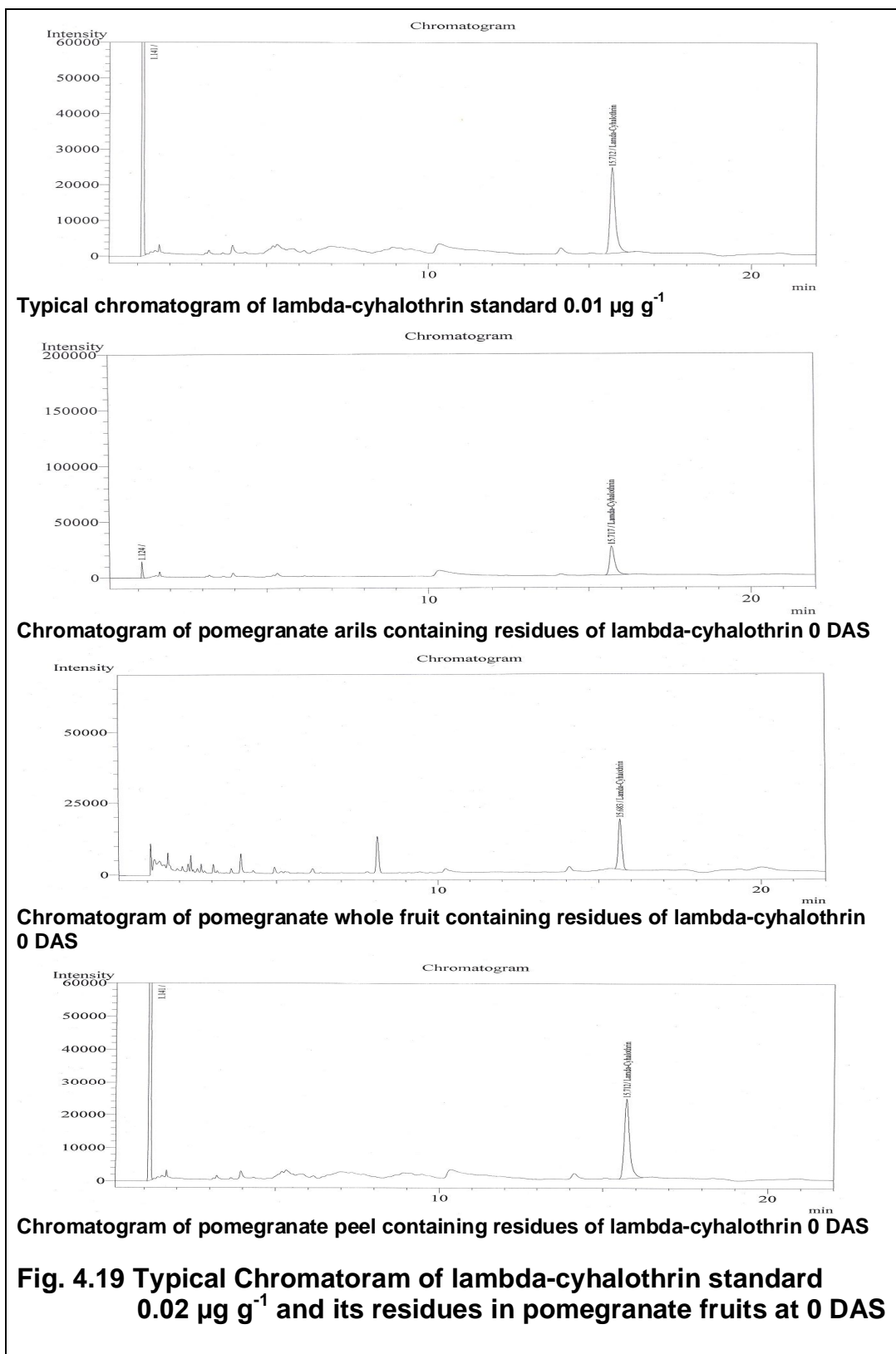
LOQ : 0.01 µg g<sup>-1</sup>

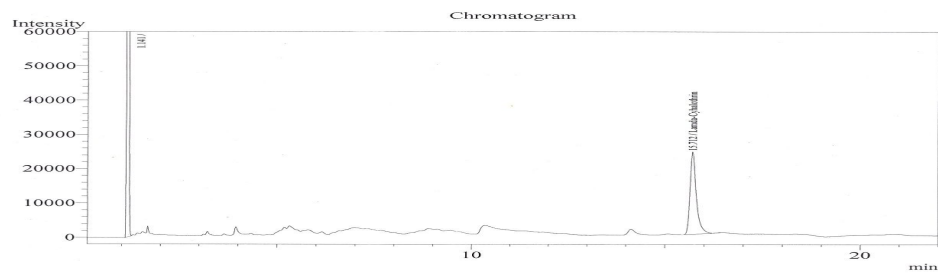
BDL : Below detection limit

MRL : Maximum residue limit : 0.02 µg g<sup>-1</sup>

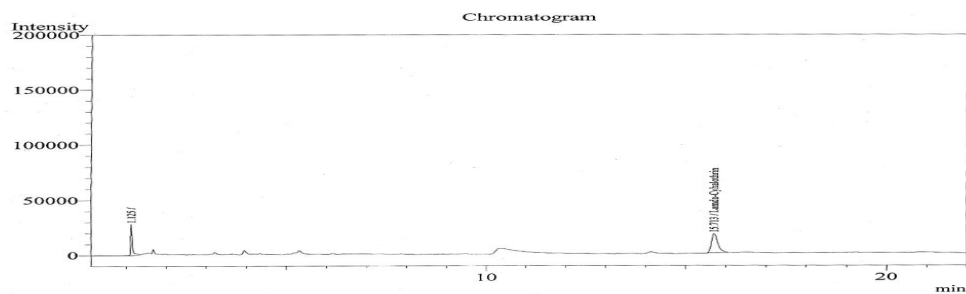
#### 4.3.5 Residues of insecticides in soil

The soil samples collected from all treatment plots 21 days after last spray did not show presence of residues of any compound at both the doses.

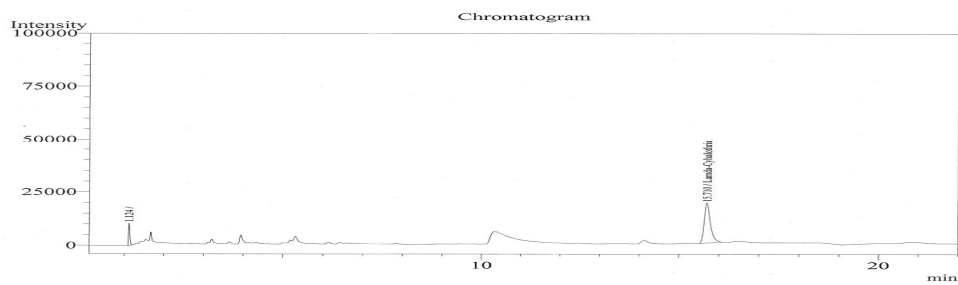




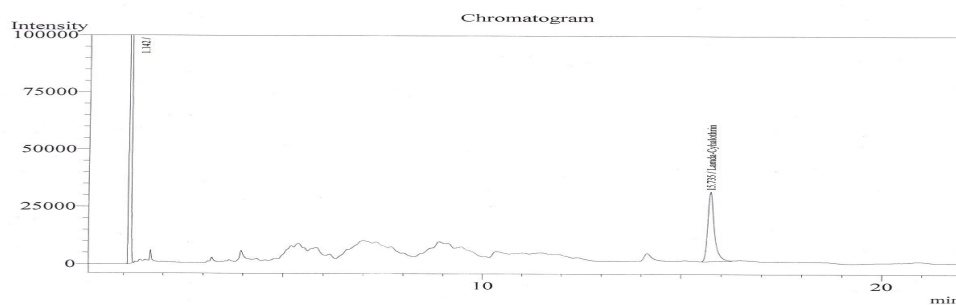
Typical chromatogram of lambda-cyhalothrin standard  $0.01 \mu\text{g g}^{-1}$



