

**PERSISTENCE OF QUINALPHOS, ETHION AND
CARBENDAZIM IN/ON TOMATO AND CROPPED SOIL**

By

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MAHARASHTRA, INDIA.**

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CROPPED SOIL**

A thesis submitted to the

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

for the award of the degree of

MASTER OF SCIENCE (AGRICULTURE)

in

AGRICULTURAL ENTOMOLOGY

by

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(Reg. No.14/160)

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MAHARASHTRA, INDIA**

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MASTER OF SCIENCE (AGRICULTURE)

in

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2016

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*I hereby declare that this thesis or part of
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
**“PERSISTENCE OF QUINALPHOS, ETHION AND
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submitted to the Faculty of Agriculture, Mahatma Phule
Krishi Vidyapeeth, Rahuri, Dist.-Ahmednagar,
Maharashtra State, for the award of the degree of
MASTER OF SCIENCE (AGRICULTURE) in
AGRICULTURAL ENTOMOLOGY, embodies the results of
a *bonafide* research carried out by **Miss. ARATI ASHOK
SALI**, under my guidance and supervision and that no
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The assistance and help received during the
course of this investigation have been acknowledged.

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Maharashtra State (India)

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Place: MPKV, Rahuri
Date :

(A. A. Sali)

CONTENTS

CANDIDATE'S DECLARATION		ii
CERTIFICATES		
1.	Research Guide	iii
2.	Associate Dean	iv
ACKNOWLEDGEMENT		v
CONTENTS		vii
LIST OF TABLES		x
LIST OF FIGURES		xi
LIST OF PLATES		xii
LIST OF ABBREVIATIONS		xiii
ABSTRACT		xvi
1.	INTRODUCTION	1
2.	REVIEW OF LITERATURE	4
	2.1 Technical information of pesticides	4
	2.2 Pesticide usage pattern	6
	2.3 Persistence of quinalphos, ethion and carbendazim in tomato and other crops	10
	2.4 Persistence of quinalphos, ethion and carbendazim in soil	21
3.	MATERIAL AND METHODS	24
	3.1 Material	24
	3.1.1 Tomato seed	24
	3.1.2 Pesticides	24
	3.1.3 Glassware	27
	3.1.4 Chemicals and reagents	27
	3.1.5 Apparatus and instruments	28
	3.1.5.1 Apparatus	28
	3.1.5.2 Instruments	28
	3.1.6 Appliance	28

3.2	Methods		28
	3.2.1	Survey of pesticide usage pattern	28
	3.2.2	Raising of tomato crop	29
	3.2.3	Application of pesticides	30
	3.2.4	Residue analysis	30
	3.2.4.1	Standard preparation	30
	3.2.4.2	Method validation	30
	3.2.4.2.1	Limit of detection and Limit of quantification	31
	3.2.4.2.2	Linearity study	31
	3.2.4.2.3	Recovery study	31
	3.2.5	Sampling	32
	3.2.6	Sample preparation	33
	3.2.6.1	Extraction and clean up of tomato fruits for quinalphos and ethion	33
	3.2.6.2	Extraction and clean up of tomato fruits for carbendazim	33
	3.2.6.3	Extraction and clean up of cropped soil for quinalphos, ethion and carbendazim	34
	3.2.7	Residue determination	34
	3.2.7.1	GC-MS analysis	35
	3.2.7.2	HPLC analysis	36
	3.2.8	Statistical analysis	37
4.	RESULTS AND DISCUSSION		38
	4.1	Survey on pesticide usage pattern on tomato	38
	4.1.1	Awareness on pesticide use	40
	4.2	Dissipation of quinalphos, ethion and carbendazim in/on tomato fruits and cropped soil	43
	4.2.1	Method validation	43

	4.2.1.1	Limit of detection and limit of quantification	43
	4.2.1.2	Linearity study	44
	4.2.1.3	Recovery study	44
	4.2.2	Residues of pesticides in tomato fruits and soil	47
	4.2.2.1	Persistence and dissipation of quinalphos in/on tomato fruits	47
	4.2.2.2	Persistence and dissipation of ethion in/on tomato fruits	51
	4.2.2.3	Persistence and dissipation of carbendazim in/on tomato fruits	54
	4.2.2.4	Persistence and dissipation of quinalphos, ethion and carbendazim in soil	57
5.	SUMMARY AND CONCLUSION		59
	5.1	Summary	59
	5.1.1	Pesticide usage pattern in tomato	59
	5.1.2	Residues of quinalphos, ethion and carbendazim in/on tomato fruits and cropped soil	59
	5.1.2.1	Recovery study	59
	5.1.2.2	Persistence and dissipation of quinalphos, ethion and carbendazim in/on tomato fruits and cropped soil	60
	5.2	Conclusion	60
6	LITERATURE CITED		62
7	APPENDICES		72
8	VITA		74

LIST OF TABLES

Table No.	Title	Page No.
1.	Particulars of the pesticides sprayed on tomato for residue studies	25
2.	Treatment details	26
3.	Usage pattern of pesticides in Ahmednager district during cropping season	41
4.	Response of farmers about the questionnaire from the surveyed area	42
5.	Recovery of quinalphos in tomato fruits and soil	46
6.	Recovery of ethion in tomato fruits and soil	46
7.	Recovery of carbendazim in tomato fruits and soil	47
8.	Persistence of quinalphos residues at different intervals in tomato fruits and soil	49
9	Dissipation pattern of quinalphos in tomato fruits	50
10.	Persistence of ethion residues at different intervals in tomato fruits and soil	52
11.	Dissipation pattern of ethion in tomato fruits	53
12.	Persistence of carbendazim residues at different intervals in tomato fruits and soil	55
13.	Dissipation pattern of carbendazim in tomato fruits	56

LIST OF FIGURES

Figure No.	Title	Between Pages
1	Per cent share of pesticides used in Ahmednagar district during cropping season	42-43
2.	Spraying interval followed by the farmers	42-43
3.	Linearity of different pesticide standard	45-46
4.	Per cent dissipation of quinalphos in tomato fruits	50-51
5.	Per cent dissipation of ethion in tomato fruits	53-54
6.	Per cent dissipation of carbendazim in tomato fruits	56-67

LIST OF PLATES

Plate No.	Title	Between Pages
1	Experimental field	29-30
2	Apparatus used during residue analysis	29-30
3	Gas chromatography - Mass Spectrometer (GCMS-QP-2010 plus, Shimadzu)	37-38
4	High Performance Liquid Chromatography equipped with DAD(LC-20AT, Shimadzu)	37-38

ABBREVIATIONS

a.i.	:	Active Ingradient
ADI	:	Acceptable Daily Intake
BDL	:	Below Detection Limit
cm	:	Centimetre
CRM	:	Certified Reference Material
DAD	:	Diode Array Detector
EC	:	Emulsifiable Concentrate
<i>et al.</i>	:	<i>et alli</i> (and other)
etc.	:	Et cetera and so on
ETU	:	Ethylenethiourea
Fig.	:	Figures (s)
g	:	Gram(s)
GCMS	:	Gas Chromatography Mass Spectrometry
HPLC	:	High Performance Liquid Chromatography
ha	:	Hectare (s)
hr	:	Hour(s)
i.e	:	<i>id est</i> (that is)
kg	:	Kilogram (s)
LC ₅₀	:	Lethal Concentration 50
LD ₅₀	:	Lethal Dose 50
lit./L	:	Litre (s)
LOD	:	Limit of Detection
LOQ	:	Limit of Quantification
Ltd.	:	Limited
M	:	Metre (s)
mg	:	Milligram (s)
Min	:	Minute (s)

ml	:	Millilitre (s)
mm	:	Millimetre (s)
MRL	:	Maximum Residual Limit
MT	:	Metric Tonne (s)
ND	:	Not Detected
nm	:	Nanometre (s)
°C	:	Degree Celcius
PHI	:	Pre Harvest Interval
ppm	:	Parts Per Million
PSA	:	Primary Secondary Amine
PDA	:	Photo Diode Array
Pvt.	:	Private
q/Q	:	Quintal (s)
QuEChERS	:	Quick Easy Cheap Effective Rugged Safe
R	:	Regression coefficient
RL ₅₀	:	Residual Life 50
rpm	:	Revolutions per minute
RSD	:	Relative Standard Deviation
RT	:	Retention Time
Sec	:	Seconds
T _{1/2}	:	Half life
Temp.	:	Temperature
µg	:	Microgram (s)
µl	:	Microlitre (s)
V	:	Volume
<i>Viz.</i>	:	Videlicet (Namely)
WP	:	Wettable powder
Wt	:	Weight
-	:	Minus

<	:	Less than
%	:	Per cent
@	:	At the rate of
+	:	Plus
±	:	Plus or minus
≤	:	Less than or equal to

ABSTRACT

**PERSISTENCE OF QUINALPHOS, ETHION AND
CARBENDAZIM IN/ON TOMATO AND CROPPED SOIL***by***ARATI ASHOK SALI***A candidate for the degree of***MASTER OF SCIENCE (AGRICULTURE)****MAHATMA PHULE KRISHI VIDYAPPETH,
RAHURI-413 722****2016**

Research Guide : Dr. B. V. Deore**Department : Agricultural Entomology**

An investigation entitled “Persistence of quinalphos, ethion and carbendazim in/on tomato and cropped soil” was undertaken during 2015-16 at the Department of Agricultural Entomology, Post Graduate Institute, Mahatma Phule Krishi Vidyapeeth, Rahuri.

Survey on pesticide use pattern indicated that farmers relied mostly on chemical pesticides to control the pest. The pesticides *viz.*, quinalphos, chlorpyrifos, ethion, indoxacarb, cypermethrin and fungicides like carbendazim were the most widely used with higher doses. It was also observed that the tomato growers from surveyed area followed routine spraying pattern. Majority of farmers did spraying at an interval of 7 to 10 days giving maximum 8 to 10 sprays.

.....
 Abstract contd....

.....
 A. A. Sali

Study on dissipation pattern of quinalphos, ethion and carbendazim in/on tomato was studied following application of pesticides at recommended and double the recommended dose at fruit initiation stage. Quinalphos @ 250 and 500 g a.i. ha⁻¹, ethion @ 500 and 1000 g a.i. ha⁻¹ and carbendazim @ 150 and 300 g a.i. ha⁻¹ were applied twice at an interval of 10 days. The mean initial residues of quinalphos (0.28, 0.58 mg kg⁻¹) and ethion (0.21, 0.46 mg kg⁻¹) reached to BDL on 7th and 10th day at recommended and double the recommended dose, respectively. Whereas, mean initial residues of carbendazim (0.99, 1.84 mg kg⁻¹) reached BDL on 10th and 15th days, at recommended and double the recommended dose, respectively

The residues dissipated with half life of 2.67 and 2.47, 2.95 and 2.47, 1.78 and 1.90 for quinalphos, ethion and carbendazim at recommended and double the recommended dose, respectively. The residue of above pesticides was found to be below detection limit in soil at harvest.

Considering this, Pre-Harvest Interval of seven days can be suggested for quinalphos and ethion. Whereas, Pre-Harvest Interval of ten days can be suggested for carbendazim.

 Total pages: 1 to 74

1. INTRODUCTION

Tomato (*Solanum lycopersicon* L.) belongs to the family Solanaceae is globally cultivated for its fleshy fruits and known as protective food because of its special nutritive value and its wide spread production. It is the world's largest vegetable crop after potato and it tops the list of canned vegetables. Tomatoes are eaten directly as raw vegetable or consumed in a variety of processed products like ketch-up, sauce, chutney, juice, soup, paste, puree etc. It plays vital role in the providing a substantial quantity of vitamin C and vitamin A in human diet (Chaudhury, 1979 and Rashid, 1999). It is also rich in the medicinal value (Bose and Som, 1986).

Previously tomatoes were grown only during favorable season, but now day's they are grown round the year. Because of its economic importance area under cultivation is increasing every year. India is the second largest producer of tomato in the world after China producing 187.35 lakh tonnes in an area of 8.82 lakh ha with a productivity of 21.2 MT ha⁻¹. In India, it is grown in a wide range of climatic conditions across states of Bihar, Karnataka, Uttar Pradesh, Orissa, Andhra Pradesh, Maharashtra, Madhya Pradesh & Assam. Among these states, Andhra Pradesh stands first which contributes 33.54 lakh tonnes of tomato from 1.68 lakh ha area with an average productivity of 20 MT ha⁻¹ (Anonymous, 2014).

In Maharashtra it is grown over an area of 50,000 ha with an annual production of 12.00 lakh tonnes having an average productivity of 24.00 MT ha⁻¹. Nasik, Ahmednagar, Pune, Beed, Satara, Solapur, Chandrapur, Latur, Parbhani and Nagpur

are the major tomato producing districts in Maharashtra (Anonymous, 2014).

The crop posse's huge domestic requirement and cultivators face several problems responsible for productivity. The tomato yield is affected due to damage caused by various pest and diseases. Mealy bugs, tobacco caterpillars, whiteflies, aphids, thrips, leaf miner, mites and fruit borer are the major insect pest whereas damping off, early blight, late blight, powdery mildew, leaf curl, spotted wilt are the major diseases of tomato. It is estimated that the pest may cause loss up to 80-100 per cent in tomato crop production in both greenhouses and fields (Korycinska and Moran, 2009). Commercial consideration of this crop unfortunately compelled the growers to use a large amount of pesticides during the entire period of growth even at fruiting stage and sometimes farmers also ignored the recommended waiting period between the harvest and last spray. Use of high levels of pesticides has caused to leave harmful residues on the crop and soil.

