

**PERSISTENCE OF TRIAZOPHOS, CHLORPYRIPHOS AND
QUINALPHOS IN/ON CHILLI AND CROPPED SOIL**

By

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(Reg. No. 014/161)**

**DEPARTMENT OF AGRICULTURAL ENTOMOLOGY,
POST GRADUATE INSTITUTE,
MAHATMA PHULE KRISHI VIDYAPEETH,
RAHURI-413722, DIST. AHMEDNAGAR,
MAHARASHTRA, INDIA.**

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A thesis submitted to the

**MAHATMA PHULE KRISHI VIDYAPEETH,
RAHURI – 413722, DIST. AHMEDNAGAR
MAHARASHTRA STATE (INDIA)**

In partial fulfillment of the requirement for the degree

of

MASTER OF SCIENCE (AGRICULTURE)

in

AGRICULTURAL ENTOMOLOGY

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This is to certify that the thesis entitled, "**PERSISTENCE OF TRIAZOPHOS, CHLORPYRIPHOS AND QUINALPHOS, IN/ON CHILLI AND CROPPED SOIL**" submitted to the Faculty of Agriculture, Mahatma Phule Krishi Vidyapeeth, Rahuri, Dist-Ahmednagar, Maharashtra, India, for the award of the degree of **MASTER OF SCIENCE (AGRICULTURE)** in **AGRICULTURAL ENTOMOLOGY**, embodies the results of a piece of *bona fide* research work carried out by **Miss. ARATI NIVRUTTI RAUT**, under my guidance and supervision and no part of the thesis has been submitted for any other Degree or Diploma. The assistance and help received during the course of this investigation has been duly acknowledged.

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CERTIFICATE

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Dated :- / /2016

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LIST OF ABBREVIATIONS

a.i.	:	Active ingredients
ADI	:	Acceptable Daily Intake
BDL	:	Below Detectable Limit
Cm	:	Centimetre
CRM	:	Certified Reference Material
EC	:	Emulsifiable concentrates
<i>et al.</i>	:	<i>et alli</i> (and other)
etc.	:	<i>Et cetera</i> and so on
ETL	:	Economic Threshold Level
Fig.	:	Figure (s)
g	:	Gram (s)
GCMS	:	Gas Chromatography Mass Spectrometry
GAP	:	Good Agricultural Practices
HPLC	:	High Performance Liquid Chromatography
Ha	:	Hectare (s)
hr	:	Hour (s)
i.e.	:	id est (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)

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mm	:	Millimetre (s)
MRL	:	Maximum Residue Limit
MT	:	Metric tone
ND	:	Not Detected
nm	:	Nanometre
ng	:	Nanogram (s)
PHI	:	Pre Harvest Interval
PPA	:	Personal Protective Equipment
ppm	:	Parts per million
PSA	:	Primary secondary amine
Pvt.	:	Private
Q/q	:	Quintal (s)
QuEChERS	:	Quick Easy Cheap Effective Rugged Safe
R	:	Regression coefficient
RL ₅₀	:	Residual life 50
rpm	:	Revolution per minute
RSD	:	Relative standard deviation
RT	:	Retention time
Sec	:	Seconds
SP	:	Soluble Powder
T _{1/2}	:	Half life
Temp.	:	Temperature
µg	:	Microgram (s)
µl	:	Microlitre (s)
V	:	Volume
Viz.	:	Videlicet (Namely)
WP	:	Wettable powder
Wt	:	Weight
-	:	Minus
<	:	Less than

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@	:	At the rate
+	:	Plus
±	:	Plus or minus
≤	:	Less than or equals to
>	:	Greater than
°C	:	Degree Celcius
%	:	Per cent

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ABSTRACT

PERSISTENCE OF TRIAZOPHOS, CHLORPYRIPHOS AND QUINALPHOS IN CHILLI AND CROPPED SOIL

by

Arati Nivrutti Raut

A candidate for the degree of

MASTER OF SCIENCE (AGRICULTURE)

**MAHATMA PHULE KRISHI VIDYAPPETH,
RAHURI-413 722**

2016

Research Guide :	Dr. C. S. Patil
Department :	Agricultural Entomology

An investigation entitled “Persistence of triazophos, chlorpyriphos and quinalphos in/on chilli and cropped soil” was undertaken during 2015-16 at the Department of Agricultural Entomology, Post Graduate Institute, M.P.K.V., Rahuri.