Chromatogram of pomegranate arils containing residues of lambda-cyhalothrin 3 DAS

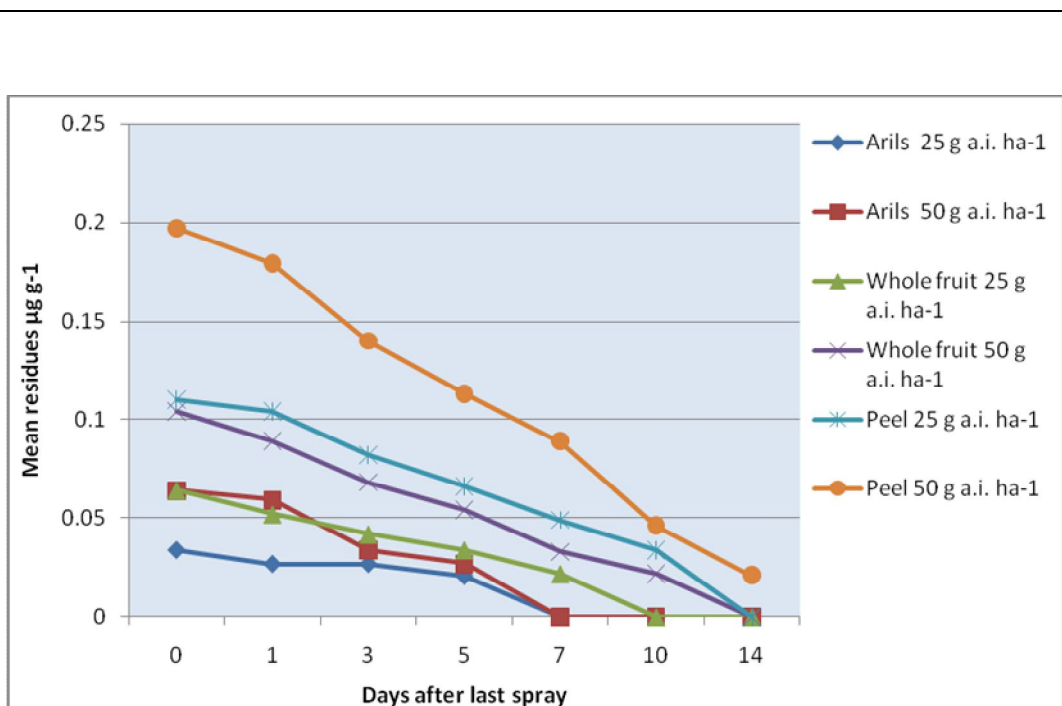


Chromatogram of pomegranate whole fruit containing residues of lambda-cyhalothrin 3 DAS

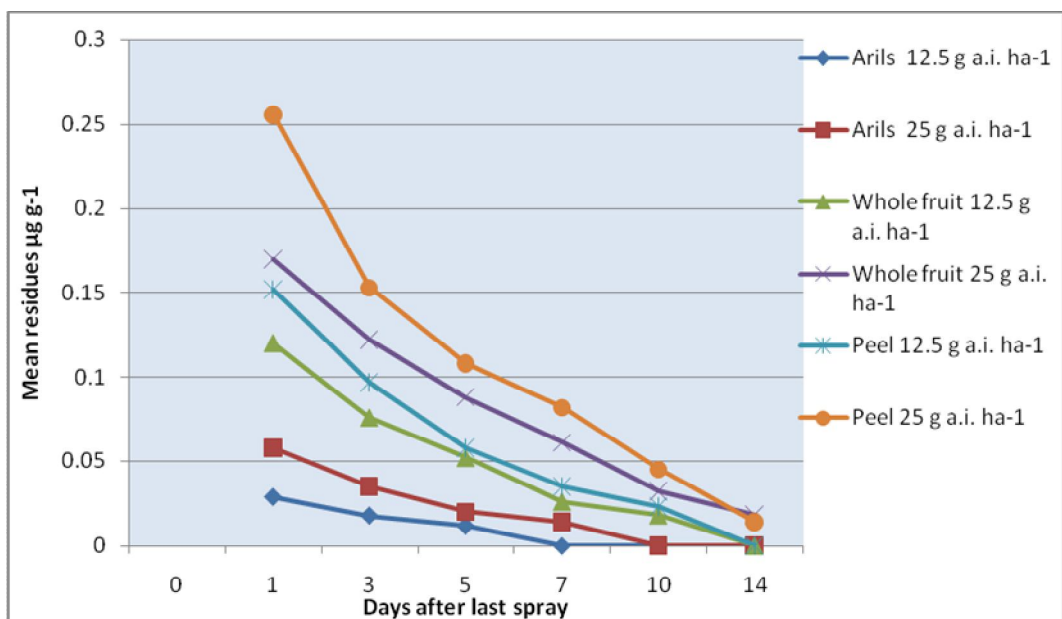


Chromatogram of pomegranate peel containing residues of lambda-cyhalothrin 3 DAS

Fig. 4.20 Typical Chromatogram of lambda-cyhalothrin standard  $0.02 \mu\text{g g}^{-1}$  and its residues in pomegranate fruits at 3 DAS



**Fig. 4.21 Residues of fipronil 5 SC (25 and 50 g a.i. ha<sup>-1</sup>) in pomegranate fruits**



**Fig. 4.22 Residues of lambda-cyhalothrin 5 EC (12.5 and 25 g a.i. ha<sup>-1</sup>) in pomegranate fruits**

#### **4.4. Leaching of lindane and chlorpyrifos used in pomegranate stem pasting**

The soil samples from the area adjacent to the tree trunk were collected and subjected to GC-ECD and GC-FTD analysis for determining the lindane and chlorpyrifos residues resulting from the stem pasting treatment. Residues of lindane and chlorpyrifos were not found in the surface layer of soil at 30 days after the treatment. The levels of quantification for lindane and chlorpyrifos were 0.01 and 0.05 ppm.

## 5. Discussion

The results obtained from the different experiments conducted during present studies are discussed in this chapter.

### 5.1 Bioefficacy and persistence toxicity of reduced risk insecticides against pomegranate thrips

Results based on pooled data obtained from two season experiments conducted at pomegranate orchard pruned for *Ambia* and *Mrig* bahar of 2010 are discussed in this chapter.

Performance of spray treatments *viz.*, imidacloprid 27 g a.i. ha<sup>-1</sup>, spinosad 56.25 g a.i. ha<sup>-1</sup>, fipronil 25 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup> was judged on the basis of infestation of thrips (No./fruit and shoot) recorded at 3, 7, 10 and 14 days after spray (DAS). Pooled data of two experiments was used for efficacy comparison. The overall initial mean count of thrips in untreated control plants was 12.85 thrips/fruit that rose to 19.84 thrips and the count on shoot was 11.29 thrips/shoot that increased to 18.07 thrips in a span of two weeks. All insecticide treatments significantly lowered the incidence of thrips. However, better efficacy of imidacloprid 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup> was noticed only upto 10 DAS as the count of thrips per fruit and shoot was below five thrips/fruit. The plants treated with spinosad 56.25 g a.i. ha<sup>-1</sup> and fipronil 25 g a.i. ha<sup>-1</sup> showed minimum incidence of thrips per fruit and shoot even at 14 DAS, since, the count was below five thrips and the insecticides found more persistent. Though, spinosad is very effective and gives better protection for longer period, it degrades quickly in the environment and has very less impact on natural enemies. It is safe and has oral

LD<sub>50</sub> value >5000 mg kg<sup>-1</sup> body weight. Considering the typical damage caused by thrips on fruits responsible for loss in aesthetic value of fruits in domestic and export market, spraying of these molecules viz., imidacloprid 27 g a.i. ha<sup>-1</sup>, lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup>, spinosad 56.25 g a.i. ha<sup>-1</sup> and fipronil 25 g a.i. ha<sup>-1</sup> can be effectively advocated in spray schedule against thrips. However, the interval between two sprays should be reduced to 10 days for imidacloprid 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup> while, spinosad 56.25 g a.i. ha<sup>-1</sup> and fipronil 25 g a.i. ha<sup>-1</sup> can be used at an interval of 14 days so that thrips incidence can be maintained below economic threshold level of 5 thrips/fruit and shoot. Fipronil is not reduced risk insecticide but selective in action.