There is currently an increasing concern and awareness on the hazards of pesticides to consumers. The application of pesticides pre-or post-harvest could, however, leave residues on food products, which pose a potential risk to the health of consumers (Lindsay 1997). The problem of residue accumulation needs more attention in vegetables because most of time these are consumed either raw or without much storage time (Kumar *et al.*, 2006).

Quinalphos and ethion are the organophosphorus insecticides most commonly used against pests on tomato. Carbendazim fungicide is also used to control fungal diseases in

tomato. However, unlike quinalphos these pesticides are not registered on tomato and have no data available on PHI and safe waiting period. The continuous use of organophosphorus pesticides increases the possibility that residues of these compound could be found in tomato fruits. Therefore, it is necessary to study the persistence of these pesticides in tomato and soil under Good Agricultural Practices which helps to workout PHI and safe waiting period.

Keeping this in mind, the investigation was undertaken with the following objectives.

1. To study the pesticide usage pattern in tomato.
2. To study the dissipation of quinalphos, ethion and carbendazim in tomato fruits.
3. To study the harvest time residues of quinalphos, ethion and carbendazim in soil.

2. REVIEW OF LITERATURE

The present research work was planned to study the pesticide usage pattern in tomato and persistence of quinalphos 25 EC, ethion 50 EC and carbendazim 50 WP in tomato and cropped soil.

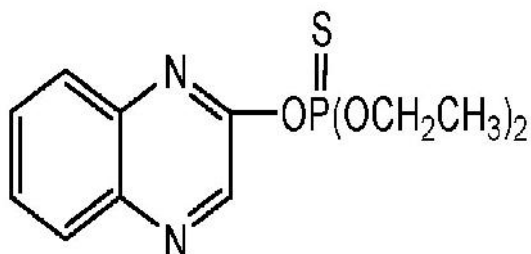
The literature pertaining to the residues of these pesticides especially in tomato and soil is very scanty hence references closely related to either pesticides or crop are reviewed and presented under different headings in this chapter.

- 2.1 Technical information of pesticides
- 2.2 Pesticide usage pattern
- 2.3 Persistence of quinalphos, ethion and carbendazim in tomato and other crops
- 2.4 Persistence of quinalphos, ethion and carbendazim in soil

2.1 Technical information of pesticides

2.1.1 Quinalphos

Chemically it is known as O,O-diethyl O-quinaxalin-2-yl phosphorothioate. Its empirical formula is $C_{12}H_{15}N_2O_3PS$ with the following structure.

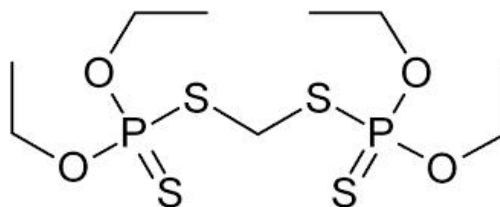


Quinalphos

It is contact poison having good penetrating power. The technical quinalphos can be produced by the reaction of O-phenylenediamine, choracetic acid and O,O-diethyl phosphorochoridithioate. The pure material is colourless crystals having vapour pressure of 3.9×10^{-12} mm Hg at 20 °C. It is soluble in acetone, ethanol and xylem and slightly soluble in light petroleum. In water, its solubility is @ 22 mg l⁻¹. Its toxicity to rats is 62-137 mg kg⁻¹ (acute oral LD₅₀) and 1250-1400 mg kg⁻¹. (acute dermal LD₅₀). It is widely used against caterpillars and borers on cotton, vegetables and other crops. It has also acaricidal properties. It can be degraded very fast in plants.

2.1.2 Ethion

Chemically it is known as O, O, O', O'-Tetraethyl S, S'-methylene bis(phosphorodithiate). Its empirical formula is C₉H₂₂O₄P₂S₄ with the following structure.



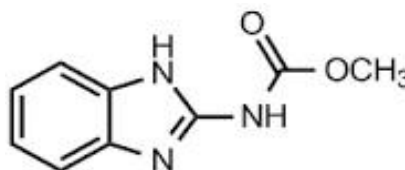
Ethion

Its molecular weight is 384.48 g mol⁻¹ with vapour pressure of 1.5×10^{-6} mm Hg at 25°C and density 1.22 g cm⁻³. Pure ethion is clear to yellowish liquid with unpleasant sulfur-like smell. It does not occur naturally in the environment. It is organophosphate insecticide and acaricide used to control a range of pests including spider mites, aphids, scale insect and leafhopper. It may be used on a wide variety of food, fiber and

ornamental crops, including greenhouse crops, lawns and turf. Ethion is often used on citrus and apples.

2.1.3 Carbendazim

Chemically it is known as Methyl 1H-benzimidazole-2-ylcarbamate. Its empirical formula is $C_9H_9N_3O_2$ with the following structure.



carbendazim

Its molecular weight is $191.187 \text{ g mol}^{-1}$ and density is 1.45 g cm^{-3} . Carbendazim is widely used, broad-spectrum benzimidazole fungicide and a metabolite of benomyl with protective and curative in action. It is used for the control of wide range of fungal diseases such as spot, powdery mildew, scorch, rot, blight etc., on cucurbits, legumes, lettuce, sunflower, cereals (rice), fruits and vegetables. In addition it can be used as a timber preservative and as a seed treatment.

2.2. Pesticide usage pattern

Yen *et al.* (1999) conducted survey of local farmers in north, central and south Trinidad, in areas where fruit and vegetable farming are well established. The survey results revealed that a wide range of pesticides are used and that the same pesticides are used on several crops to control different pests. Application rates exceeding manufacturers'

recommendation are also common, as is the disregard of recommended pre harvest intervals after pesticide application.

Epstein and Bassein (2003) studied the use of fungicides, bactericides, fumigants and selected insecticides primarily for vegetable, fruit and nut production. There have been reductions in use of organophosphate insecticides, largely by substitution with pyrethroids. Theoretically, replacement of “calendar spray” pesticide programs with “environmentally driven” programs could reduce pesticide use in years with lower disease pressure, but this assumes that the majority of growers currently use a “calendar spray” program and that growers who use less than recommended by an environmentally driven program would not increase their use.

Plianbangchang *et al.* (2009) conducted survey of 130 small-scale farmers regarding pesticide use patterns. The results indicated that pesticides are readily available and widely used in crop production including the use of endosulfan which has been banned by the Thai government since 2004. Overall, pesticide use was inappropriate. Farmers did not wear suitable personal protection, apply pesticide in an appropriate fashion, or discard the waste safely. They frequently relied on commercial advertisements for the best pesticide to use. Pesticide use patterns among small-scale farmers in Thailand need improvement.

Shetty *et al.* (2010) conducted survey of 1039 farmers from 12 states of India. The results revealed that most of the farmers in the surveyed area followed their own spraying schedules and pesticide dosages to manage ever increasing insect pests and disease problems.

Amoako *et al.* (2012) reported that as many as 26 different pesticides were used to control insect pests in cabbage production. Further, they reported that 8 per cent of the farmers sprayed pesticides between 1 and 5 times in a growing season. Majority (45%) of the farmers, however, sprayed pesticides between 11 and 15 times within a single growing season of cabbage cultivation to control insect pests. Twenty seven per cent farmers sprayed pesticides between 16 and 20 times within a growing season of cabbage cultivation.

Tibugari *et al.* (2012) reported that, in African countries, there is a great reliance on broad spectrum insecticides such as pyrethroids, organophosphates and carbamates, that are applied weekly or twice per week. Use of unregistered insecticides has also been reported.

Patil (2012) conducted survey pesticide usage pattern in Ahmednagar district revealed that the farmers used 5.504 kg a.i/ha/year synthetic insecticides against *S. litura*. Organophosphates, carbamates, synthetic pyrethroids and oxadiazines were used at 2.231, 0.400, 0.767 and 0.036 kg a.i/ha/year, respectively.

Banerjee *et al.* (2014) studied the pesticide use pattern among the farmers in the district of Burdwan of West Bengal, India. They observed that alpha cypermethrin (46%) was the most commonly used pesticide followed by methyl parathion (25.6%), imidachloprid (16.4%), dichlorvos (7.8%) and phorate (4.2%).

Odhiambo *et al.* (2014) studied the insecticide use pattern in cabbage and observed that the growers sprayed the insecticides frequently and at short intervals with 70 per cent of them spraying at a frequency less than a week. This high

frequency of spraying was reflected by 46 per cent farmers who observed pre-harvest interval as short as less than a week. In addition, some of the farmers during heavy pest infestation could spray the cabbage and sell them immediately.

Odhiambo *et al.* (2014) conducted a survey at three localities in eastern region of Ghana to determine insecticide use pattern in cabbage farms. The results showed that use of organophosphates was on the rise in the surveyed locations. On the contrary, pyrethroids and the biopesticides i.e. *Bt* formulations (Biobit and Dipel) usage has declined over the years. Further, they also reported that insecticides were either sprayed alternatively by 63.3 per cent of the farmers or applied as cocktail mixtures by 36.7 per cent of them.

Tandi *et al.* (2014) studied the perception of small scale tomato cultivators on pesticide usage and practices in Buea Cameroon. A standardized questionnaire, interviews, field observations and an analytical ranking game were used to describe the pesticide use of 93 tomato farmers. Many farmers (47.6%) used pyrethroid and organophosphorus insecticides and identified these chemicals as the most effective in pesticide control.

Afari Sefa *et al.* (2015) reported that 43 pesticides were found in use for vegetable farming in the Ashanti and Western regions of Ghana. The pesticides consisted of 7 fungicides, 9 herbicides and 30 insecticides. It is important to note that one systemic insecticide, carbofuran is used by the most farmers both as an insecticide and nematocide as they perceive and have also found it effective in the short run. The class of pesticides commonly used by vegetable farmers in the surveyed area was

insecticide (61.7%), followed by fungicide (32.7) and herbicides (5.5%).

Deviprasad *et al.* (2015) studied the pesticide use pattern in four districts of Karnataka. The results indicate that majority of the farmers are using synthetic pesticide formulations as crop protection to combat various pests and insects. The widely used insecticides were chlorpyrifos, monocrotophos, cypermethrin, quinalphos, fungicides included copperoxide, bavistin, mancozeb, glyphosate and paraquate were used under herbicide group. Survey results further revealed that for a single crop multiple formulations of pesticides were used.

Tyagi *et al.* (2015) studied the pattern of pesticide usage, management and their health effects on farmers from the district Faridabad, Haryana, India. A survey was conducted among 100 farmers in cauliflower and tomato cultivating areas. Cypermethrin (62%) and profenofos (58%) were found as the most popular insecticides while captan (74%) and carbendazim (53%) were the most widely used fungicides by the farmers in this area. However, biological pesticides like azadirachtin (34%) and *Bacillus thuringiensis* (16%) were also observed. Manual application was reported as the method of choice for pesticide application by 70 per cent farmers and 56 per cent of the farmers confirmed that no requisite safety measures and precautions were adopted while applying the pesticides.

2.3. Persistence of quinalphos, ethion and carbendazim in tomato and other crops

Maes *et al.* (1974) studied the GLC determination of ekalux residues in various crops. They observed that the initial

deposits of quinalphos soon after treatment varied from 0.28 ppm on tomatoes to 5.67 ppm on wheat plants, but after 10 days the residue levels on all crops (except cherries, 0.14 ppm at 21 days) dropped to <0.1 ppm (range 0.07 ppm in beans to 0.01 ppm in leek).

Rajukkannu *et al.* (1979) studied the residues of phosalone, quinalphos, methyl parathion and fenitrothion in/on tomato and evaluated the waiting periods when 0.7 kg a.i. ha⁻¹ phosalone, 0.5 kg a.i. ha⁻¹ quinalphos, 0.5 kg a.i. ha⁻¹ methyl parathion and 1.0 kg a.i. ha⁻¹ fenitrothion were sprayed on tomato fruits. The half life and total values were worked out and based on these data, waiting period of 4.75 days for methyl parathion, 3.89 days for phosalone, 2.23 days for fenitrothion and 2.01 days for quinalphos have been suggested for safe consumption.

Singh *et al.* (1980) studied the residues of quinalphos and phosalone in tomato. They observed that quinalphos spray resulted in the initial deposit of 1.8 ppm which dissipated to the level of 1.2, 0.5 and 0.2 ppm in 1, 2 and 4 days respectively.

Gupta and Singh (1988) studied the residues of quinalphos on okra applied at 500 and 250 g a.i.ha⁻¹. Residues were determined colorimetrically at 0-9 days after application. The results revealed that residues fell below the tolerance limit of 2 ppm after 1.5 and 0.73 days at application rates of 500 and 250 g a.i. ha⁻¹, respectively.

Awasti and Ahuja (1989) recorded that quinalphos persisted for 125 days with half life of 5 days in acid lime fruits.