Survey on pesticide use pattern indicated that farmers relied mostly on chemical insecticides to control the chilli pest. The insecticides *viz.*, chlorpyriphos, triazophos, cypermethrin, thiamethoxam *etc.*, were most widely used with higher doses. It was also observed that the chilli grower from surveyed area followed routine spraying pattern. Majority of farmers sprayed the crop at an interval of 6 to 10 days giving maximum 7-9 sprays during cropping season.

Studies on the dissipation of triazophos, chlorpyriphos and quinalphos in/on chilli were undertaken by following application of

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Abstract contd.....**A. N. Raut**

insecticides at recommended and double the recommended dose at fruit initiation stage. Triazophos @ 500 and 1000 g a.i. ha⁻¹, chlorpyriphos @ 300 and 600 g a.i. ha⁻¹ and quinalphos 250 and 500 g a.i. ha⁻¹, were applied twice at an interval of 10 days. The mean initial residues of triazophos (1.12 and 2.34 mg ka⁻¹), chlorpyriphos (0.85 and 1.70 mg kg⁻¹) and quinalphos (0.96 and 1.83 mg ka⁻¹) reached to BDL on 10th and 15th days at recommended and double the recommended dose, respectively.

The residue dissipated with half life of 1.72 and 1.99, 2.05 and 2.74 and 1.99 and 2.07 for triazophos, chlorpyriphos and quinalphos were at recommended and double the recommended dose, respectively. The residue of above insecticides was found to be below detection limit (BDL) in soil at harvest.

Considering this, Pre-Harvest Interval (PHI) of seven days can be suggested for triazophos, chlorpyriphos and quinalphos in chilli.

Total pages: 1 to 78

1. INTRODUCTION

Chilli (*Capsicum annum* L.) also called “red pepper” is an important cash crop in India and is grown for its pungent fruits, which are used both green and ripe to impart pungency to the food. The pungency is due to the active principle ‘capsicin’ contained in the skin and septa of the fruit.

Chilli is rich in vitamin ‘A’ and ‘C’, whereas seeds contain traces of starch which has medicinal significance in dyspepsia and to prevent blood cancer. Capsicin extracted from chilli is used in pharmaceutical industry. Oleoresin and essential oils of chilli are active constituents for providing characteristic pungency, flavour, aroma and have number of uses in industries. Different varieties of chilli are grown for vegetables, spices, condiments, sauces and pickles. It is an important ingredient in day-to-day curries, pickles and chutneys. As a condiment, it has become indispensable in every Indian home.

In India, chilli is grown in almost all the states covering an area of 7,75,000 ha producing 10,18,000 tones dry chilli with an average productivity of 1.9 MT in year 2013-14 (Anon; 2014). India is one of the largest chilli producer which contributes about 36 per cent (0.45 million tones) of global production (Anon; 2010). Andhra Pradesh, Karnataka, Tamil Nadu and Maharashtra are the major chilli producing states in India. Andhra Pradesh is leading both in area and production contributing 25 per cent of an area and 40 to 50 per cent of production.

In Maharashtra, chilli crop is grown over an area of 1,43,000 ha. The average yield of chilli in Maharashtra is only 2.15 q ha⁻¹. The low production of chilli in the country could be attributed to several factors. One of the most important being the damage caused by various insect pests. The insect pests attacking chilli crop includes thrips, mites and pod borers.

Insects and mites were responsible for about 34 per cent destruction in chilli crop. In order to control the damage caused by these pests, pesticides are being used by the farmers even during fruiting stage. Organophosphates and pyrethroids are most commonly and frequently used insecticides for these pests (Sanap and Nawale, 1986).