The reports on chemical control of pomegranate thrips are very few. Spraying of 0.05% monocrotophos was reported to be effective (Bagale, 1993). However, use of monocrotophos on fruit and vegetable crops has been prohibited by the Central Insecticide Board. In the present study the new compounds spinosad and fipronil were found better and more consistent against thrips. These compounds are basically claimed to be effective against thrips on other crops as well (Sparks *et al.*, 1995 and Salgado, 1997). In studies conducted by Kadam (2006) spraying of spinosad (0.025% and 0.018%) was found effective against thrips infesting pomegranate. Several other insecticides have shown better efficacy against thrips, *Scirtothrips dorsalis* (H.) infesting chilli (Asokan and Venugopal, 1992; Manjunatha *et al.*, 2000; Patil *et al.*, 2002; Jayewar *et al.*, 2003; Jadhav *et al.*, 2004; Mishra *et al.*, 2005 and Seal *et al.*, 2005). Nderitu *et al.* (2007) observed that Tracer® 48 SC (spinosad) and Regent® 5 SC (fipronil) sprayed plots of

French bean had lowest incidence of thrips. Shitole *et al.* (2002) reported that imidacloprid 17.8 SL @ 20 g a.i. ha<sup>-1</sup> was effective against onion thrips. Bhadane *et al.* (2007) found that Confidor® (imidacloprid) 200 SL @ 100, 125 and 150 ml ha<sup>-1</sup> was significantly effective against groundnut thrips as compared to conventional insecticides, dimethoate and acephate. Jadhav (2003) reported that fipronil 5 SC 100 g a.i. ha<sup>-1</sup> was more effective than imidacloprid 17.8 SL @ 20 g a.i. ha<sup>-1</sup> against chilli thrips. Reddy *et al.* (2005) observed that fipronil 5 SC (0.01%) treated chilli plots were minimally damaged by thrips as compared to crop sprayed with thiamethoxam 25 WS (0.005%) and acetamiprid 20 SP (0.002%). Dhanlaxmi and Mallapur (2008) reported spinosad 45 SC @ 0.1 ml L<sup>-1</sup>, imidacloprid 0.5 ml L<sup>-1</sup> and acetamiprid 0.2 g L<sup>-1</sup> as the best treatments against thrips infesting okra crop. Branco (1996) reported that lambda-cyhalothrin was the most effective treatment in suppressing thrips on tomato followed by permethrin and deltamethrin. Sule *et al.* (2008) reported that lambda-cyhalothrin was the most effective treatment against *T. tabaci* on onion crop.

The insecticide molecules tested in the present investigation are designated as organophosphate alternatives or reduced risk insecticides. Organophosphate insecticides are banned in many developed countries due to their greater risk to user, environment, non-targets, natural enemies and high levels of residues. Reduced risk insecticides are the compounds which are effective at low doses, have low impact on human health, environment and non-targets. They have low potential for development of pest resistance and are IPM compatible. These compounds belonging to different groups *viz.*, chloronecotinyl neonicotinoid-imidacloprid,

naturally macrocyclic lactone-spinosad, phenylpyrazole-fipronil and synthetic pyrethroid-lambda-cyhalothrin are included in the list of reduced risk pesticides by the US Government except fipronil which is an organophosphate alternative. Imidacloprid and fipronil are systemic in action whereas, spinosad and lambda-cyhalothrin are contact and stomach poisons. Thrips, with their rasping and sucking type of mouth parts feed on the oozing cell sap from the developing fruits and shoots of pomegranate resulting from their injuries.

The tested insecticides were found effective on this pest. However, spinosad was highly effective due to its additional translaminar action on plant. It is a macrolide compound produced during fermentation by naturally occurring soil actinomycete bacterium *Saccharopolyspora spinosa*. It is selective, environmentally safe due to low persistence, less harmful to non-targets and showed less residues in pomegranate fruits. Fipronil was the second best compound found during the present studies against thrips. It has unique mode of action of interference with GABA regulated chloride channel in target pest and is systemic nature. However, it took more than twenty days in peel of pomegranate to reach the residues below maximum residue limits specified for this crop by Agricultural and Processed Food Products Export Development Authority (APEDA). Due to its residues in fruit crops, this compound is banned in spray schedule of grapes. But it can be very well utilized in spray schedule of pomegranate as initial spray against thrips at the time of fruit setting, since, the fruits require 5-6 months for maturity and harvest. Imidacloprid, a chloronicotinyl neonicotenoid insecticide has specificity for insect

and vertebrate nicotine receptors. It strongly binds to insect nicotine receptors ( $IC_{50} = 4.6$ ) as compared to vertebrate receptors ( $IC_{50} = 2600$ ). Hence, it is relatively safe to human beings. It is active as foliar spray, seed treatment or soil application and also has translaminar systemic movement in leaves, these properties give it an edge over other insecticides. Thus, these compounds, with novel modes of action can be alternated with other selectively effective insecticides in resistance management programmes on pomegranate and other crops. Moreover, all these insecticides have a broad spectrum activity and are equally effective against lepidopterous pests, they can be advocated against other major pests infesting pomegranate viz., aphids, leaf hoppers, fruit sucking moth and fruit borer. There will be an added advantage if they will be incorporated in IPM of pomegranate.

### **5.1.1 Persistence toxicity of insecticides to thrips on pomegranate shoots**

The results of the laboratory experiment indicated that spinosad and fipronil persisted more than 10 days and recorded PT value of 819.94 and 786.62, respectively. Whereas, imidacloprid was least persistent insecticide (PT= 452.76) after lambda-cyhalothrin (PT= 497.20). These results are in conformity with Jadhav (2003) and Jadhav *et al.* (2004). Rajkumar *et al.* (2005) found that fipronil was the most effective chemical against rose thrips as compared to imidacloprid. Nderitu *et al.* (2007) observed that spinosad and fipronil were the best treatments against thrips infesting French beans followed by lambda-cyhalothrin.

## 5.2 Comparison of different methods of insecticide residue analysis

In the present study California Department of Food and Agriculture, QuEChERS and Single Residue Method were compared for their efficiency on the basis of recovery percentage. The fruits of pomegranate (arils, whole fruit and peel) were fortified at 0.05 and 0.1  $\mu\text{g g}^{-1}$  levels with standards of imidacloprid, spinosad, fipronil and lambda-cyhalothrin. Imidacloprid at both the levels of fortification gave good recovery by all the methods under study in arils, whole fruits and peel of pomegranate. CDFA and Single Residue Method were the best methods of analysis for this insecticide on pomegranate as compared to QuEChERS method. Fan-ZhiXian *et al.* (2003) reported 80 to 120 per cent recovery of imidacloprid in soil and tomato. Diao-Chuan Yun *et al.* (2007) analysed imidacloprid residue in pear by a modified HPLC method. They found that when a mobile phase of acetonitrile: water in the ratio of 40:60 (v:v) was used and the wavelength for detection was set at 268 nm, the recovery rate of imidacloprid residues in pear varied from 83.3 to 116.6 per cent with a low relative standard deviation of less than 5.06 per cent. The pomegranate fruit samples fortified with spinosad at both the levels showed highest recovery by SRM followed by QuEChERS method. CDFA method was less efficient. Yeh *et al.* (1997) observed average recovery of spinosad in the range between 77 and 97 per cent in leafy vegetables, pepper and tomato. Schwedler *et al.* (2000) found average recovery of spinosad ranged between 69 to 96 per cent from wheat straw and sorghum fodder. Kale (2003) showed 91 per cent recovery of spinosad from fortified samples of okra.