Sangama *et al.* (1989) studied the effect of quinalphos residue on egg plant. The results revealed that the mean initial

deposits by the 2 assay methods were 10.33 ppm at 0.5 kg ha⁻¹ and 11.75 ppm at 1.0 kg ha⁻¹. These decreased to 6.71 and 8.83 ppm, respectively after 1 day. Residues dissipated by 95.35 and 95.66, 87.80 and 84.94 per cent respectively in the 1st week. On the 15th day residues exceeded the limit of 0.25 ppm, with levels of 0.45-0.50 ppm and 0.4-0.62 ppm for applications of 0.5 and 1.0 kg ha⁻¹, respectively.

Yadav *et al.* (1990) studied the quinalphos residues in/on cauliflower and cabbage. They observed that residues resulting from the recommended dose were below the detectable level after 7 days on these crops. The residue half life ($T_{1/2}$) was 1.53 days on cauliflower curds and 1.41 days on cabbage heads.

Mohapatra *et al.* (1998) studied the persistence and dissipation of carbendazim residue in/on grape berries following spray applications at 250 and 500 g a.i. ha⁻¹. They observed that the residues persisted beyond 15 day and dissipated with a half life of 5 days. A waiting period of 2 to 5 day is suggested for the lower and the higher doses, respectively.

Yirong *et al.* (2003) studied carbendazim and metalaxyl residues in post-harvest treated apples. They reported that the concentration of carbendazim residues in apple flesh was ≤ 0.43 mg kg⁻¹ in all treatments. The concentration of carbendazim residues in flesh increased with 6-month storage. The mean concentration of carbendazim residue in apple core and in apple peel was 2.2 ± 1.1 and 5.2 ± 2.2 mg kg⁻¹, respectively, for all treatments, and increased after 3 months and decreased after 6 months of storage.

Arora *et al.* (2004) studied the residues of ethion on pear fruits. They reported that initial deposit of ethion was

observed to be less than its maximum residue limit of 2.0 mg kg⁻¹ when sprayed at recommended dose (0.05 % a.i. ha⁻¹). Based on acceptable daily intake (ADI) of ethion at 0.002 mg kg⁻¹, a waiting period of 10 days is recommended for safe consumption of pear fruits following application at recommended dose.

Banerjee (2005) studied the residue dynamics of carbendazim and mancozeb in grape and reported that the half-life of carbendazim and mancozeb were 7.3 and 8.1 days at recommended dose and 4.6 and 5.7 days at double dose. The pre-harvest intervals for carbendazim and mancozeb were found to be 26 and 12 days at recommended dose and 33 and 17 days at double dose, respectively.

Mahalingappa *et al.* (2006) studied the dissipation of ethion (0.1 %) and chlorpyrifos (0.05 %) on chilli by spraying the crop four times at fortnight interval starting from 45 days after transplanting. The results reported that the initial deposits of ethion and chlorpyrifos on chilli were 1.84 mg kg⁻¹ and 0.67 mg kg⁻¹ respectively, dissipated to 0.17 (90.8 %) and 0.07 (89.6 %) mg kg⁻¹ by 30 days after fourth spray, respectively. Half-life (RL₅₀) values of 9.4 and 9.9 days and the waiting periods of 17.6 and 21.2 days were calculated for ethion and chlorpyrifos, respectively. The residues in shade dried red chilli on 30th day after last spray were 1.29 and 0.62 mg kg⁻¹, which dissipated to 0.35 and 0.02 mg kg⁻¹, respectively, for ethion and chlorpyrifos on 90th day.

Singh *et al.* (2007) studied the persistence of ethion on cucumber and reported that the average initial deposits of ethion on cucumber fruits were found to be 2.40 and 4.97 mg kg⁻¹ at single and double dose, respectively. Residues of ethion

dissipated below the maximum residue limit (MRL) of 0.5 mg kg⁻¹ in 7 days. Half-life ($T_{1/2}$) for degradation of ethion on cucumber was observed to be 2.92 days at recommended dose. A waiting period of 7 days is suggested for safe consumption of cucumber.

Battu *et al.* (2008) studied the dissipation of quinalphos in kinnow mandarin fruits under subtropical conditions of Punjab, India. They observed that quinalphos residue deposited at application rate of 10.0 and 20.0 ml per tree on kinnow mandarin fruits were found to be 0.05 and 0.16 mg kg⁻¹, respectively. These initial deposits were found to be less than its maximum residue limit (MRL) of 0.25 mg kg⁻¹. The corresponding values in the rind were found to be 0.65 and 1.64 mg kg⁻¹, respectively. These residue levels in the rind dissipated below the MRL in 5 and 15 days, respectively. The half-life values for quinalphos in the rind at single and double dosages were found to be 3.2 and 4.0 days, respectively.

Kumari *et al.* (2009) studied the harvest time residues of ethion in wheat and reported that no residues were detected in wheat grain at single dose but the residues at double dose were 0.031 µg g⁻¹ which exceeded the maximum residue limit (MRL) of 0.025 µg g⁻¹.

Bhattacharjee and Pandey (2010) studied the dissipation of carbendazim in mango after pre and post-harvest treatments. They observed that carbendazim dissipated to 1.01 and 2.14 mg kg⁻¹ in mature whole fruit after harvest (12 days after second spray) at 0.05 and 0.1 per cent concentrations, respectively, following first order rate kinetics. The corresponding values in fruit pulp after 12 days were 0.57 and 1.26 mg kg⁻¹. In another experiment, cold water dip treatment in carbendazim

solution @ 0.05 and 0.1 per cent was given for 10 min to a separate lot of fruits having no pre harvest spray. Dissipation of carbendazim in whole fruit again followed first order rate kinetics with 0.92 and 2.06 mg kg⁻¹ of the fungicide recovered after 10 days of storage from 0.05 and 0.1 per cent doses, respectively. The corresponding values in fruit pulp after same days of storage were 0.51 and 1.05 mg kg⁻¹. The residual half-life values of carbendazim in whole fruit were calculated as 4 and 3 days at both the concentrations from pre harvest spray and post harvest dip treatment, respectively.

Nasrin *et al.* (2010) studied the dissipation of ethion applied on greenhouse cucumbers. They observed that the average initial deposits of ethion on cucumber fruits were found to be 2.40 and 4.97 mg kg⁻¹ at single and double dose, respectively. Residue levels in samples, which were collected post application of the pesticide throughout a period of 15 days showed a gradual and significant ($p < 0.05$) decrease in contents for ethion. Residues of ethion dissipated below the maximum residue limit (MRL) of 0.5 mg kg⁻¹ in 7 days. Half-life ($T_{1/2}$) for degradation of ethion on cucumber was observed to be 2.1 and 1.8 at single and double dosages, respectively. A waiting period of 7 days is suggested for safe consumption of cucumber.

Aktar *et al.* (2010) studied the risk assessment and decontamination of quinalphos under different culinary processes in/on cabbage. They revealed that the initial deposits (3 h after spraying) of quinalphos in cabbage heads were found to be 4.42 and 9.75 ppm at lower and higher doses, respectively, irrespective of any season. More than 60 per cent of the initial deposit was dissipated within 48 hrs except double the recommended doses.

The half-life values ($t_{1/2}$) for field dissipation study were found to be 1.27–1.38 and 1.12– 1.24 days for cabbage heads and cropped soil, respectively. The corresponding waiting periods were found to be 5.28 and 6.7 days.

Zheng *et al.* (2010) studied the residue dynamics of carbendazim in strawberry. The results showed that the limit of determination was 0.05 mg kg⁻¹. Carbendazim degrades comparatively fast and the half life were 4.2-6.7 days for rice.

Chahil *et al.* (2011) studied the degradation dynamics of quinalphos on cabbage under subtropical conditions of Ludhiana, Punjab, India. They reported that average initial deposits of quinalphos on cabbage were found to be 0.41 and 0.75 mg kg⁻¹ at single dose and double dosages, respectively. Residues of quinalphos dissipated below determination limit of 0.01 mg kg⁻¹ in 7 and 10 days, respectively at single and double dose. The half-life of quinalphos on cabbage was observed to be 3.02 and 2.70 days for single and double dose, respectively. The study suggested a waiting period of 7 days for safe consumption of cabbage.

Chandel *et al.* (2011) studied the dissipation of quinalphos in cabbage, cauliflower and potato from treatment @ 500 and 1000 g a.i. ha⁻¹; on onion, from treatment @ 300 and 600 g a.i. ha⁻¹. The initial deposits of quinalphos were found to be 0.740 and 1.250 mg kg⁻¹ in cabbage heads, 0.475 and 0.888 mg kg⁻¹ in cauliflower curds and 1.058 and 1.359 mg kg⁻¹ in green/immature onion at the lower and higher doses, respectively. Initial deposits dissipated to half in 1.80- 2.20, 1.21- 1.26 and 2.46-3.00 day from cabbage, cauliflower and onion, respectively, at both doses. The residues persisted for 3 and 5

days on cauliflower and cabbage, respectively, at lower dose and for 5 days at higher dose. In immature onion, quinalphos persisted up to 7 days at lower dose and 10 days at higher dose. The residues were below detection limit (0.05 mg kg^{-1}) on potato tubers at 0 day sampling, although its cropped soil contained detectable residues.

Utture *et al.* (2011) studied the dissipation and distribution behavior of azoxystrobin, carbendazim and difenoconazole in pomegranate fruits. The results revealed that the dissipation of azoxystrobin, carbendazim, and difenoconazole followed first order kinetics at both standard and double doses, with preharvest intervals being 9, 60, and 26 days at standard dose. At double dose, the preharvest intervals extended to 20.5, 100 and 60 days, respectively.

Varghese *et al.* (2011) studied the dissipation of dimethoate, ethion and oxydemeton methyl in chilli. They reported that mean initial deposit of ethion on the day of spraying was found to be 5.79 mg kg^{-1} . About 75 per cent of the initial residues get dissipated on the 3rd day of spraying. On the 10th day 87.92 per cent of the residues gets dissipated and 96.72 per cent of the residues get dissipated on the 15th day. The residues were below detection level on the 20th day of spraying.

Parmar *et al.* (2012) studied the dissipation and decontamination of some pesticides in/on okra. They observed that the average initial deposit of deltamethrin, alphamethrin, deltamethrin in combination, triazophos, ethion, cypermethrin and profenophos was 0.152, 0.136, 0.025, 0.543, 0.254, 0.172 and 4.519 mg kg^{-1} , respectively which dissipated to 0.025 (83.55%), 0.023 (83.09%), 0.01 (60.00%), 0.015 (0.015%), 0.013

(94.88%), 0.02 (88.37%) and 0.508 (88.76%) mg kg⁻¹ on 5th and 7th day. The half-life values for respective pesticides were 2.09, 2.09, 2.61, 1.68, 1.27, 2.59 and 1.88 day, respectively.

Pathan *et al.* (2012) studied the dissipation of quinalphos in brinjal and soil. They observed that the initial deposit of quinalphos in brinjal at 375 and 750 g a.i. ha⁻¹ were recorded as 0.0866 and 0.1517 mg kg⁻¹, respectively which reached to below detection level (0.01 mg kg⁻¹) in 7 and 10 days at recommended (375 g a.i. ha⁻¹) and double of the recommended dose (750 g a.i. ha⁻¹), respectively. The half life values (RL₅₀) were found to be 2 days for lower dose and 3 days for higher dose. Hence 6 and 9 days waiting period was suggested for recommended and double of the recommended dose, respectively.

Mohapatra *et al.* (2013) studied the persistence and dissipation of quinalphos residues in/on cauliflower under semi arid climatic conditions of Karnataka, India after giving spray application at 2 concentrations, i.e. recommended dose (500 g a.i ha⁻¹) and double the recommended dose (1000 g a.i ha⁻¹). Residue analysis of cauliflower curd was carried out after third spray over a period of 15 days. Initial residues of quinalphos on cauliflower from the two treatments were 1.19 and 1.84 mg kg⁻¹. The residues persisted up to 15 days from both the treatments with half life of 4.8 and 5.3 days. Based on the persistence study and maximum residue limit value of 0.05 mg kg⁻¹ the safe pre-harvest interval was worked out as 17 and 22 days from the treatment at recommended and double the recommended dose, respectively.

Salghi *et al.* (2013) studied the dissipation of carbendazim and iprodion during cultivation of peaches in the region of Souss Massa Valley (Morocco). The results revealed that

residue levels in the plantation ranged between 0.28 and 0.10 mg kg⁻¹ for carbendazim and between 0.52 and 0.06 mg kg⁻¹ for iprodion. The residual concentrations after the pre harvest intervals (PHI) were below the legal limits.

Sharma and Parihar (2013) studied the dissipation and persistence of dimethoate and ethion residues in/on chilli. The results revealed that the initial deposit of dimethoate was found to be 3.12 and 5.16 mg kg⁻¹ with the half life values of 1.74 and 1.51 days at 300 and 600 g a. i. ha⁻¹, respectively. In case of ethion, initial deposit were found to be 2.40 and 4.84 mg kg⁻¹, with half life values of 1.81 and 2.32 days at 500 and 1000 g a. i. ha⁻¹ respectively.

ZhouWei (2013) studied the dissipation of carbendazim, chlorothalonil and chlorpyrifos in vegetables and soil inside and outside the greenhouse. The results revealed that the dissipation of carbendazim, chlorothalonil and chlorpyrifos in pakchoi, tomato, cucumber and soil was fitted to the first-order model. The dissipation rates of these three pesticides in the vegetables and soils were much slower in the greenhouse than those in the open field. Furthermore, their dissipation rates were much slower in the winter than those in the summer. The residual amounts of three pesticides in the soil increased with their increasing application concentrations under the same application frequency. An obvious accumulation of carbendazim, chlorothalonil and chlorpyrifos was observed with application times.