Recently, it has been revealed that samples of chilli fruits collected from market and farmgate were contaminated with pesticides like chlorpyrifos, triazophos and quinalphos. These pesticides are not recommended for use on chilli fruit in India. In order to fix MRL's of these pesticides in/on chilli fruits, it is necessary to generate information on persistence of these pesticides by conducting supervised field trial as per Good Agricultural Practices (GAP).

Indiscriminate and repeated use of conventional insecticides accumulate the toxic pesticide residues on an agricultural produce and pose serious threat to the health of consumers. India is dominating the world market in chilli as a spice product. The trend in the export of chilli is very encouraging, but on other hand, the exports are rejected due to pesticide residues

(Reddy, *et al.*, 2007 b). In 2001, Germany and Greece rejected red chilli and chilli powder due to pesticide residues (Rao, *et al.*, 2005).

There has been an increasing concern and awareness on hazards of pesticide to consumers. Even with adoption of integrated pest management practices, farmers still believe in the control of pests using pesticides because of its quick effect. The application of pesticide or post harvest application could however, leave residues on food products, which pose a potential risk to the health of consumers (Lindsay, 1997). The presence of pesticide residues in food commodities is the concern to human health due to the toxic nature of pesticides. Hence, it is imperative to study the persistence of pesticides on edible crop to ensure that the levels of harvest time residues are within prescribed limits in domestic as well as international trade.

Keeping this in mind, studies were undertaken with the following objectives

1. To study the pesticide usage pattern in chilli.
2. To study the persistence of triazophos, chlorpyrifos and quinalphos in/on chilli.
3. To study the harvest time residues of triazophos, chlorpyrifos and quinalphos in cropped soil.

2. REVIEW OF LITERATURE

Chilli crop is seriously affected by sucking pests like thrips, mites and also pod borers. In order to control the damage caused by these pests, pesticides are being used by the farmers even during fruiting stage.

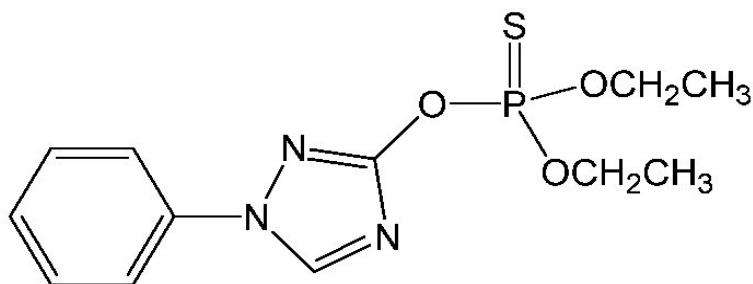
Excessive use of insecticides resulted in the development of resistance in insect, resurgence, destruction of natural enemies and pollution in the environment. However, chemical control is still the first line of defense against insect pests of chilli.

The technical information of these insecticide and available literature on pesticide usage pattern and work done on persistence of insecticides in chilli, other vegetables and cropped soil have been reviewed and presented in this chapter.

2.1 Technical information of insecticides

2.1.1 Triazophos

Chemically it is known as O, O-diethyl O-1-phenyl-1, 2, 4-triazol-3-yl phosphorothioate. Its empirical formula is $C_{12}H_{16}N_3O_3PS$ with the following chemical structure.

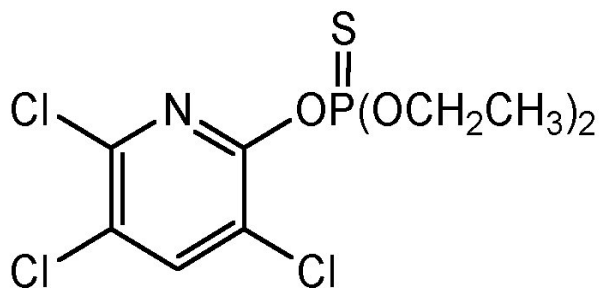


Triazophos

It is light brown yellowish liquid having vapour pressure of 2.9×10^{-6} mm Hg. It is soluble in most organic solvents. The water solubility is 39 mg L⁻¹. It has insecticidal and acaricidal properties as well as some nematicidal properties. It is effective against a variety of pests particularly lepidopteran larvae on fruits and vegetables. It is usually recommended @ 500 g a.i. ha⁻¹ on cotton against boll worm. It has also been reported effective against cutworms.