The recovery data of fipronil and metabolites showed variable results on pomegranate fruits. The Single Residue Method gave highest recovery whereas CDFFA and QuEChERS methods were less efficient in recovering fipronil and its metabolites. A gas chromatography (GC) method was developed by Luo Gongshu *et al.* (2005) for the analysis of fipronil in soil planted with vegetables. They found average recovery in the range of 87.79 and 98.45 per cent. Recovery of fipronil and three of its metabolites ranged from 80 to 88 per cent (Debashis Dutta *et al.* 2008). At both the levels of fortification ( $0.05$  and  $0.1 \mu\text{g g}^{-1}$ ), all the methods showed good recovery of lambda-cyhalothrin. CDFFA was the best method observed for this insecticide followed by Single Residue Method and QuEChERS. Colume *et al.*, (2001) observed average recovery of lambda-cyhalothrin  $89 \pm 8$  per cent in fruits by GC-MS, while Esteve-Turrillas *et al.*, (2006) found 84 to 120 per cent recovery of lambda-cyhalothrin in soil.

Presently, there are more than 228 pesticides registered in India for use. Development of multiple residue (multi-residue) methods for estimating residues of several pesticides in a single run is most desired because specific or single residue methods are time consuming, expensive and labourious. Residue analysis is a complex process because of chemical-matrix characteristics. Recovery of some chemicals is very good (beyond 80%) whereas, some chemical give poor recovery ( $< 75\%$ ). Hence, the selection of residue analysis method is very important for getting reliable data. The multiresidue methods after simplicity, cost reduction miniaturization and automation. They have low limits of detection, good accuracy, robustness and safety. Therefore, these three

methods were selected for comparison. Though in some matrices, SRM gave good recovery, there is a scope for improvement in MRMs by modifying the extraction and cleanup techniques.

In the present investigation, two multiresidue analysis methods *viz.*, CDFA and QuEChERS were compared with Single Residue Method provided by the manufacturer specified for each compound. QuEChERS is recently developed method with certain advantages over other methods. In this method very small quantity of analytical solvent is utilized. It makes this method cheaper and and risk free to the analyst as well as for the environment, since in India, till today, there are no facilities to recycle these chemical solvents or their safe disposal. It is also quick method and an analyst can analyse more than 25 to 30 samples per day. The studies regarding recovery of insecticides from the fortified samples of pomegranate fruits revealed that the multiresidue methods proved their efficiency for most of the insecticides. These methods can be successfully utilized for the analysis of residues of the different insecticide groups tested in the present study.

### **5.3 Residues of insecticides in pomegranate fruits and soil**

Residues of evaluated insecticides were determined by well standardized analytical methods. The representative fruit samples of pomegranate harvested periodically after third spray *i.e* 0 (2 hr), 1, 3, 5, 7, 10, 14 and 21 days, were subjected to analytical steps *viz.*, extraction, cleanup and determination. The arils, whole fruits and peel were separately extracted to evaluate extent of residues in different parts of the fruits. The limit of detection was 0.02 ppm in respect of spinosad and fipronil. However, such limit was 0.05 ppm

for analytical method used for imidacloprid and 0.01 ppm for lambda-cyhalothrin. All used methods were considered to be most suitable because of their ability to detect insecticide residues well below or equal to the maximum residue limits (MRLs) legally specified by different national and international authorities.

In field experiment on bioefficacy of pesticides against thrips, residue levels were studied in respect of periodically harvested fruits from the pomegranate plants treated with imidacloprid, spinosad, fipronil and lambda-cyhalothrin. Out of these insecticides initial residues of imidacloprid were 0.097 and 0.167 mg kg<sup>-1</sup> at the spray dose of 27 and 54 g a.i. ha<sup>-1</sup>, respectively which reached to 0.05 mg kg<sup>-1</sup> in 1 day and 3 days in arils suggesting a pre-harvest interval of 1 day. In whole fruits the initial residues of 0.156 mg kg<sup>-1</sup> (normal dose) and 0.284 mg kg<sup>-1</sup> (double dose) took 5 and 7 days to reach below detectable limit of 0.05 mg kg<sup>-1</sup>. The whole fruits of pomegranate treated with recommended dose of imidacloprid were not risk free immediately after spraying and a waiting period of 5 days was estimated. In peel the initial residues of 0.286 mg kg<sup>-1</sup> and 0.429 mg kg<sup>-1</sup> at normal and double dose required 7 and 10 days, respectively to reach below detectable limit. Reports on residue data on pomegranate are not available in the literature reviewed. However, Arora *et al.* (2000) reported the residues of imidacloprid (0.008 and 0.016 % a.i.) in fruits of kinnow mandarin. The initial deposits at both the dosage on the rind were 2.40 and 3.90 mg kg<sup>-1</sup> and corresponding values in the pulp were 0.03 and 0.04 mg kg<sup>-1</sup>. Gupta *et al.* (2005) studied persistence of imidacloprid seed dressing @ 3 and 6 g a.i kg<sup>-1</sup> seed and foliar application (20 and 40 g a.i. ha<sup>-1</sup>) on chickpea and found that the residues of

imidacloprid persisted beyond 3 days but no residues were detected on 5<sup>th</sup> day. Battu *et al.* (2007) found that acephate and imidacloprid, when applied on cotton using ready-mix SP formulation of acephate 50% + imidacloprid 1.8% (Lancer Gold) at acephate 500 and 1000 and imidacloprid 18 and 36 g a.i. ha<sup>-1</sup>. Imidacloprid residues reached below detectable level of 0.02 mg kg<sup>-1</sup> after 5 and 7 days of its application at normal and double doses of application, respectively.

The immediate post application spinosad residues in pomegranate arils, whole fruits and peel were 0.030, 0.036 and 0.045 mg kg<sup>-1</sup> at normal dose and 0.037, 0.062 and 0.099 mg kg<sup>-1</sup> at double dose. The residues were present in pomegranate arils at 0 DAS for normal dose and 1 DAS for double dose of application indicating that the spinosad residues were not found in pomegranate arils at normal dose and such arils can be considered safe from consumer's health view point. In whole fruits residues were detected at 0, 1 and 3 days for both the doses. The pomegranate whole fruits at recommended rate of application (56.25 g a.i. ha<sup>-1</sup>) were not risk free and a waiting period of 3 days is suggested. The peel showed residues up to 3 DAS at normal dose and 5 DAS at double dose suggesting a pre-harvest interval of 4 days. The initial residues of spinosad were 0.18 and 0.30 mg kg<sup>-1</sup> at 15 and 30 g a.i. ha<sup>-1</sup>, respectively on okra fruits (Kale, 2003). The initial deposit of spinosad 45 SC (96.4 g a.i. ha<sup>-1</sup>) on cauliflower were 0.08 and 0.05 mg kg<sup>-1</sup> at 0 and 1 DAS, respectively (Sable, 2005).

Fipronil and its metabolites were studied for their residues at normal (25 g a.i. ha<sup>-1</sup>) and double dose (50 g a.i. ha<sup>-1</sup>) in fruits of

pomegranate. The parent compound fipronil dissipated gradually. The residues of fipronil in arils reached below detectable limit in 3.22 days at normal dose and 6.38 days in respect of double dose in arils. A pre-harvest interval of 13 days must be followed for normal dose of fipronil. The residues of fipronil in whole fruits were  $0.064 \text{ mg kg}^{-1}$  and  $0.104 \text{ mg kg}^{-1}$  initially at normal and double doses. The samples collected 10 DAS did not show any detection residues of fipronil. Thus, fruits treated with fipronil @  $25 \text{ g a.i. ha}^{-1}$  should not be harvested upto 18 days after application. Higher residues were recovered from the peel of pomegranate and were  $0.110$  and  $0.197 \text{ mg kg}^{-1}$  at 0 DAS (2 hr) at normal and double dosages, respectively that dissipated in 14 days to below detectable level. At normal application rate of fipronil  $25 \text{ g a.i. ha}^{-1}$  a waiting period of 27 days must be followed before harvesting. There are no reports on residues of fipronil on pomegranate. However, in a study conducted by Stevens, *et al.* (1998) in rice crop fipronil ( $12.5 \text{ g a.i. ha}^{-1}$ ) residue levels in the water column in small rice plots under glasshouse condition declined from  $2.1 \mu\text{g L}^{-1}$  to  $0.01 \mu\text{g L}^{-1}$  in 14 days after treatment. Kale (2003) reported initial deposit of fipronil on okra fruits at  $15$  and  $30 \text{ g a.i. ha}^{-1}$  to the extent of  $0.17$  and  $0.3 \text{ mg kg}^{-1}$ , respectively. Zhou *et al.* (2004) studied fipronil residues in vegetables under field condition in China and reported that degradation of fipronil was faster in Pakchoi (half-life 2.6 days) than in soil (half-life 7.3 days). They also reported faster degradation of fipronil metabolites in soil. Debashis Dutta *et al.* (2008) standardized a method for the extraction and estimation of residues of fipronil and its three metabolites from cabbage and soil. They found that desulfonyl and sulfone derivatives of fipronil were

the major metabolites found in the field samples of cabbage and soil which were formed after one day and reached their maximum amount on third day after application. The half-life of fipronil on cabbage varied from 7.5 to 7.6 days.