Mutkule *et al.* (2014) studied the persistence and dissipation of quinalphos applied to brinjal. Initial amounts of quinalphos were 1.20 and 2.98 mg kg⁻¹ on brinjal fruits which

dissipated to below detection level on 7th and 10th day, respectively. The residual half life for quinalphos was 1.32 and 1.55 days, respectively. For safety waiting period of 1.07-2.99 days for quinalphos has been suggested.

Devi *et al.* (2015) studied the degradation pattern and risk assessment of carbendazim and mancozeb in mango fruits. A supervised field trial was conducted at four different agro climatic locations at Tamil Nadu, Himachal Pradesh, West Bengal and Maharashtra in India, following foliar application of mixed formulation of carbendazim 12 per cent and mancozeb 63 per cent fungicides (SAAF-75WP) at recommended dose (90+472.5 g a.i. ha⁻¹) and double the recommended dose (180+945 g a. i. ha⁻¹). The results revealed that average initial deposition of carbendazim was in the range of 1.12 to 2.7 and 1.95 to 4.09 mg kg⁻¹ and for mancozeb in the range of 2.25 to 2.71 and 4.17 to 5.96 mg kg⁻¹, given at respective doses. Residues of carbendazim and mancozeb were dissipated to the below detection limit on 7 days after spray at recommended dose in all locations.

Gleissy *et al.* (2015) studied the pesticide residues in conventionally and organically grown tomatoes in Espirito Santo (Brazil). They reported that the pesticides acephate, carbaryl (0.23 mg kg⁻¹; exceeding maximum residue levels), carbendazim, chlorpyrifos, dichlorvos, fenpropathrin (0.41 mg kg⁻¹; exceeding maximum residue levels), methamidophos and permethrin (0.51 mg kg⁻¹, exceeding maximum residue levels) were found in conventional tomatoes. In organic tomatoes, only one sample exhibited the presence of permethrin (0.21 mg kg⁻¹).

Huidong *et al.* (2016) investigated the dissipation behaviors and residues of carbendazim and diethofencarb in

tomato. The half-life values were 2.1-3.4 days for carbendazim and 1.8-3.2 days for diethofencarb at a dose of 1.5 times of the recommended dose.

2.4. Persistence of quinalphos, ethion and carbendazim in soil

Babu *et al.* (1998) studied the persistence of quinalphos and occurrence of its primary metabolite in soil. They concluded that the rate of constant and half life for disappearance of quinalphos in black cotton soil and red sandy loam-sandy clay soil under aerobic conditions were 0.0533 and 0.0462 day⁻¹ and 13 and 15 days, respectively. Quinalphos persisted for 2 weeks in soil under aerobic conditions in the present investigation. This insecticide was short-lived with 5 days of half life even in horticultural fruit.

Kumari *et al.* (2009) studied the harvest time residues of ethion in soil and wheat crop. The results revealed that the residues of ethion were 0.048 and 0.082 µg g⁻¹, 0.257 and 0.472 µg g⁻¹ in soil and straw, respectively.

Wei *et al.* (2009) studied the residue dynamics of carbendazim in soil and reported that the half life of carbendazim were 5.74-7.07 days in the cultivated soil.

Yu *et al.* (2009) studied the effects of repeated applications of fungicide carbendazim on its persistence and microbial community in soil. The results indicated that dissipation of carbendazim in soil was accelerated with its application frequency. The degradation rate constant of carbendazim was increased significantly from 0.074 day⁻¹ to 0.79 day⁻¹. The corresponding half-life was shorten markedly from 9.3 day to 0.9 day after four repeated applications.

Soad *et al.* (2010) studied the dissipation and persistence of fungicides, carbendazim and metalaxyl in Egyptian soil under biotic and abiotic conditions. They observed that the carbendazim and metalaxyl dissipation were found to be higher in non-sterilized soils than that in sterilized soils. The degradation of metalaxyl at different concentration levels were ranged between 21.99 to 29.24% in sterilized soil and from 64.22 to 79.93% in non-sterilized soil after 60 days from treatments, while, the dissipation of carbendazim were ranged from 62.8 to 70.98 % in sterilized soil and from 81.55 to 87.13% in non-sterilized one. There was a direct correlation between the fungicides concentrations and the degradation rate. The value of the ($T_{1/2}$) decreased significantly from 41.01, 40.77 and 35.91 days in sterilized soil to 27.50, 22.80 and 21.19 days in non-sterilized soil treated with carbendazim at 1.0, 5.0 and 10.0 $\mu\text{g g}^{-1}$ soil respectively.

Wu *et al.* (2010) studied the dynamics of carbendazim residue in soil. They observed that the half lives of carbendazim were 5.92 and 6.82 days at 1.000 and 0.675 kg a.i ha⁻¹ respectively in the cultivated soil.

Liu *et al.* (2012) studied the residue and degradation of carbendazim in rice and soil. The results showed that degradation of carbendazim in paddy water, soil and rice conformed to chemical kinetic equation. The half-life was 2.53-3.41 days in paddy water, 6.20-7.27 days in soil and 3.27-3.91 days in plant. The original deposition was closely related to application rate and spraying frequency. Carbendazim was sprayed twice or three times at a 7 days interval with the application dose of 231 g a.i ha⁻¹ and 346.5 g a. i. ha⁻¹, the final maximum residue of

carbendazim after 21 days were ND(not detected) in soil, 0.524 mg kg⁻¹ in rice straw, 0.528 mg kg⁻¹ in rice shell and ND in brown rice, respectively.

Pathan *et al.* (2012) studied the dissipation of quinalphos in soil. They reported that no residues were detected in soil in treated plots at both the treatment levels 30 days after the spray of insecticide to the crop.

Mohapatra *et al.* (2013) studied the persistence and dissipation of quinalphos residues in soil. They observed that on 15th day the residues were found to be 0.013 and 0.044 mg kg⁻¹.

3. MATERIAL AND METHODS

Present investigation entitled “Persistence of quinalphos, ethion and carbendazim in/on tomato and cropped soil were carried out to study the pesticide usage pattern, dissipation of quinalphos, ethion and carbendazim in tomato and harvest time residues in cropped soil. Field experiment was conducted during Kharif-2015 at the Instructional Farm of Post Graduate Institute, M.P.K.V., Rahuri. The dissipation and harvest time residues of pesticides were studied at Pesticide Residue Laboratory, AINP on Pesticide Residues. Department of Entomology, M.P.K.V., Rahuri. The material used and methods followed during the research experiment are given below.

3.1 Material

3.1.1 Tomato seeds

The seed of tomato variety-Namdhari was procured from local market.

3.1.2 Pesticides

In this experiment seven treatments including treated control were maintained. Ethion and carbendazim are not registered in India for usage on tomato, hence, no PHIs are recommended. However, the pest management practices of farmers revealed their usage on tomato due to their effectiveness for management of pests and diseases. The test pesticides were obtained from the Modern Pesticide Testing Scheme, Department of Entomology, MPKV, Rahuri. Particulars of evaluated pesticides *viz.*, common name, chemical name, trade name, formulation and manufacturer of product/source are presented in Table 1. The treatment details *viz.*, name of pesticides, its formulation, dose in g a.i. ha⁻¹ and concentration of spray solution are given in Table 2.

Table.1.Particulars of the pesticides sprayed on tomato for residue studies

Sr. No.	Common Name	Chemical Name	Trade Name	Formulation	Source
1	Quinalphos	O,O-diethyl O-2- quinoxaliny phosphorothiote	Ekalux	25 EC	M/s. Syngenta, India Ltd., Pune
2	Ethion	O,O,O',O'tetraethyl S, S- methylene di (phosphorothiote)	Fosmite	50 EC	M/s. PI Industries Ltd., Gujarat
3	Carbendazim	Methyl 1H-benzimidazol-2-yl carbamate	Wilzim	50 WP	M/s. Syngenta India Ltd., Mumbai

Table 2: Treatment details

Treatment No.	Treatment Name	Formulation	Dose (g a.i. ha⁻¹)	Spray Conc. (ml lit⁻¹)
T ₁	Quinalphos	25 EC	250*	0.9
T ₂	Quinalphos	25 EC	500**	1.8
T ₃	Ethion	50 EC	500*	0.9
T ₄	Ethion	50 EC	1000**	1.8
T ₅	Carbendazim	50 WP	150*	0.27
T ₆	Carbendazim	50 WP	300**	0.54
T ₇	Untreated control	Water spray		

* Recommended dose

** Double the recommended dose

3.1.3 Glassware

All glass items were of 'A' grade. Glassware was initially cleaned with aqueous soap solution and was rinsed thoroughly with tap water. Acetone rinsed glassware was oven-dried prior to use.

3.1.4 Chemicals and Reagents

- a. Ethyl acetate (HPLC Grade), Avantor Performance Materials India Limited, Thane (MS)
- b. Sodium sulphate anhydrous purified, SDFCL, Mumbai
- c. PSA (Primary secondary amine)-Agilent Technology, Bangalore
- d. Acetone (Analytical Reagent grade), Merck Specialties Private Limited, Mumbai
- e. Toluene (Analytical Reagent grade), Avantor Performance Materials India Limited, Thane
- f. η -Hexane (HPLC grade), Thermo Fisher Scientific India Pvt. Ltd., Mumbai
- g. Water (HPLC grade), Avantor Performance Materials India Limited, Thane
- h. Magnesium sulphate (Laboratory Reagent), Avantor Performance Materials India Limited, Thane (MS)
- i. Acetonitrile (HPLC grade), Merck Life Science Private Limited, Mumbai
- j. Acetic acid (ExcelaR grade), Thermo Fisher Scientific India Pvt. Ltd., Mumbai
- k. Sodium acetate (Analytical Reagent grade), Avantor Performance Materials India Limited, Thane (MS)

1. CRM: Certified Reference Materials of quinalphos, ethion and carbendazim with purity 99.40, 97.20 and 98.50 per cent, respectively were obtained from Sigma-Aldrich

3.1.5 Apparatus and instruments

3.1.5.1 Apparatus

- a. Analytical balance-Citizen.
- b. Grinder-Robot Coupe (Blixer 6 v.v.)
- c. Laboratory Centrifuge, Remi make
- d. Vortex-Spinix
- e. Refrigerator-SANYO [-20°C]
- f. Low Volume Concentrator (TurboVap LV, Caliper Life Sciences, USA)

3.1.5.2 Instruments

- a. Gas Chromatography-MS
(GCMS-QP 2010 plus-Shimadzu)
- b. High Performance Liquid Chromatography-PDA
(LC-20AT- Shimadzu)

3.1.6 Appliance

Manually operated knapsack sprayer (Aspee make) with hollow cone nozzle was used for spraying of pesticides on tomato crop.

3.2 Methods

3.2.1 Survey of pesticide usage pattern

Pesticide usage pattern in tomato against different pest and diseases was studied during Kharif-2015 through a survey by using structured questionnaire (Appendix I)

Twenty five farmers randomly selected from major tomato growing areas of Ahmednagar district were interviewed. Survey questionnaire covered type of pesticides used to control pest and diseases in tomato, active ingredient of the pesticides, doses of application and frequency of spraying, etc.

3.2.2 Raising of tomato crop

The experiment was laid out at Instructional Farm of Post Graduate Institute, MPKV, Rahuri, District-Ahmednagar, Maharashtra state (Plate 1). Tomato seedlings were grown on raised beds by sowing disease free seeds of variety Namdhari. Seedlings were ready for transplanting on 30 days after sowing. Land for planting the experiment was ploughed once and latter given two harrowing. The layout of the experiment was done by preparing ridges and furrows. All the cultural practices were carried out as per recommendation. The experimental details are given below.

Treatments	7
Replications	3
Plot size	3.6 m × 3.6 m
Spacing	60 cm × 30 cm
Variety	Namdhari
Date of sowing	20 th June 2015
Date of transplanting	20 th July 2015
Time of application	Fruit initiation stage
Number of applications	Two at 10 days interval
Dates of application	31.08.2015 and 10.09.2015

3.2.3 Application of pesticides

The spraying was done manually by hand operated knapsack sprayer fitted with hollow cone nozzle. Two foliar sprays of each pesticide were given at an interval of 10 days. First spray was given at fruit initiation stage. Quantity of spray fluid required per plot was calculated by spraying control plot with water. The due care was taken to wash the spray pump with water, in the beginning and while switching over from one pesticide to another during spraying. All sprayings were done during morning hours to avoid drift due to heavy winds from one treatment plot to other.

3.2.4 Residue Analysis

3.2.4.1 Standard Preparation

An accurately weighed 10 mg of an individual analytical grade pesticide was dissolved in 10 ml volumetric flask using suitable solvent to prepare the standard stock solution to 1000 mg kg⁻¹. Standard stock solution of each pesticide was further diluted to obtain immediate lower concentrations of 100 and 10 mg kg⁻¹. They were stored in a refrigerator at -20°C. From intermediate standards, working standards of 0.50, 0.40, 0.25, 0.10 and 0.05 mg kg⁻¹ were prepared by suitably diluting the stock solution in n-hexane and acetonitrile for organophosphates (quinalphos, ethion) and carbendazim, respectively and used as standard check in residue determination, linearity and recovery studies.