2.1.2 Chlorpyrifos

Chlorpyrifos is an organophosphorous insecticide chemically known as 0,0-diethyl-0-3,5,6-trichloro-2-pyridyl phosphorothioate. Its empirical formula is C₉H₁₁Cl₃NO₃PS with the following structure.



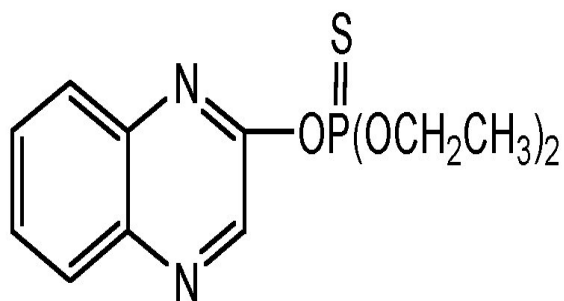
Chlorpyrifos

It is colourless crystals with a mild mercaptan odour. Its solubility at 35°C is 2 mg L⁻¹ water and readily soluble in most other organic solvents. It is compatible with non-alkaline pesticides but is corrosive to copper and brass. It has a broad range of insecticidal activity and is effective by contact, ingestion and vapour action. It is

non-systemic, used for the control of mosquitoes, flies, various soil insects and many foliar crop pest and household pests. It is also used for ectoparasite control on cattle and sheep. In India, it is widely recommended as seed treatment against white grub and termites. It is non-phytotoxic at insecticidal concentration and persists in soil for 60-120 days. The acute oral LD₅₀ for rats is 135-163 mg kg⁻¹. The acute dermal LD₅₀ in solution for rabbit is 2000 mg kg⁻¹. It is rapidly detoxified in the animal body. It is toxic to shrimps and fish. Chlorpyriphos is formulated as wettable powder (250 g a.i kg⁻¹), emulsifiable concentrate (240 and 480 g a.i.L⁻¹) and granules (10 and 100 g a.i. kg⁻¹).

2.1.3 Quinalphos

Chemically it is known as 0,0-diethyl 0-quinoxalin-2-yl phosphorothioate. Its empirical formula is C₁₂H₁₅N₂O₃PS with the following structure.



Quinalphos

It is contact poison having good penetrating power. 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 rat 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. 2 Pesticide usage pattern in chilli crop

Pesticides are with their enormous benefits; but their indiscriminate application by the producers has raised serious concerns about environment and human health. In this regard, the survey undertaken on usage pattern of the different region has been revised and presented hereunder.

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

Muzlon and Mumford (2005) investigated Cameron Highland's cabbage farmers' knowledge and practices of pest management, particularly the use of pesticides against *Plutella xylostella*. A survey of 99 cabbage farmers was conducted in five different zones in the Cameron Highlands. This survey and others conducted by previous researchers showed little change in farming systems over the past decade. *P xylostella* remained the major pest in cabbage and more than 90 per cent of farmers used pesticides for control. There were 11 types of insecticides used to control this pest and each farmer usually used 3–4 types of insecticides to control the pest over a season. Both high and low toxicity pesticides were commonly used. The study also revealed that more than 50 per cent of farmers observed 10–14 day pre-harvest intervals, while 4 per cent observed a pre-harvest interval of only 1–4 days.

Mukherjee and Singh (2005) conducted surveys in the villages of Karsara, Madaon and Tikari in Varanasi, Uttar Pradesh, India, to determine the type and quantity of insecticides used by the farmers. The most commonly used insecticides included endosulfan, methyl parathion, carbofuran, dimethoate, phosphamidon, quinalphos, HCH and in some cases cartap hydrochloride and DDT.