Lambda-cyhalothrin residues were detected up to 3 days in arils of pomegranate, when the insecticide was applied at normal dose ( $12.5 \text{ g a.i. ha}^{-1}$ ) suggesting a waiting period of 1 day for harvesting and up to 5 days at double dose of  $25 \text{ g a.i. ha}^{-1}$ . Whole fruits showed dissipation of initial residues of  $0.12 \text{ mg kg}^{-1}$  and  $0.17 \text{ mg kg}^{-1}$  to below detection limit of  $0.01 \text{ ppm}$  in 7 and 10 days at normal and double doses, respectively. Whole fruits treated with lambda-cyhalothrin  $12.5 \text{ g a.i. ha}^{-1}$  should not be harvested upto 7 days after insecticide application. Peel of pomegranate showed initial residues of  $0.152 \text{ mg kg}^{-1}$  which fell to  $0.023 \text{ mg kg}^{-1}$  in 7 days ( $12.5 \text{ g a.i. ha}^{-1}$ ). A pre-harvest interval of 8 days should be followed for such treated fruits. At double dose the residues were not found in the samples collected at 10 DAS. In absence of data on pomegranate, there is a limitation on discussion on present findings. Residues of lambda-cyhalothrin ( $35 \text{ g a.i. ha}^{-1}$ ) on brinjal fruits were studied by Dixit *et al.*, (2001). They found that residues were below detectable limit after 7 days and the half-life of lambda-cyhalothrin on brinjal fruits was 1.45 to 2.54 days. The residues of lambda-cyhalothrin persisted in tomato fruits up to 5 days at  $7.5 \text{ g a.i. ha}^{-1}$  and 7 days at  $15$  and  $30 \text{ g a.i. ha}^{-1}$  (Mathirajan, 2002). Debi Sharma *et al.*, (2002) studied residues of lambda-cyhalothrin on cauliflower and reported that initial residues ( $0.81$  to  $1.59 \text{ mg kg}^{-1}$ ) dissipated quickly to reach below detectable limits within 10 to 15 days with the half-life ( $RL_{50}$ ) of 2.2 to 2.4 days. Sureshkumar *et al* (2002)

reported that residues of lambda-cyhalothrin (12.5 and 25g a.i. ha<sup>-1</sup>) were below detectable levels in rice, bran, husk and straw at harvest. Kaushik Banerjee *et al.* (2006) reported that residues of lambda-cyhalothrin at 25 and 50 g a.i. ha<sup>-1</sup> were lost in grapes with a pre-harvest interval of 12.0 to 12.5 and 15.0 to 15.5 days, respectively.

#### **5.4 Leaching of lindane and chlorpyrifos used in pomegranate stem pasting**

Soil surrounding the stem of pasted pomegranate plant (paste containing lindane and chlorpyrifos) was studied for the residues of lindane and chlorpyrifos. However, residues of lindane as well as chlorpyrifos were below detectable limit of 0.01 ppm 30 days after pasting. This indicated that both insecticides used in pasting of stem did not show the residues in soil and hence, it can be assumed that they degrade within 30 days.

## 6. Summary and Conclusions

Pomegranate crop is prone to attack by many insect pests. Thrips, *Scirtothrips dorsalis* (H.) is the most important one. It not only reduces the yield but also deteriorates the quality of fruits. Intensive cultivation of a fruit crop often leads to pest build up necessitating more rigid pest control. Pomegranate growers rely on insecticides and resort to prophylactic applications at regular intervals throughout the season to ensure minimum fruit damage. This renders insecticides ineffective in a long run due to selection of insecticide resistance in strains of target pest species. The present study was designed to study the bioefficacy of imidacloprid, spinosad, fipronil and lambda-cyhalothrin against infestation of thrips on pomegranate. Similarly from consumers' safety point of view their residues in pomegranate fruits were studied. At the same time different methods of pesticide residue analysis were studied for their efficiency.

### 6.1 Summary

- **Bioefficacy and persistence toxicity of reduced risk insecticides against pomegranate thrips**

Four insecticides imidacloprid 17.8 SL 27 g a.i. ha<sup>-1</sup>, spinosad 45 SC 56.25 g a.i. ha<sup>-1</sup>, fipronil 5 SC 25 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 5 EC 12.5 g a.i. ha<sup>-1</sup> were studied for their bioefficacy against thrips on developing fruits and shoots of pomegranate during *Summer* and *Kharif* 2010. The pooled data on incidence of thrips (No./fruit and shoot) of two seasons revealed that the count of thrips before initiation of spray treatments was in the range of 12.77 to 13.22 on fruits

and 10.57 to 11.29 thrips on shoots. The untreated control plants showed an increasing thrips population from 12.85 to 19.84 (thrips/fruit) and 11.29 to 18.07 (thrips/shoot) during a span of 14 days. The count of thrips in the insecticide treatments was significantly lower indicating that all evaluated insecticides were significantly effective against thrips. The minimum pest population was observed in plants treated with spinosad 56.25 g a.i. ha<sup>-1</sup> followed by fipronil 25 g a.i. ha<sup>-1</sup>. These treatments were found effective upto 14 DAS whereas, the treatments imidacloprid 27 g a.i. ha<sup>-1</sup>, and lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup> were found effective only upto 10 DAS. Similarly their persistence on fruits and shoots was also studied. Spinosad 56.25 g a.i. ha<sup>-1</sup> was found to be the most persistent treatment followed by fipronil 25 g a.i. ha<sup>-1</sup>. Imidacloprid 27 g a.i. ha<sup>-1</sup> was the least persistent chemical treatment.

- **Comparison of different methods of insecticide residue analysis**

The comparative efficiency of methods of California Department of Food and Agriculture (CDFA), QuEChERS and Single Residue Method (SRM) of insecticide residue analysis was studied by fortifying arils, whole fruits and peel separately at a fortification level of 0.05 and 0.1 µg g<sup>-1</sup>. The recovery percentage of insecticide was taken into account to judge the merit of the methods. Considering the overall performance of each method, imidacloprid gave good recovery by all three methods under study at both the levels of fortification. However, the CDFA and Single Residue methods were the

best methods for this product compared to QuEChERS method. Spinosad also gave good recovery by all three methods. Single Residue method yielded highest per cent recovery followed by QuEChERS method whereas, CDFA was comparatively less efficient. Fipronil and its metabolites showed variable results in recovery studies. Single Residue method was the most superior method in extracting maximum residues of fipronil and its metabolites whereas, CDFA and QuEChERS methods were found to be less efficient. Lambda-cyhalothrin gave good recovery by all three methods under study at both the levels of fortification in arils, whole fruits and peel.