3.2.4.2 Method validation

Prior to analysis of samples, linearity of quinalphos and ethion was established on GCMS and carbendazim on HPLC.

Accuracy and precision of the methods was determined by per cent mean recovery and per cent relative standard deviation.

3.2.4.2.1 Limit of Detection and Limit of Quantification

The limit of detection of quinalphos, ethion and carbendazim was determined by considering a signal-to-noise ratio of three with reference to the background noise obtained for the blank sample. The limits of quantification determined as 3 times of LOD.

3.2.4.2.2 Linearity study

Five linear concentrations i.e. 0.05 (LOQ) , 0.10, 0.25 0.40 and 0.05 mg kg⁻¹ of quinalphos, ethion and carbendazim standard were injected in triplicate in order to find out calibration range of an instrument. The linearity curve was drawn by plotting the graph of detector response against concentration.

3.2.4.2.3 Recovery study

The analytical method for estimation of quinalphos, ethion and carbendazim residues in tomato and soil has been validated by conducting recovery studies using control samples of tomato and soil. Ten gram each of control sample of blended tomato fruits and soil was taken in 50 ml centrifuge tubes in three replicates each were spiked with quinalphos, ethion and carbendazim separately at the required fortification levels *i.e.* LOQ, 5 x LOQ and 10 x LOQ, adding an appropriate volume of working standard of 10 mg kg⁻¹. This mixture was then shaken, in order to attain a proper homogeneity of pesticides in the

samples. The extraction and cleanup procedures were followed as described under 3.2.6 of this chapter. Per cent recovery was calculated by using following formula.

$$\text{Per cent recovery} = \frac{\text{Quantity of pesticide recovered}}{\text{Quantity of pesticide added}} \times 100$$

3.2.5 Sampling

The medium marketable size tomato fruit samples (1 kg) were collected at random from each replicate of the treated and control plots separately at regular time interval of 0 (2 hr after spraying), 1, 3, 5, 7, 10 and 15 days after the second spray, whereas, soil samples from each treatment plot were collected at final harvest. The collected samples (tomato and soil) were transferred immediately to the laboratory in an ice box. The samples were homogenized and kept at -20°C in deep freezer until used for analysis. The dates of collection of tomato and soil samples are mentioned below.

Substrate	Interval between last application and sampling	Date of sample collection
Tomato	0 day	10.09.2015
	1 day	11.09.2015
	3 day	13.09.2015
	5 day	15.09.2015
	7 day	17.09.2015
	10 day	20.09.2015
	15 day	25.09.2015
Soil	30 day	10.10.2015

3.2.6 Sample preparation

The tomato samples were extracted and cleaned up using QuEChERS methodology (acronym for quick easy cheap effective rugged safe) (Anastassiades *et al.*, 2003).

3.2.6.1 Extraction and clean up of tomato fruits for quinalphos and ethion:

The entire laboratory sample was crushed thoroughly in a grinder and approximately 10 g homogenized sample weighed in a 50 ml polypropylene tube and tube was kept in deep freezer for 10 min. Homogenised sample was extracted with 10 ml ethyl acetate in presence of 10 g anhydrous Na₂SO₄ and centrifuged at 3500 rpm for 5 min. Transferred 2 ml supernatant to the 15 ml tube containing 50 mg PSA. The content was vortexed for 30 sec and then centrifuged for 2 min at 2500 rpm. The supernatant was filtered through 0.2 micron filter and GC-MS analysis was carried out.

3.2.6.2 Extraction and clean up of tomato fruits for carbendazim:

A modified version of the QuEChERS method (Ahumada & Zamudio, 2011) was carried out in order to obtain carbendazim extracts by the following procedure. In a centrifuge tube, 10 g of homogenized sample was weighed, 15 ml of solvent was poured into it and then it was shaken on vortex for 1 min. The extraction solvent consisted of acetonitrile and acetic acid 1 per cent (v/v). Thereafter, 6 g of anhydrous MgSO₄ and 1 g of sodium acetate were added, and it was shaken again. The tube was centrifuged to 4500 rpm for 5 min and 10 ml of the

supernatant (solution A) was measured using a pipette and then transferred to a 15 ml centrifuge tube. In case of the clean-up procedure, 25 mg of PSA (primary secondary amine) and 150 mg of anhydrous MgSO₄ were added for each extract milliliter of solution A. Afterward; it was shaken for 30 seconds and centrifuged by 2 min at 4500 rpm. Finally, the supernatant was filtered through a 0.22 mm PTFE filter and HPLC analysis was carried out.

3.2.6.3 Extraction and clean up of cropped soil for quinalphos, ethion and carbendazim

A representative 10 g soil sample was taken in 50 ml polypropylene tube. Add 20 ml acetonitrile shake vigorously for 1 min. To this 4 g magnesium sulphate and 1 g sodium chloride added then centrifuged at 3300 rpm for 5 minute. Transferred 10 ml supernatant to the 15 ml tube containing 1.5 g MgSO₄ and 0.250 g PSA. Afterward it was shaken for few minutes and sonicated for 1 min and then centrifuged again for 10 minute at 4400 rpm. From this 4 ml aliquot of supernatant was taken and 1 ml was used for HPLC analysis and remaining 3 ml aliquot was evaporated to dryness using nitrogen concentrator at 40°C (water bath temp.). Reconstituted the dry residues in 1.5 ml of ethyl acetate and filtered through 0.2 micron filter in GC vials and performed GC-MS analysis.

3.2.7 Residue determination

Residue estimation of quinalphos and ethion was performed using GC-MS while carbendazim was estimated on HPLC. Identification of pesticide residue was accomplished by

retention time and compared with known standard at the same conditions. The quantities were calculated on peak area basis by using following formula.

$$\text{Residues (mg kg}^{-1}\text{)} = \frac{\text{Area of sample}}{\text{Area of standard}} \times \frac{\mu\text{l of sample injected}}{\mu\text{l of standard injected}} \times \frac{\text{Con. of standard (ppm)}}{\text{Wt. of sample (g)}} \times \text{Final Vol. (ml)}$$

$$\text{Wt. of sample (g)} = \frac{\text{Sample Wt. (g)} \times \text{Aliquot taken (ml)}}{\text{Volume of solvent added (ml)}} = \text{g}$$

3.2.7.1 GC-MS analysis:

Analysis of quinalphos and ethion was carried out by Gas Chromatography-Mass Spectrometry equipped with automatic injection system (Plate 3). GC-MS solution software was used as the data analysis system. Typical GC-MS conditions used for analysis of are as below.

Column Type	VF-5MS-30m × 0.25 μm × 0.25 mm
Oven	0 80° C..... 1 min hold
Programming	@ 11° C/min 140° C 3 min hold @ 5° C/min 225° C 5 min hold @ 8° C/min 280° C 7 min hold
Detector	Interface temperature - 285° C Ion source temperature - 250° C Mass range (M/Z) 40 - 400° C.
Injector	Injector temperature- 250° C Injection Volume - 1 μl Injection Mode- split less
Column flow	1.48 ml min ⁻¹
Carrier gas	Helium (99.999%)
Retention time	Quinalphos - 10.60 min Ethion - 12.64 min

3.2.7.2 HPLC analysis:

The analysis of samples for carbendazim residues were carried out with Shimadzu make High-Performance Liquid Chromatography system equipped with a diode array detector and quaternary pump (Plate 4). LC solution software was used as the data analysis system. The typical HPLC conditions used for analysis are as follow.

Column Type	Purospher @ STAR (Hibar) RP-18 -5 µm-150-4.6
Mobile phase	Acetonitrile : Water (80:20)
Flow rate	0.6 ml min ⁻¹
Wavelength	210 nm
Injection Volume	20 µl
Retention time	5.4 min

3.2.8 Statistical Analysis

The simple statistical analysis was carried out in the Microsoft Excel programme with the help of computer. The mean residues, standard deviation, regression equation, R² value and half life were calculated in excel programme.

4. RESULT AND DISCUSSION

The present investigation entitled “Persistence of quinalphos, ethion and carbendazim in/on tomato and cropped soil” was undertaken at Department of Agricultural Entomology, MPKV, Rahuri during 2015-2016. Results are presented in this chapter.

4.1 Survey on pesticide usage pattern on tomato

The results of survey conducted with 25 farmers on pesticide use pattern in predominant tomato growing area, Rahuri (Ahmednagar district) during June to August, 2015 are presented in Table 3 and Table 4. Data were recorded on number of sprays, pesticides used and frequency of spray.

Survey reports revealed that share of conventional insecticides (Table 3 and Fig. 1) was highest (42.69 %) followed by fungicides (27.20 %), novel insecticides (16.96 %) and biopesticides (13.15 %). Majority of the farmers generally used combination of pesticides. The data on quantity of pesticide used in respect of tomato (Table 3) revealed that total consumption of conventional insecticides was 6.170 kg a.i. ha⁻¹. Whereas, total consumption of novel insecticides, biopesticides and fungicides was 4.451, 1.90 and 3.933 kg a.i. ha⁻¹, respectively in tomato crop.

Survey on pesticide usage pattern on tomato revealed wide range of pesticide use by the farmers in tomato growing areas. Farmers relied upon conventional insecticides, novel insecticides, biopesticides and fungicides. The usage of pesticides, largely depends on the incidence of pest and diseases of the

location. Farmers used organophosphates, neonicotinoids for the control of sucking pests, organophosphates and synthetic pyrethroids for the lepidopteran pest control. The quantity of organophosphate insecticides used was 5.67 kg a. i. ha⁻¹ as against 3.933 kg a. i. ha⁻¹ of fungicides for the control of insect pest/diseases in tomato. Among the insecticide groups, share of organophosphate and synthetic pyrethroid was 39.23 and 3.46 per cent, respectively. Whereas, novel insecticides *viz.*, neonicotinoids, avermectin, diamides, oxadizines, diamides and spinosad were 2.42, 3.53, 4.82, 1.28 and 4.91 per cent, respectively. Among these pesticides, quinalphos, chlorpyrifos, imidacloprid, thiamethoxam, lambda cyhalothrin, emamectin benzoate, indoxacarb, spinosad, chlorantraniliprole flubendiamide and carbendazim were used more commonly and frequently.

Findings of the survey conducted by Patil (2012) in Ahmednagar district revealed that the farmers used 5.504 kg a.i./ha/year synthetic insecticides against *S. litura*. Organophosphates, carbamates, synthetic pyrethroids and oxadiazines were used @ 2.231, 0.40, 0.767 and 0.036 kg a.i./ha/season, respectively.

The usage pattern of pesticides in tomato as evidenced in the present survey cannot be discussed due to lack of literature.

As regards the frequency of spraying depicted in Table 4 and Fig. 2 majority of farmers (52 %) adopted 7 to 10 sprays during cropping season, whereas only 8 per cent farmers gave more than 10 sprays in cropping season.

The application of pesticides frequently at short intervals as observed in the present investigation is in agreement with Odhiambo *et al.* (2014). They reported that cabbage growers sprayed the insecticides frequently and at short intervals with 70 per cent of them spraying at a frequency less than a week. It was observed in case of 46 per cent farmers that Pre-Harvest Interval (PHI) was as short as less than a week. During heavy pest infestation, some farmers sprayed the pesticides and harvested on the succeeding day.

4.1.1 Awareness on pesticide use

From the survey reports, it was revealed that majority (88 %) of the farmers did not know about safe waiting period. Further, only 8 per cent farmers were aware of harmful effects of pesticide residues (Table 4). In a similar study, Odhiambo *et al.* (2014) reported that with regards to insecticide residues awareness, 63.33 per cent had no idea about it.

It was also observed that most of the farmers used non recommended pesticides. The data revealed that only 8 per cent farmers knew regarding recommended pesticides (Table 4).

The finding of the present survey is in corroboration with Afari-Sefa *et al.* (2015) who studied the pesticide use pattern in vegetables. The study revealed that most vegetable farmers (76.3 %) harvest their produce within 7 days of spraying pesticides with some (1.4 %) harvesting their produce even on the same day after spraying.

Table 3 Usage pattern of pesticides in Ahmednagar district during cropping season

Sr. No	Pesticide category	Pesticides group	Total quantity of Pesticides used (kg a.i. ha⁻¹)	Per cent share
1	Conventional insecticides	Organophosphate	5.670	39.23
		Synthetic pyrethroid	0.500	3.46
		Total (A)	6.170	42.69
2	Novel insecticides	Neonicotinoid	0.350	2.42
		Avermectin	0.510	3.53
		Diamide	0.696	4.82
		Oxadiazine	0.185	1.28
		Spinosad	0.710	4.91
		Total (B)	4.451	16.96
3	Biopesticides	Neem based formulation	1.900	13.15
		Total (C)	1.900	13.15
4	Fungicides	Benzimidazole	3.500	24.21
		Phthalimide	0.233	1.61
		Carbamate	0.200	1.38
		Total (D)	3.933	27.20
		Total (A+B+C+D)	14.454	100

Table 4: Response of farmers about the questionnaire from the surveyed area

Sr.No.	Variables	Response of farmers (%)
1.	i) Conventional insecticides (quinalphos, chlorpyriphos, ethion, cypermethrin etc.) ii) Novel insecticides (imidacloprid, acetamiprid etc.) iii) Fungicides (carbendazim, captan, mancozeb) iv) Biopesticides (Neem oil and Nimbicidine)	60 44 32 8
2.	Spraying interval followed by farmers 1) 1-3 times 2) 4-6 times 3) 7-10 times 4) More than 10 times	16 24 52 8
3.	Awareness about natural enemies	0
4.	Awareness about recommended dose of pesticides	8
5.	Knowledge of safe waiting period	12
6.	Awareness about the harmful effect of pesticide residues	8

4.2 Dissipation of quinalphos, ethion and carbendazim in/on tomato fruits and cropped soil

Dissipation of quinalphos, ethion and carbendazim was determined by conducting a supervised field trial during Kharif-2015 at the Instructional Farm of Post Graduate Institute, MPKV, Rahuri. Two sprays of pesticides were given at an interval of ten days, first being at fruit initiation stage. The fruits were collected at 0, 1, 3, 5, 7, 10 and 15 days after second application and subjected to QuEChERS method of analysis to determine residues as explained under section 3.2.6 of the chapter III (Material and Methods). The relevant meteorological data *viz.*, temperature, RH and rainfall were recorded during the period of experimentation and mentioned in Appendix-II.