- **Residues of insecticides in pomegranate fruits and soil**

The validated Gas Chromatography method was used for the analysis of residues of fipronil and lambda-cyhalothrin where as High Performance Liquid Chromatography analytical method was followed for imidacloprid and spinosad. The limit of detection used for fipronil and spinosad was 0.02 ppm and such limit for imidacloprid was 0.05 ppm and 0.01 ppm for lambda-cyhalothrin. The residues from arils, whole fruits and peel were separately studied. In arils initial residues of imidacloprid reached below detectable limit on 3 and 5 DAS for normal and double dose. Spinosad residues in arils of pomegranate were observed only in the samples collected at 0 and 1 DAS for normal and double dose. Fipronil and its metabolites were detected in arils of pomegranate up to 5 and 7 days for normal and double dose. The initial residues of

lambda-cyhalothrin took 5 days at normal dose whereas 7 days were required at double dose to reach the residues below detection limit. Thus, the pomegranate fruits harvested from the plants treated with imidacloprid 27 g a.i. ha<sup>-1</sup>, spinosad 56.25 g a.i. ha<sup>-1</sup>, fipronil 25 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup>, 2 hr after application were not risk free from the residue point of view and certain waiting period must be followed before harvesting and consumption. Whole fruits showed nearly 2-fold residues as compared to arils. Imidacloprid residues were detected up to 5 and 7 days at normal and double dose. Spinosad residues remained in the fruits of pomegranate up to 3 DAS at normal dose and 5 DAS at double dose. Fipronil and its metabolites were detected in the fruits collected at 7 DAS and 10 DAS for both the doses. Lambda-cyhalothrin residue was observed in the whole fruits up to 7 days at normal application rate and up to 10 days at double dose. Imidacloprid residue was noticed up to 7 and 10 days, spinosad up to 5 and 7 days, fipronil up to 10 and 14 days and lambda-cyhalothrin up to 7 and 10 days at normal rate of application and at double dose respectively in peel of pomegranate. Residues of these insecticides were not detected in the soil collected 21 days after last spray.

- **Leaching of lindane and chlorpyrifos used in pomegranate stem pasting**

Residues of lindane and chlorpyrifos used in pomegranate stem pasting were not found in the soil samples collected at 30 days after pasting.

## 6.2 Conclusions

On the basis of results and discussion of the present investigation the following recommendations/conclusions are proposed,

1. Spinosad 45 SC 56.25 g a.i. ha<sup>-1</sup> was the most superior and persistent treatment against thrips as compared to evaluated insecticides followed by fipronil 5 SC 25 g a.i. ha<sup>-1</sup>.
2. Spinosad 45 SC 56.25 g a.i. ha<sup>-1</sup> and fipronil 5 SC 25 g a.i. ha<sup>-1</sup> were found effective upto 14 DAS and therefore, spray interval rotational sprays in combination with other insecticides may be fixed at 15 days for managing thrips on pomegranate. Similarly, imidacloprid 17.8 SL 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 5 EC 12.5 g a.i. ha<sup>-1</sup> can also be incorporated in the rotational sprays for management of thrips.
3. Imidacloprid, a neonecotinoid insecticide gave satisfactory recovery by all three methods viz., CDFA, QuEChERS and Single Residue Method and hence, these methods can be very well adopted for estimating the residues of imidacloprid in fruits of pomegranate.
4. The recovery of spinosad was acceptable by all three methods under study. QuEChERS and Single Residue Method were good for this insecticide compared to CDFA.
5. Fipronil and its three metabolites showed excellent recovery by Single Residue method; however, performance of CDFA and QuEChERS method for this insecticide and its metabolites was not consistent.
6. Lambda-cyhalothrin, a synthetic pyrethroid provided good recovery by Single Residue Method and CDFA method but

QuEChERS method was less efficient in recovering this insecticide.

7. Residues of imidacloprid were found in arils of pomegranate up to 1 DAS (27 g a.i. ha<sup>-1</sup>) whereas it persisted in whole fruits up to 5 DAS and in peel up to 7 DAS for normal dose.
8. Spinosad residues were noticed in the arils of pomegranate up to 0 DAS (56 g a.i. ha<sup>-1</sup>) and 1 DAS (112.5 g a.i. ha<sup>-1</sup>). In whole fruits deposits were observed up to 1 DAS and 3 DAS for normal and double doses. The peel showed residues of spinosad up to 3 DAS at normal application rate and 5 DAS at double dose.
10. Fipronil and its metabolites showed variable results in their residues in pomegranate fruits. Residues of fipronil were found in arils of pomegranate up to 3 DAS (25 g a.i. ha<sup>-1</sup>) and 5 DAS (50 g a.i. ha<sup>-1</sup>) and metabolites were found only at 1 DAS. In whole fruits residues were found up to 7 and 10 days for normal and double dose.
11. Residues of lambda-cyhalothrin were detected in arils up to 3 days (12.5 g a.i. ha<sup>-1</sup>) and 5 days (25 g a.i. ha<sup>-1</sup>). Residues were noticed in whole fruits up to 7 and 10 DAS for normal and double dose. The peel showed residues up to 7 and 10 DAS at normal and double dose.
12. Residues of imidacloprid (27 and 54 g a.i. ha<sup>-1</sup>) spinosad (56.25 and 112.5 g a.i. ha<sup>-1</sup>), fipronil (25 and 50 g a.i. ha<sup>-1</sup>) and lambda-cyhalothrin (12.5 and 25 g a.i. ha<sup>-1</sup>) were not detected in the surface layer of the soil below the canopy of the plant at 21 DAS.

13. Residues of lindane and chlorpyrifos used in stem pasting of pomegranate were not found in the surface layer of the soil at 30 days after pasting.
14. In view of the efficacy and safety to consumers, spinosad at 56.25 g a.i. ha<sup>-1</sup> found to be the best treatment for managing pomegranate thrips. It may be alternated with fipronil 25 g a.i. ha<sup>-1</sup>, imidacloprid 27 g a.i. ha<sup>-1</sup> and lambda-cyhalothrin 12.5 g a.i. ha<sup>-1</sup>.

### **Future strategy**

*Scirtothrips dorsalis* (H.) is one of the most damaging insect pests responsible for reduction in pomegranate yield and aesthetic quality. The management of this pest needs the integrated pest management approach and hence the most effective and IPM compatible insecticides should be incorporated in its IPM programme. Recently, many new insecticides with novel chemistry are introduced in the market as 'Reduced Risk Pesticides'. They are selective in nature and affect the natural enemies minimally. Such new insecticides should be investigated for incorporating in pomegranate IPM. Furthermore, the multiresidue methods are very efficient, less expensive, fast and reliable. They may be further investigated for optimum recovery by manipulating extraction and/or cleanup steps of residue analysis.

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# Appendix

## Meterological data Jan. 2010 to Sept. 2010

Month	Met. Week No.	Meterological parameters					
		Temperature (°C)		Humidity (%)		Sunshine (hrs)	Rainfall (mm)
January	1	28.0	11.7	90	46	0.0	08.6
	2	28.6	11.9	91	39	0.0	07.7
	3	28.1	9.8	91	38	0.0	08.9
	4	28.1	8.1	90	34	0.0	09.6
	5	29.7	11.9	89	37	0.0	08.4
	<b>Average</b>	28.5	10.7	90	39	0.0	8.6
February	6	29.9	14.3	89	44	0.0	07.1
	7	31.2	13.9	91	41	0.0	08.6
	8	32.8	13.6	89	33	0.0	09.9
	9	33.6	13.9	88	31	0.0	10.0
	<b>Average</b>	31.9	13.9	89	37	0.0	8.9
March	10	34.3	14.5	88	32	0.0	09.4
	11	35.4	16.2	89	29	20.2	09.0
	12	37.8	17.2	88	23	0	09.7
	13	37.7	17.3	87	22	0	09.3
	<b>Average</b>	36.3	16.3	88	27	5.04	9.4
April	14	38.1	18.2	86	21	0.0	09.8
	15	39.5	21.0	90	19	0.0	07.7
	16	40.5	22.3	87	17	0.0	10.3
	17	40.3	21.2	86	16	0.0	10.6
	18	37.2	21.2	87	27	1.03	07.4

Contd.....