4.2.1 Method validation

Method validation refers to the process used to confirm the suitability of analytical method employed for specific test and is an integral part of any good analytical procedure (Huber, 2007). Validation parameters *viz.*, linearity, LOD and LOQ, accuracy and precision were determined before analysis of tomato samples.

For the linearity study a graph of detector response versus concentration of pesticides was plotted and correlation equation and coefficients were determined.

4.2.1.1 Limit of Detection and Limit of Quantification

The limit of detection of the tested pesticides was 0.01 mg kg⁻¹ resulted by considering a signal-to-noise ratio of compound with reference to the background noise (3:1) obtained for the blank sample. The limits of quantification determined as

the lowest concentration in tomato of a given compound giving a response that could be quantified with RSD lower than 20 per cent, was 0.05 mg kg⁻¹ for all tested pesticides.

4.2.1.2 Linearity study

Five linear concentrations (0.05, 0.10, 0.25, 0.40 and 0.50 mg kg⁻¹) of each working standard *i.e.*, quinalphos, ethion and carbendazim were injected 3 times and the linearity lines were drawn. The response was linear over the range tested and R² values were 0.998, 0.998 and 0.992 for quinalphos, ethion and carbendazim, respectively as given in Fig 3.

These results indicated that the GCMS and HPLC analysis is a valid method for residue determination of the tested pesticides in tomato fruits and soil.

4.2.1.3 Recovery studies

Accuracy of the analytical method was determined by recovery studies. Mean recovery obtained from the studies reflect the accuracy of the method. Precision of the method was reflected by the relative standard deviation.

Recovery experiments were conducted on untreated tomato fruits and soil fortified with three concentrations *i.e.*, 0.05, 0.25 and 0.50 mg kg⁻¹ of individual pesticide. The extraction and clean-up were performed as described earlier (3.2.6). Recoveries of three tested pesticides were determined in three replicates to confirm the validity of the method. The recovery percentages and relative standard deviation (RSD) values are presented in Table 5 to 7.

The mean of recovery of quinalphos carried out at the levels of 0.05, 0.25 and 0.50 mg kg⁻¹ (Table 5) on tomato fruits and

soil were 97.18, 97.06, 107.35 per cent and 89.95, 87.61, 95.05 per cent, respectively.

For ethion, mean of recovery at the levels of 0.05, 0.25 and 0.50 mg kg⁻¹ (Table 6) on tomato fruits and soil were 85.71, 109.75, 99.02 per cent and 80.20, 104.40, 97.14 per cent, respectively.

For carbendazim, mean of recovery at the levels of 0.05, 0.25 and 0.50 mg kg⁻¹ (Table 7) on tomato fruits and soil were 91.71, 82.25, 94.96 per cent and 79.50, 82.06, 83.99 per cent, respectively.

These results indicated that the QuEChERS method is valid method for residue determination of the tested pesticides on tomato fruits and soil.

The analytical method employed for the extraction and clean up of tomato fruits and soil samples was found accurate and precise as mean recovery percentage and relative standard deviation (RSD) were within the limits prescribed by SANCO (2011). According to SANCO (2011) guidelines, analytical method which records mean recovery in the range of 70-120 per cent and relative standard deviation below 20 per cent is accurate and precise.

Table 5. Recovery of quinalphos in tomato fruits and soil

Substrate	Fortification Level (mg kg ⁻¹)	Recovery (%)			
		R-I	R-II	R-III	Mean
Tomato fruits	0.05	91.60	101.57	98.37	97.18 (±5.09)
	0.25	99.15	93.14	98.90	97.06 (± 3.40)
	0.50	109.16	100.00	112.90	107.35 (±6.64)
Soil	0.05	91.60	91.95	86.31	89.95 (±3.16)
	0.25	90.21	86.24	86.39	87.61 (±2.25)
	0.50	95.09	89.60	100.47	95.05 (±5.44)

Table 6. Recovery of ethion in tomato fruits and soil

Substrate	Fortification Level (mg kg ⁻¹)	Recovery (%)			
		R-I	R-II	R-III	Mean
Tomato fruits	0.05	87.84	83.19	86.09	85.71 (±2.35)
	0.25	117.29	105.81	106.16	109.75 (±6.53)
	0.50	100.91	97.03	99.12	99.02 (±1.94)
Soil	0.05	80.03	78.91	81.67	80.20 (±1.39)
	0.25	102.62	104.85	105.73	104.40 (±1.60)
	0.50	96.25	97.03	98.15	97.14 (±0.70)

Table 7. Recovery of carbendazim in tomato fruits and soil

Substrate	Fortification Level (mg kg⁻¹)	Recovery (%)			
		R-I	R-II	R-III	Mean
Tomato fruits	0.05	88.53	94.02	92.58	91.71 (±2.85)
	0.25	83.62	82.11	81.01	82.25 (±1.31)
	0.50	95.49	96.54	92.85	94.96 (±1.90)
Soil	0.05	80.58	80.24	77.69	79.50 (±1.58)
	0.25	87.06	78.99	80.14	82.06 (±4.37)
	0.50	81.99	85.79	84.20	83.99 (±1.91)

4.2.2 Residues of pesticides in tomato fruits and soil

Dissipation of quinalphos, ethion and carbendazim was studied after two applications at the recommended dose and double the recommended dose on tomato crop. The results obtained indicated that residues decreased with different day intervals after application.

4.2.2.1 Persistence and dissipation of quinalphos in/on tomato fruits

Dissipation of residues in plant depends on climatic conditions, type of application, dosage and intervals between

application and time of harvest. The results revealed reduction in residue levels of these tested pesticides in tomato fruits with time.

In case of quinalphos 25 EC @ 250 and 500 g a.i.ha⁻¹, initial deposits were recorded as 0.28 and 0.58 mg kg⁻¹ and they are found to be BDL on 7th and 10th day, respectively. The half-life (RL₅₀) values of quinalphos for tomato fruits were 2.67 and 2.47 days, respectively (Table 8). The residues dissipated to 75.00 and 89.65 per cent at both the doses of application (Table 9 and Fig.4). The samples taken from control plot contained no detectable amounts of quinalphos residues.

These results were in agreement with those of Maes *et al.* (1974) who reported the initial deposit of quinalphos as 0.28 ppm following application of Ekalux at 0.2 per cent. Rajukkanu *et al.* (1979) studied the residues of quinalphos in tomato and suggested the waiting period of 2.01 days for safe consumption of tomato. Chahil *et al.* (2011) studied the degradation dynamics of quinalphos on cabbage and reported that average initial deposit of quinalphos on cabbage were found to be 0.41 and 0.75 mg kg⁻¹, following application at 500 and 1000 g a. i. ha⁻¹ respectively. The residues of quinalphos dissipated below its determination limit of 0.01 mg kg⁻¹ in 7 and 10 days at recommended and double the recommended doses, respectively. The half-life of quinalphos on cabbage was observed to be 3.02 and 2.70 days, respectively, in single and double dose.

Table 8. Persistence of quinalphos residues at different intervals in tomato fruits and soil

Interval between last application and sampling	Residues (mg kg ⁻¹)											
	Control				Quinalphos @ 250 g a.i. ha ⁻¹				Quinalphos @ 500 g a.i. ha ⁻¹			
	R-I	R-II	R-III	Mean	R-I	R-II	R-III	Mean	R-I	R-II	R-III	Mean
0 day (2 hr)	ND	ND	ND	ND	0.28	0.29	0.27	0.28 (±0.01)*	0.58	0.57	0.61	0.58 (±0.02)
1 day	ND	ND	ND	ND	0.17	0.18	0.17	0.17 (±0.01)	0.28	0.31	0.29	0.30 (±0.02)
3 day	ND	ND	ND	ND	0.12	0.11	0.13	0.12 (±0.01)	0.22	0.23	0.22	0.22 ±0.01)
5 day	ND	ND	ND	ND	0.08	0.06	0.07	0.07 (±0.01)	0.17	0.17	0.18	0.17 (±0.01)
7 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	0.06	0.06	0.06	0.06 (0)
10 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
15 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
RL _{50(days)}	-				2.67				2.47			
Soil (at harvest)	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

ND-Not Detected BDL= Below Detection Limit LOQ 0.05 mg kg⁻¹ * Standard deviation

Table 9. Per cent dissipation of quinalphos in tomato fruits

Interval between last application and sampling	Quinalphos			
	Recommended dose		Double the recommended dose	
	Mean Residues (mg kg ⁻¹)	Dissipation (%)	Mean Residues (mg kg ⁻¹)	Dissipation (%)
0 day (2 hr)	0.28	-	0.58	
1 day	0.17	39.28	0.30	48.27
3 day	0.12	57.14	0.22	62.06
5 day	0.07	75	0.17	70.68
7 day	BDL	-	0.06	89.65
10 day	BDL	-	BDL	-
15 day	BDL	-	BDL	-

4.2.2.2 Persistence and dissipation of ethion in/on tomato fruits

As regards ethion 50 EC @ 500 and 1000 g a.i. ha⁻¹, initial deposits were recorded as 0.21 and 0.46 mg kg⁻¹. The ethion residues were below detectable limit (BDL) on 7th and 10th day, respectively. The residual half-life (RL₅₀) values recorded were 2.95 and 2.47 days, respectively (Table 10). The residues of ethion dissipated to 71.42 and 89.13 per cent (Table 11 and Fig.5) at recommended and double the recommended dose, respectively. None of the sample from control plot recorded the detectable amounts of ethion residues.

Parmar *et al.* (2012) reported that the average initial deposit of ethion in okra as 0.254 mg kg⁻¹ which are in line with the present investigation. However Singh *et al.* (2007) studied the persistence of ethion on cucumber and reported the high mean initial deposit of ethion on cucumber fruits i.e. 2.40 and 4.97 mg kg⁻¹ following three applications at 10 days interval at 375 and 750 g a. i. ha⁻¹. More than 80 per cent and 90 per cent of these ethion residues dissipated after 7 and 10 days, respectively, at single and double dosages. Arora *et al.* (2004) also estimated residues of ethion on pear fruits following its application at 0.05 per cent and 0.1 per cent a.i. Average initial deposits were observed to be 1.53 and 3.11 mg kg⁻¹, respectively. These residues were less than the MRL value of 2.0 mg kg⁻¹ of ethion on pear fruits. Half life of ethion was observed to be 1.95 and 2.21 days at single and double the dosages, respectively.

Table 10. Persistence of ethion residues at different intervals in tomato fruits and soil

Interval between last application and sampling	Residues (mg kg ⁻¹)											
	Control				Ethion @ 500 g a.i. ha ⁻¹				Ethion @ 1000 g a.i. ha ⁻¹			
	R-I	R-II	R-III	Mean	R-I	R-II	R-III	Mean	R-I	R-II	R-III	Mean
0 day (2 hr)	ND	ND	ND	ND	0.19	0.26	0.18	0.21 (±0.04)*	0.47	0.47	0.43	0.46 (±0.02)
1 day	ND	ND	ND	ND	0.13	0.12	0.12	0.12 (±0.01)	0.21	0.21	0.21	0.21 (±0.02)
3 day	ND	ND	ND	ND	0.10	0.07	0.07	0.08 (±0.02)	0.12	0.14	0.11	0.12 (±0.02)
5 day	ND	ND	ND	ND	0.05	0.05	0.06	0.06 (±0.01)	0.09	0.10	0.10	0.10 (±0.05)
7 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	0.05	0.06	0.05	0.05 (±0.01)
10 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
15 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
RL 50 (days)					2.95				2.47			
Soil (at harvest)	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BD	BDL	BDL

ND-Not Detected BDL= Below Detection Limit LOQ 0.05 mg kg⁻¹ * Standard deviation

Table 11. Per cent dissipation of ethion in tomato fruits

Interval between last application and sampling	Ethion			
	Recommended dose		Double the recommended Dose	
	Mean Residues (mg kg⁻¹)	Dissipation (%)	Mean Residues (mg kg⁻¹)	Dissipation (%)
0 day (2 hr)	0.21	-	0.46	-
1 day	0.12	42.85	0.21	54.34
3 day	0.08	61.90	0.12	73.91
5 day	0.06	71.42	0.10	78.26
7 day	BDL	-	0.05	89.13
10 day	BDL	-	BDL	-
15 day	BDL	-	BDL	-

4.2.2.3 Persistence and dissipation of carbendazim in/on tomato fruits

In case of carbendazim 50 WP @ 150 and 300 g a.i.ha⁻¹, the initial deposits were recorded as 0.99 and 1.84 mg kg⁻¹. The residual half-life (RL₅₀) values were 1.78 and 1.90 day, respectively at both rates of application (Table 12). More than 93.93 and 97.28 per cent (Table 13 and Fig.6) carbendazim residues dissipated after 10 and 15 days, which were below detection limit (BDL) respectively, at both rate of application. The samples from control plot didn't record any amount of residues.