Month	Met. Week No.	Meterological parameters					
		Temperature (°C)		Humidity (%)		Sunshine (hrs)	Rainfall (mm)
May	19	40.6	20.3	87	22	0.0	10.3
	20	41.2	22.1	88	23	0.0	10.3
	21	41.2	24.6	89	26	0.0	09.7
	22	37.5	23.8	91	26	3.8	10.1
	<b>Average</b>	40.1	22.7	89	27	0.095	10.1
June	23	36.1	23.0	93	38	025.2	09.7
	24	32.4	22.7	93	60	075.9	02.7
	25	33.4	22.9	93	54	015.2	04.6
	26	33.3	23.0	94	57	132.8	06.5
	<b>Average</b>	33.8	22.9	93	52	62.27	5.9
July	27	30.5	22.1	93	67	035.4	03.2
	28	31.6	22.4	93	68	084.9	05.2
	29	30.9	22.3	93	64	018.7	04.5
	30	29.5	22.3	94	65	011.4	01.7
	31	30.0	21.9	93	66	018.2	01.9
	<b>Average</b>	30.5	22.2	93	66	42.07	3.3
August	32	29.8	21.1	93	63	026.6	05.4
	33	30.1	21.9	93	67	020.2	04.5
	34	29.1	21.1	92	70	011.9	02.1
	35	28.7	21.6	94	75	138.3	02.2
	<b>Average</b>	28.9	21.4	93	69	49.25	3.6
September	36	29.0	21.5	92	68	46.3	02.8
	37	31.0	20.6	91	53	0.00	07.8
	38	30.8	21.6	94	62	105.8	06.4
	39	30.8	21.5	94	64	103.4	07.4
	<b>Average</b>	30.4	21.3	93	62	63.75	6.1

# Vita

## KADAM DHIRAJKUMAR RAJARAM

A candidate for the degree of Doctor of Philosophy (Agriculture) in  
Agricultural Entomology

**Title of thesis** : “Bioefficacy, persistence toxicity and residues of reduced risk insecticides against pomegranate thrips *Scirtothrips dorsalis* Hood”

**Major field** : Agricultural Entomology

### Biographical information

**Personal data** : Born at Koli, Tal. Hadgaon, Dist. Nanded on 6<sup>th</sup> November, 1978. Son of Late Adv. Rajaram Dattarao Kadam, residing at A-13, Sakhar Nagar, Pashan-Sus Road, Pune-21 (Phone 9850192356).  
Married with Monica on 8<sup>th</sup> May 2004.

**Educational** : Attended Primary and Secondary School at Mahatma Phule High School, Vijay Nagar, Nanded and Higher Secondary School at Yeshwant Mahavidyalaya Nanded. Received Bachelor of Science (Agriculture) degree with first class and awarded Master of Science (Agriculture) degree in the discipline of Agricultural Entomology with first class, Hexamer Foundation Gold Medal from Marathwada Krishi Vidyapeeth, Parbhani during 1999 and 2001.

**Research work** : Worked on efficacy of newer insecticides against pests of soybean.

**Publications** : Published 10 research papers in the national journals and 15 popular articles in various magazines and leading newspapers. Delivered 04 All India Radio talks and 2 TV programmes.

**Extension Work**: Delivered several lectures on intergrated pest management of cotton, soybean during farmer’s rallies in Marathwada region. Attended various farmers queries regarding pest problems and rendered proper advice.



**Tab.4.1 Bioefficacy of insecticides against thrips on pomegranate fruits-Summer 2010**

Treatment	Dose (g a.i. ha <sup>-1</sup> )	Count before first spray	Average number of thrips per fruit											
			First Spray				Second Spray				Third Spray			
			3 DAS	7 DAS	10 DAS	14 DAS	3 DAS	7 DAS	10 DAS	14 DAS	3 DAS	7 DAS	10 DAS	14 DAS
Imidacloprid 17.8 SL	27	15.03 (3.94)	3.72 (2.05)	4.41 (2.21)	5.44 (2.44)	9.97 (3.24)	2.34 (1.68)	3.53 (2.01)	3.53 (2.01)	5.56 (2.46)	2.56 (1.75)	2.94 (1.85)	3.53 (2.00)	5.16 (2.38)
Spinosad 45 SC	56.25	14.78 (3.91)	2.84 (1.83)	3.40 (1.97)	4.16 (2.16)	7.00 (2.74)	1.47 (1.40)	2.06 (1.59)	2.66 (1.77)	4.19 (2.16)	1.59 (1.44)	2.06 (1.60)	2.53 (1.74)	3.00 (1.87)
Fipronil 5 SC	25	14.66 (3.89)	3.41 (1.98)	3.94 (2.11)	4.81 (2.30)	7.03 (2.74)	1.56 (1.43)	2.28 (1.66)	2.59 (1.76)	4.06 (2.13)	1.69 (1.48)	2.22 (1.65)	2.69 (1.78)	3.62 (2.03)
Lambda- cyhalothrin 5 EC	12.5	14.94 (3.93)	3.15 (1.91)	4.28 (2.19)	5.19 (2.38)	9.47 (3.16)	2.03 (1.59)	3.06 (1.89)	3.50 (2.00)	5.65 (2.48)	2.22 (1.65)	3.00 (1.87)	3.44 (1.98)	4.90 (2.32)
Untreated Control	---	14.75 (3.90)	16.19 (4.08)	16.09 (4.07)	17.19 (4.20)	17.72 (4.27)	19.12 (4.43)	19.09 (4.43)	21.15 (4.65)	22.47 (4.79)	22.44 (4.79)	21.78 (4.72)	23.25 (4.87)	25.25 (5.07)
S.E. ±		0.04	0.04	0.05	0.05	0.04	0.04	0.07	0.03	0.04	0.05	0.04	0.04	0.02
C.D. at 5%		NS	0.14	0.15	0.16	0.13	0.13	0.20	0.11	0.14	0.14	0.12	0.12	0.06

Figures in parentheses are  $\sqrt{n+0.5}$  transformed values  
DAS = Days after spray

**Tab.4.2 Bioefficacy of insecticides against thrips on pomegranate fruits-Kharif 2010**

Treatment	Dose (g a.i. ha <sup>-1</sup> )	Count before first spray	Average number of thrips per fruit											
			First Spray				Second Spray				Third Spray			
			3 DAS	7 DAS	10 DAS	14 DAS	3 DAS	7 DAS	10 DAS	14 DAS	3 DAS	7 DAS	10 DAS	14 DAS
Imidacloprid 17.8 SL	27	11.37 (3.44)	3.44 (1.98)	4.44 (2.22)	5.47 (2.44)	7.65 (2.85)	2.22 (1.65)	2.94 (1.85)	3.97 (2.11)	5.37 (2.42)	1.97 (1.57)	2.72 (1.79)	3.37 (1.97)	4.63 (2.63)
Spinosad 45 SC	56.25	11.22 (3.42)	2.41 (1.70)	3.16 (1.91)	4.28 (2.19)	5.50 (2.45)	1.47 (1.40)	2.03 (1.59)	2.72 (1.79)	3.37 (1.97)	0.84 (1.15)	1.34 (1.36)	2.00 (1.58)	2.47 (1.72)
Fipronil 5 SC	25	10.87 (3.46)	2.63 (1.77)	3.40 (1.97)	4.31 (2.19)	4.81 (2.29)	1.75 (1.50)	2.22 (1.65)	3.03 (1.88)	3.97 (2.11)	1.25 (1.32)	1.81 (1.52)	2.31 (1.67)	2.75 (1.80)
Lambda-cyhalothrin 5 EC	12.5	11.50 (3.46)	3.54 (2.01)	4.22 (2.17)	5.31 (2.41)	7.59 (2.84)	2.53 (1.74)	3.19 (1.92)	4.28 (2.19)	5.62 (2.47)	2.09 (1.61)	2.84 (1.83)	3.97 (2.11)	4.87 (2.32)
Untreated Control	---	10.94 (3.38)	11.81 (3.51)	12.16 (3.56)	13.00 (3.67)	14.00 (3.81)	15.37 (3.98)	16.34 (4.10)	17.15 (4.20)	18.06 (4.31)	19.3 (4.42)	19.87 (4.51)	20.72 (4.61)	21.58 (4.70)
S.E. ±		0.05	0.04	0.04	0.04	0.09	0.05	0.04	0.04	0.03	0.05	0.04	0.05	0.05
C.D. at 5%		NS	0.13	0.13	0.12	0.28	0.16	0.12	0.12	0.11	0.14	0.13	0.17	0.14