The results are in line with those of Huidong *et al.* (2016) who reported the half life values as 2.1-1.4 days in tomato. Devi *et al.* (2015) recorded the average initial deposition of carbendazim in mango in the range of 1.12 to 2.7 and 1.95 to 4.09 mg kg⁻¹ following application at 90 and 180 g a.i ha⁻¹ respectively. However, Banerjee (2005) studied the residue dynamics of carbendazim in grape berries and reported very high initial deposits of 4.8 and 6.7 mg kg⁻¹ with half life of 7.3 and 8.1 days following application at 0.7 and 1.4 kg a.i ha⁻¹. Zheng *et al.* (2010) reported that the half life were found to be 4.2-6.7 days in rice. Mohapatra *et al.* (1998) reported that residues persisted beyond 15 days and dissipated with a half life of 5 days in grape berries.

Table 12. Persistence of carbendazim residues at different intervals in tomato and soil

Interval between last application and sampling	Residues (mg kg ⁻¹)											
	Control				Carbendazim @ 150 g a.i.ha ¹				Carbendazim @ 300 g a.i. ha ⁻¹			
	R-I	R-II	R-III	Mean	R-I	R-II	R-III	Mean	R-I	R-II	R-III	Mean
0 day (2 hr)	ND	ND	ND	ND	0.92	1.08	0.97	0.99 (±0.08)*	1.72	1.96	1.84	1.84 (±0.12)
1 day	ND	ND	ND	ND	0.85	0.78	0.81	0.81 (±0.04)	1.52	1.47	1.40	1.46 (±0.06)
3 day	ND	ND	ND	ND	0.46	0.59	0.48	0.51 (±0.07)	0.68	0.75	0.88	0.77 (±0.10)
5 day	ND	ND	ND	ND	0.22	0.21	0.23	0.22 (±0.01)	0.32	0.38	0.42	0.37 (±0.05)
7 day	ND	ND	ND	ND	0.08	0.06	0.05	0.06 (±0.02)	0.21	0.12	0.17	0.16 (±0.05)
10 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	0.07	0.06	0.05	0.05 (±0.01)
15 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
RL 50 (days)	1.78								1.90			
Soil (at harvest)	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

ND-Not Detected BDL= Below Detection Limit LOQ 0.05 mg kg⁻¹ * Standard deviation

Table 13. Dissipation pattern of carbendazim in tomato

Interval between last application and sampling	Carbendazim			
	Recommended dose		Double the recommended dose	
	Mean Residues (mg kg ⁻¹)	Dissipation (%)	Mean Residues (mg kg ⁻¹)	Dissipation (%)
0 day (2 hr)	0.99	-	1.84	-
1 day	0.81	18.18	1.46	20.65
3 day	0.51	48.48	0.77	58.15
5 day	0.22	77.77	0.37	79.89
7 day	0.06	93.93	0.16	91.30
10 day	BDL	-	0.05	97.28
15 day	BDL	-	BDL	-

4.2.2.4 Persistence and dissipation of quinalphos, ethion and carbendazim in soil

Analysis of soil samples for the residues of quinalphos, ethion and carbendazim was carried out on the 30th day after second application and are presented in Table 8, 10 and 12. No residues were detected in untreated samples. The residues of all three pesticides (*i.e.*, quinalphos, ethion and carbendazim) in soil at harvest were found to be below detection limit (BDL) in both the dosages.

Pathan *et al.* (2012) studied the dissipation of quinalphos in brinjal and soil. They reported that no residues were detected in soil in treated plots at both the treatment *i.e.* 375 and 750 g a.i ha⁻¹, 30 days after the spray of insecticide to the crop. The half-life values for quinalphos were found to be 1.12–1.24 days for cropped soil (Aktar *et al.* 2010). Kumari and Bhanot (2009) reported that the harvest time residues of ethion in soil were 0.048 and 0.082 µg g⁻¹. Liu *et al.* (2012) reported that the final maximum residue of carbendazim after 21 days were ND (not detected) in soil. These results lend support to the present findings.

The use of pesticides has become indispensable in present agriculture to control insect pests. Survey reports revealed that farmers give 7 to 10 applications of pesticides in/on tomato during cropping season. In order to minimize risk from exposure of pesticide residues, farmers must observe safe waiting period/Pre-Harvest Interval (PHI) before harvesting tomato fruits. They may be advised to prefer non chemical methods of pest control and apply only recommended (label claim) doses of

pesticides when pest population crosses economic threshold level (ETL).

Studies on dissipation of pesticides reveal that quinalphos and ethion persisted upto five and seven days on tomato at recommended and double the recommended doses, respectively. Persistence of carbendazim was for seven and ten days, respectively.

Half-life (RL_{50}) values calculated for quinalphos on tomato were 2.67 and 2.47 days, for both the doses, respectively. As there are no MRL's available for quinalphos in tomato, LOQ of 0.05 mg kg^{-1} is taken as MRL. Considering this, Pre-Harvest Interval (PHI) of seven days can be suggested for quinalphos for safe consumption of tomato fruits.

Half-life (RL_{50}) recorded for ethion in/on tomato were 2.95 and 2.47 days for recommended and double the recommended dose, respectively. As there is no MRL available for ethion in tomato, 0.05 mg kg^{-1} may be taken as a MRL. On the basis of this, Pre-Harvest Interval (PHI) of seven days can be suggested for ethion.

As regards carbendazim, half-life (RL_{50}) values calculated were 1.78 and 1.90 days for recommended and double the recommended dose, respectively. There is no prescribed MRL for carbendazim in tomato and hence 0.05 mg kg^{-1} may be taken as MRL. On this basis, Pre-Harvest Interval of ten days may be suggested for carbendazim in tomato for safe consumption of tomato fruits.

5. SUMMARY AND CONCLUSION

5.1 Summary

5.1.1 Pesticide usage pattern in tomato

During survey, the pesticide usage pattern in tomato indicated that the farmers from selected location of Ahmednagar district of Maharashtra relied mostly on chemical pesticides to control the pests and diseases of tomato. Survey reports revealed that farmers used different chemical pesticides most frequently viz., quinalphos, chlorpyrifos, ethion, indoxacarb, cypermethrin and fungicides like carbendazim.

Majority of the farmers sprayed at an interval of 7-10 days giving maximum 10 sprays during cropping season. Most of the farmers used conventional insecticides and very few farmers used novel insecticides. Majority of the farmers generally inclined to use combination of pesticides.

None of the farmers were aware of natural enemies, whereas only 8 and 12 per cent farmers were aware of effect of pesticide residues in/on food and safe waiting periods for harvesting, respectively. Few (8 %) farmers knew about recommended dose of insecticides. Most of the farmers used non recommended insecticides with higher doses.

5.1.2 Residues of quinalphos, ethion and carbendazim in/on tomato fruits and cropped soil.

5.1.2.1 Recovery study

In case of quinalphos, ethion and carbendazim in/on tomato fruits and soil, the mean per cent recovery at 0.05, 0.25 and 0.5 mg kg⁻¹ fortification levels varied between 87.61 and

107.35, 80.20 and 109.75, 79.50 and 94.96 respectively, which is within the acceptable range of 70-120 per cent.

5.1.2.2 Persistence and dissipation studies of quinalphos, ethion and carbendazim in/on tomato fruits and cropped soil.

The mean initial residues of quinalphos 25 EC @ 250 and 500 g a.i. ha⁻¹ in tomato fruits were found to be 0.28 and 0.58 mg kg⁻¹ which dissipated to BDL on 7th and 10th day after 2nd spray. The half life values were 2.67 and 2.47 days. The residues of quinalphos were found to be BDL in soil at harvest at both doses, respectively

As regards ethion 50 EC @ 500 and 1000 g a.i. ha⁻¹ the initial residues of 0.21 and 0.46 mg kg⁻¹ reached BDL at 7th and 10th day after 2nd spray. The half life values calculated were 2.95 and 2.47 days for both the doses, respectively. The residues of ethion were found to be BDL in soil at harvest.

As in respect of carbendazim 50 WP @ 150 and 300 g a.i. ha⁻¹, the initial residues of 0.99 and 1.24 mg kg⁻¹ reached BDL at 10th and 15th days after 2nd spray. The half life values calculated of 1.78 and 1.90 days. The residues of carbendazim were found to be BDL in soil at harvest.

5.3 Conclusion

Pesticides are toxic to substances and are likely to leave behind residues in crops. Hence, farmers may be advised to use pesticides judiciously by following Good Agricultural Practices. At present, no MRL's are prescribed for quinalphos, ethion and carbendazim in tomato. Pre harvest intervals of seven

days for quinalphos and ethion, whereas ten days for carbendazim be observed, if these pesticides are recommended on tomato.

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and soil inside and outside the greenhouse to Zhejiang University.

7. APPENDICES

APPENDIX I

Questionnaire of pesticide usage pattern on tomato

Pesticide Residues Laboratory, PGI Mahatma Phule Krishi Vidyapeeth, Rahuri		
1.	Name of Farmer
2.	Area under tomato crop
	➤ Major pest occurred on tomato
	➤ Other pest
	➤ Natural enemies	
3.	Insecticides used against fruit borer
4.	Insecticides used against mite and other sucking pest
5.	Do you know about fungicides used against disease?
6.	Information on application of biopesticides
7.	Do you know about recommended pesticides in tomato?
8.	Source of information for recommended pesticides - Agril. Dept/ Neighbour / Media / Dealers/ Scientists/ University.
9.	Do you know safe waiting period?
10.	Do you know about harmful effects of pesticide?

APPENDIX II

Meteorological data during experimental field

June 2015 - December 2015

Month	Meteorological Week	Date	Temperature (°C)		Humidity %		Rain Fall (mm)
			Max	Min	I	II	
June, 2015	22	28-03	39	23	56	26	03
	23	04-10	36	23	68	52	36
	24	11-17	32	23	72	65	26
	25	18-24	32	24	71	57	12
	26	25-01	34	23	66	45	00
July, 2015	27	02-07	35	24	66	43	00
	28	08-14	34	24	68	41	00
	29	15-21	33	24	74	58	17
	30	22-28	31	24	71	60	08
August, 2015	31	29-04	31	23	77	59	07
	32	05-11	30	22	76	60	04
	33	12-18	28	23	71	50	00
	34	19-25	33	22	71	49	01
	35	26-01	33	22	71	47	03
September, 2015	36	02-08	33	23	81	45	21
	37	09-15	31	22	79	58	48
	38	16-22	30	23	79	60	55
	39	3-29	34	20	68	41	00
October, 2015	40	30-06	33	21	76	50	21
	41	7-13	34	21	71	39	00
	42	14-20	35	19	56	30	00
	43	21-27	32	22	57	38	00
November, 2015	44	28-03	32	17	57	38	00
	45	04-10	33	17	58	38	00
	46	11-17	32	15	50	30	00
	47	18-24	30	18	71	59	26
	48	5-01	32	18	72	44	00
December, 2015	49	02-08	33	14	59	33	00
	50	09-15	32	16	49	33	00
	51	16-22	31	14	64	36	00

8. VITA

Miss. Sali Arati Ashok

A candidate for the degree

of

MASTER OF SCIENCE (AGRICULTURE)

in

AGRICULTURAL ENTOMOLOGY

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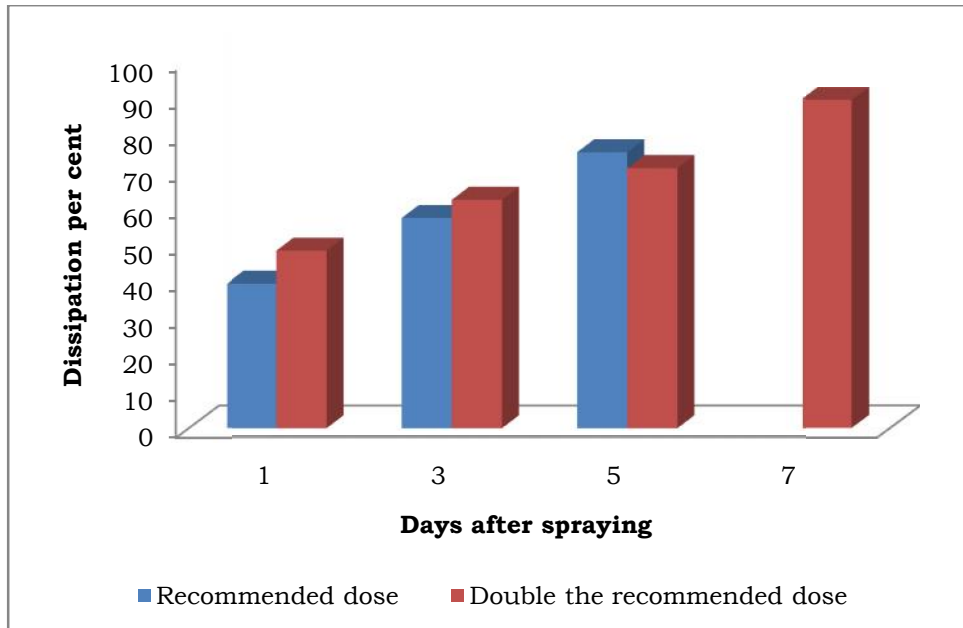


Fig. 4 Per cent dissipation of quinalphos in tomato

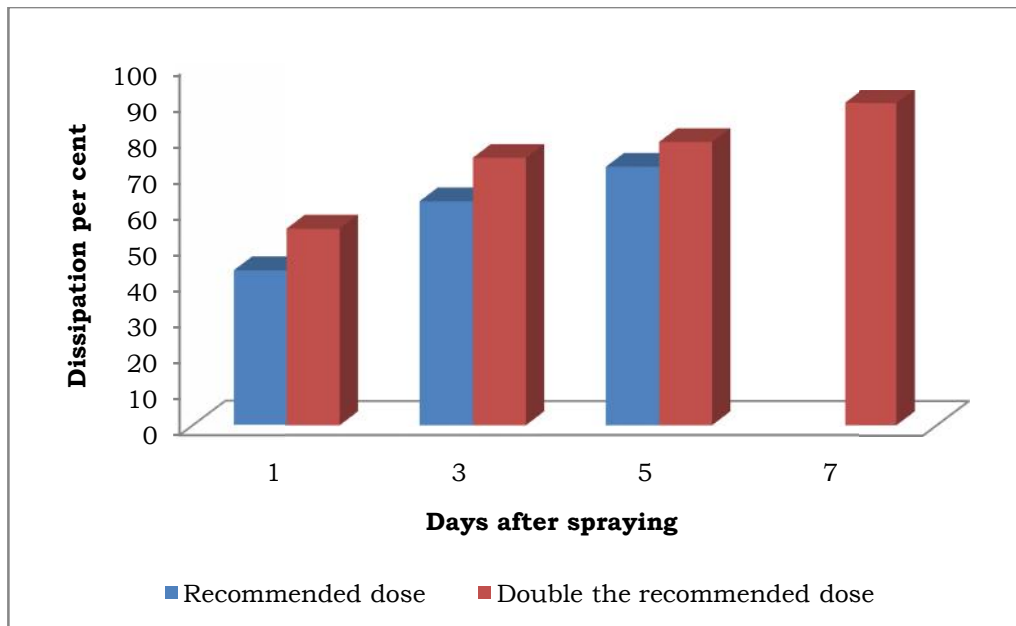


Fig. 5 Per cent dissipation of ethion in tomato

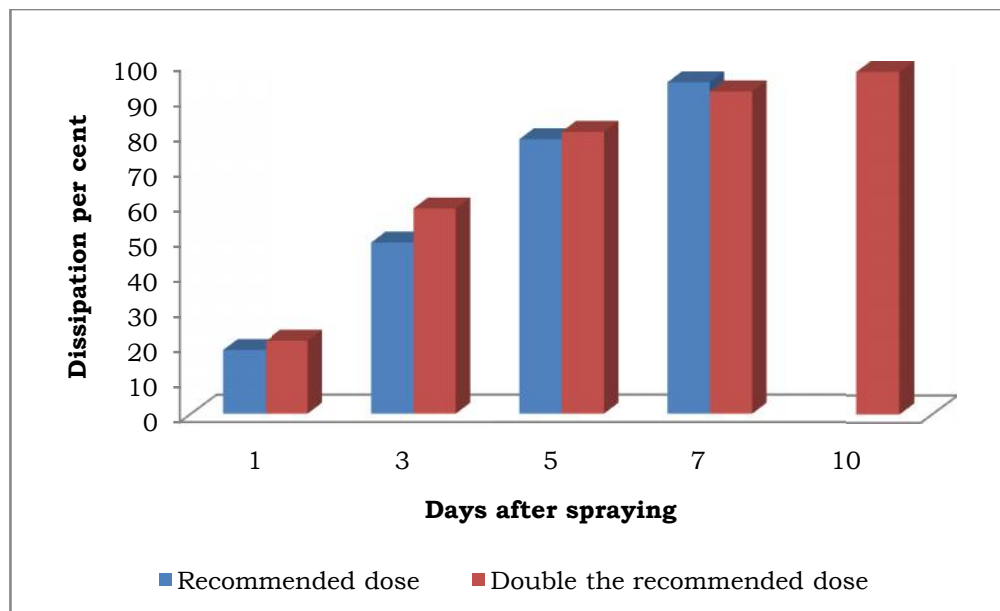


Fig. 6 Per cent dissipation of carbendazim in tomato

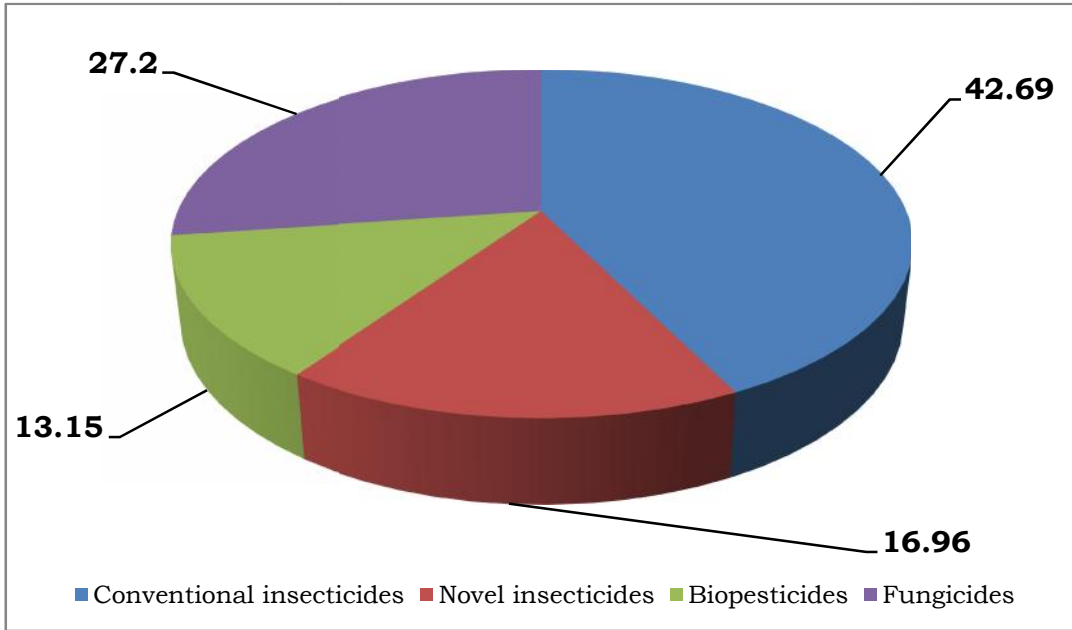


Fig. 1 Per cent share of pesticides used in Ahmednagar district during cropping season

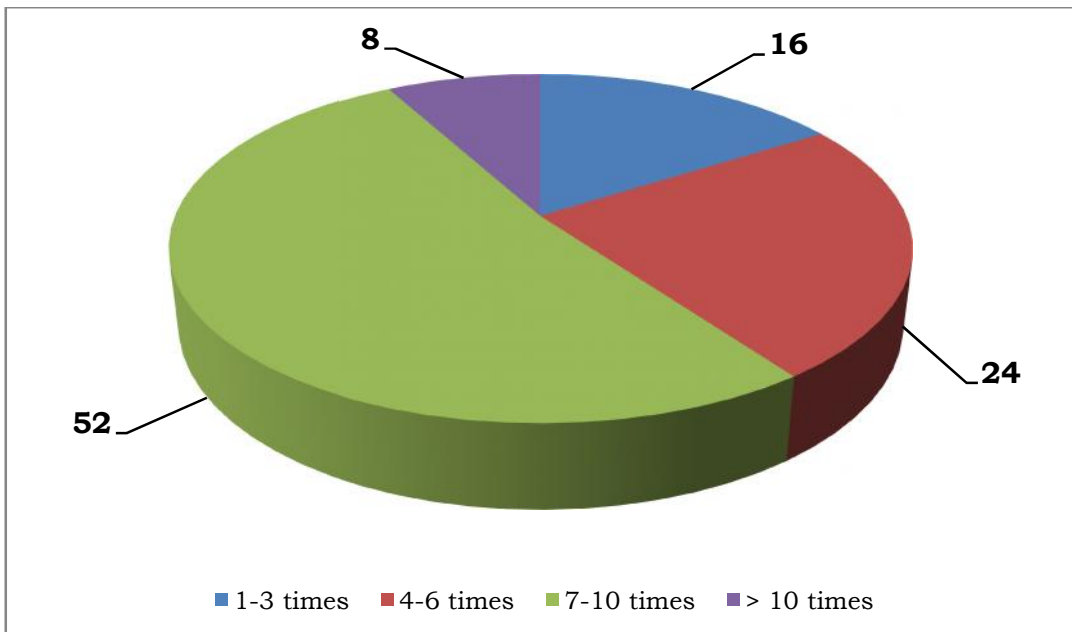


Fig. 2 Spraying interval followed by the farmers

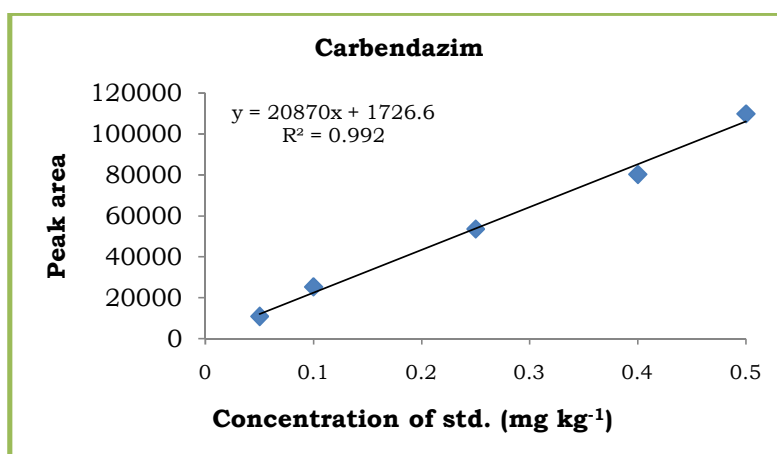
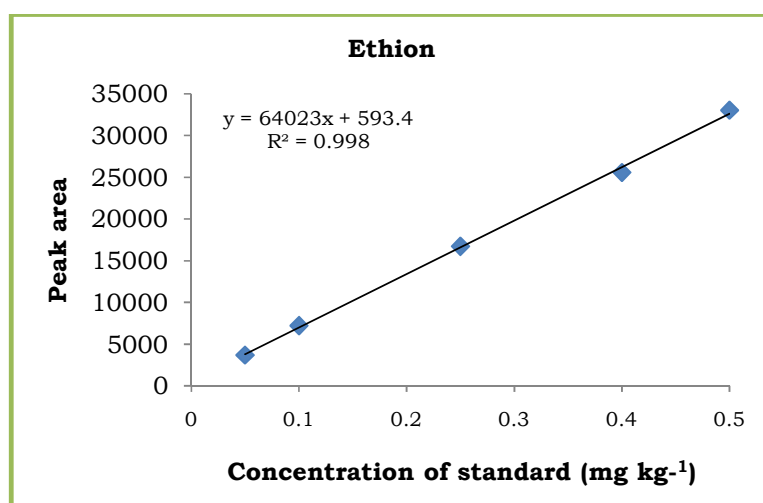
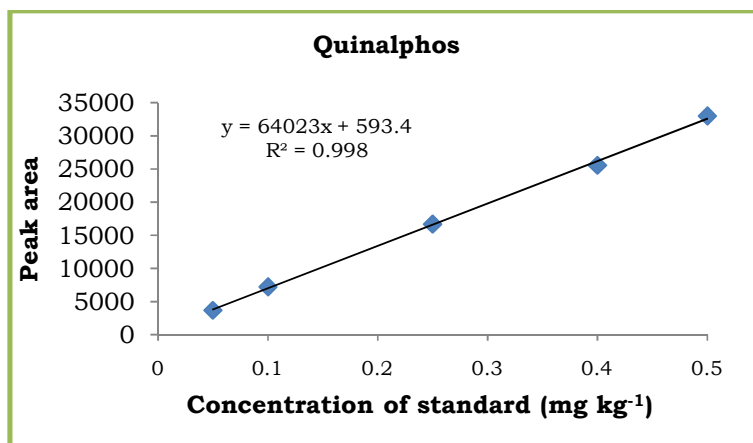


Fig. 3. Linearity of different pesticide standard



Grinder



Digital balance



Vortex



Centrifuge



Low volume concentrator



Biomedical deep freezer

Plate 2. Apparatus used during residue analysis



**Plate 3. Gas Chromatography – Mass Spectrometer
(GCMS-QP 2010 plus, Shimadzu)**



Plate 4. High Performance Liquid Chromatography equipped with DAD (LC-20 AT, Shimadzu)



Plate 1. Experimental field