Figures in parentheses are  $\sqrt{n+0.5}$  transformed values

DAS = Days after spray

**Tab.4.4 Bioefficacy of insecticides against thrips on pomegranate shoots-Summer 2010**

Treatment	Dose (g a.i. ha <sup>-1</sup> )	Count before first spray	Average number of thrips per shoot											
			First Spray				Second Spray				Third Spray			
			3 DAS	7 DAS	10 DAS	14 DAS	3 DAS	7 DAS	10 DAS	14 DAS	3 DAS	7 DAS	10 DAS	14 DAS
Imidacloprid 17.8 SL	27	12.31 (3.58)	4.75 (2.29)	5.50 (2.45)	6.06 (2.56)	7.06 (2.75)	2.38 (1.69)	3.25 (1.93)	3.88 (2.09)	5.25 (2.40)	1.88 (1.54)	2.88 (1.84)	4.00 (2.12)	5.00 (2.34)
Spinosad 45 SC	56.25	11.75 (3.50)	2.94 (1.85)	3.69 (2.04)	4.25 (2.18)	5.56 (2.46)	1.56 (1.43)	2.19 (1.63)	2.63 (1.77)	3.38 (1.97)	0.88 (1.17)	1.69 (1.48)	2.44 (1.71)	3.13 (1.90)
Fipronil 5 SC	25	12.50 (3.60)	3.38 (1.97)	3.69 (2.04)	4.38 (2.21)	5.44 (2.44)	1.63 (1.46)	2.13 (1.62)	2.50 (1.73)	3.63 (2.03)	1.25 (1.32)	2.06 (1.60)	2.88 (1.84)	3.63 (2.03)
Lambda- cyhalothrin 5 EC	12.5	12.19 (3.56)	4.38 (2.21)	5.38 (2.42)	6.00 (2.55)	6.81 (2.70)	2.81 (1.82)	3.63 (2.03)	3.75 (2.06)	4.81 (2.30)	1.63 (1.45)	2.56 (1.75)	3.88 (2.09)	4.81 (2.30)
Untreated Control	---	13.19 (3.70)	14.06 (3.81)	13.19 (3.70)	15.25 (4.20)	16.75 (4.15)	16.13 (4.08)	14.81 (3.91)	16.75 (4.15)	17.81 (4.28)	18.63 (4.37)	19.69 (4.49)	21.06 (4.64)	22.38 (4.78)
S.E. ±		0.05	0.07	0.05	0.03	0.04	0.05	0.08	0.06	0.04	0.05	0.03	0.02	0.03
C.D. at 5%		NS	0.21	0.16	0.10	0.13	0.14	0.23	0.17	0.13	0.17	0.10	0.08	0.11

Figures in parentheses are  $\sqrt{n+0.5}$  transformed values  
DAS = Days after spray

#### 4.5 Bioefficacy of insecticides against thrips on pomegranate shoots *Kharif 2010*

Treatment	Dose (g a.i. ha <sup>-1</sup> )	Count before first spray	Average number of thrips per shoot											
			First Spray				Second Spray				Third Spray			
			3 DAS	7 DAS	10 DAS	14 DAS	3 DAS	7 DAS	10 DAS	14 DAS	3 DAS	7 DAS	10 DAS	14 DAS
Imidacloprid 17.8 SL	27	9.13 (3.10)	2.75 (1.80)	3.94 (2.10)	4.56 (2.25)	6.25 (2.60)	1.94 (1.56)	2.44 (1.71)	3.25 (1.94)	4.13 (2.15)	1.13 (1.27)	1.63 (1.45)	2.44 (1.71)	3.13 (1.90)
Spinosad 45 SC	56.25	10.06 (3.25)	1.38 (1.36)	2.63 (1.77)	3.69 (2.04)	4.50 (2.23)	0.88 (1.17)	1.31 (1.34)	1.94 (1.55)	2.63 (1.76)	0.19 (0.82)	0.81 (1.14)	1.56 (1.43)	2.06 (1.60)
Fipronil 5 SC	25	9.44 (3.15)	1.88 (1.54)	3.06 (1.88)	4.00 (2.12)	4.88 (2.32)	0.94 (1.20)	1.56 (1.43)	2.25 (1.66)	2.75 (1.80)	0.56 (1.03)	1.13 (1.27)	1.81 (1.52)	2.38 (1.69)
Lambda- cyhalothrin 5 EC	12.5	8.94 (3.07)	2.94 (1.85)	4.06 (2.13)	4.75 (2.29)	5.88 (2.52)	1.81 (1.52)	2.56 (1.75)	3.19 (1.92)	4.06 (2.14)	1.44 (1.39)	2.13 (1.62)	2.88 (1.84)	3.69 (2.05)
Untreated Control	---	9.38 (3.14)	10.44 (3.30)	11.44 (3.45)	12.56 (3.61)	13.81 (3.78)	14.56 (3.88)	15.56 (4.01)	16.50 (4.12)	17.44 (4.23)	18.25 (4.33)	19.31 (4.45)	19.88 (4.51)	20.25 (4.55)
S.E. ±		0.07	0.08	0.08	0.07	0.06	0.06	0.06	0.06	0.06	0.08	0.06	0.05	0.03
C.D. at 5%		NS	0.24	0.26	0.21	0.18	0.19	0.18	0.19	0.19	0.24	0.19	0.14	0.11

Figures in parentheses are  $\sqrt{n+0.5}$  transformed values  
DAS = Days after spray

**Tab. 4.7 Persistence toxicity of insecticides against thrips on pomegranate shoots**

Treatment	Per cent mortality of thrips after treatment in days									
	0	1	3	5	7	10	14	P	T	PT
Imidacloprid 17.8 SL 0.0055%	75.00	65.00	53.33	40.00	35.00	3.33	0.00	10	45.27	452.76
Spinosad 45 SC 0.0112%	91.66	83.33	78.33	71.66	55.00	21.66	8.33	14	58.57	819.94
Fipronil 5 SC 0.005%	88.33	81.66	75.00	68.33	58.33	16.66	5.00	14	56.19	786.62
Lambda-cyhalothrin 5 EC 0.0025%	78.33	71.66	60.00	45.00	38.33	5.00	0.00	10	49.72	497.20



**Plate 1 : Experimental field of Pomegranate**



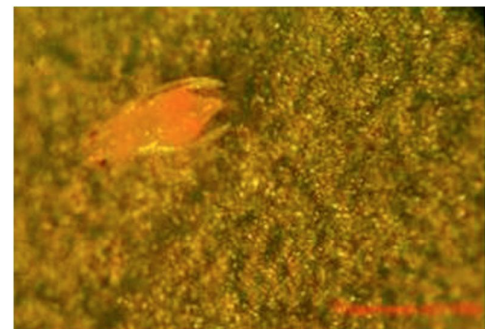
**First instar nymph & eggs of thrips**



**Second instar nymph**



**Adult**



**Pupa**

**Plate 2 : Different life stages of pomegranate thrips *Scirtothrips dorsalis* (H.)**





**Plate 6 : Collection of fruits and soil samples for residue analysis**



**Blending**



**Cleanup**



**Centrifuge**



**Rotary vacuum evaporator**

**Plate 7 : Procedural steps of residue analysis**



**Plate 8 : Gas Liquid Chromatograph**



**Plate 9 : High Performance Liquid Chromatograph**



# Introduction



# Review of Literature



# Material and Methods



# Experimental Results



# Discussion



## Summary and Conclusions



Literature cited



# Appendix



Vita