Borjan *et al.* (2006) conducted pesticide use survey of licensed pesticide applicators in New Jersey every three years since 1985 for the purpose of tracking pesticide use amounts and patterns. Information collected indicated slow increase with golf course and mosquito control pesticide use and slow decrease in

agriculture use over the past 20 years, with lawn care pesticide use remaining relatively even.

Willam *et al.* (2006) surveyed pesticide use practices of 137 vegetables growing farmers in Ghana. The results revealed that 43 pesticides were used for crop production. The pesticide comprised, herbicides (44 %), insecticides (23 %) and fungicides (23 %). The majority of farmers ranked cypermethrin as the most effective insecticide against insect pests followed by lambda cyhalothrin and endosulfan in that order. The number of spray application per crop, season, however, varied widely among crops, location and the farmer interviewed in the survey. For instance, in a tomato, farmer sprayed an average of 6-12 application with 3-6 insecticides on a calendar basis in 90 days season of tomato.

Magdoleen (2007) studied the seasonal variation of pesticide residues in some salad vegetables in Khartoum State – Sudan. Study revealed that out of the 77 farmers checked for such practices, almost more than one fourth of these farmers used the pesticide malathion with all the salad vegetables although most of the latter group used this pesticide with tomatoes. About 20 per cent of these farmers used Sevin with all salad vegetables, with emphasis on tomatoes. The remaining farmers exhibited variations in using other pesticides such as cypermethrin (11%), sumicidin (8 %) etc.

Plianbangchang *et al.* (2009) surveyed 130 farmers to study pesticide usage in rural Phstsanulok of northern Thailand during 2007-08. The results indicated that 94.6 per cent

respondents using pesticides in crop production, while 66 farmers (50.8%) used chemicals only and 57 farmers (43.8%) used combined pesticides with biological control agents. Chlorpyrifos was the most frequently used by the farmers followed by cypermethrin.

Survey of pesticide usage pattern against bitter gourd in Kerala revealed that out of 15 pesticides, eight insecticides, four fungicides, one herbicide and rest were plant growth stimulators. Further, farmers changed the chemicals in each spray. Acetamiprid was used six times, phorate and dimethoate five times each. Quinalphos and indoxacarb four times each and rest 3 to 4 times during a crop cycle of 90 days in bitter gourd in all total 50 spray (Devi, 2010).

Shetty *et al.* (2010) conducted intensive survey involving 1039 farmers belonging to 28 districts of 12 states in India, to study the influence of farmer's awareness, education and practices related to pesticide use as well as Integrated Pest Management (IPM) measures. Survey revealed that more than 50 per cent of the respondents applied both single and cocktail pesticides to manage their crop pests. Only 20 per cent of the respondents obtained their information on plant protection aspect from the agricultural extension officer.

Nyakundi *et al.* (2011) surveyed 100 respondents for pesticide usage pattern against major horticultural crops in Kenya during 2009-10. Results indicated that 62 per cent respondents using recommended dosage of pesticide dosage and 12 per cent used above recommended dosage. Most commonly used insecticides

were methomex 90 SP and diazo 60 EC. All pesticides were stated by their trade names without any awareness of the common names.

Al-Sayed *et al.* (2011) carried out a survey of farmers (n=126) in five districts of the West Bank and Gaza Strip, where pesticides were mostly used on irrigated land cultivated with vegetables. Data analysis of received questionnaires revealed that total number of 217 pesticides including 13 soil sterilizers, while 134 kinds with different active ingredients (insecticides 62; fungicides 45; herbicide 20) were applied in all districts. Based on the total irrigated land cultivated, the rate of pesticides per annum per farmer reached 0.77 L in Gaza Strip and 0.18 L in the West Bank districts.

Chandi *et al.* (2012) reported that eighteen insecticides singly and four mixtures were being used extensively by the vegetable growers of the Ludhiana. On an average, 4.9 sprays (range 3-11 sprays) were done by each cabbage/cauliflower grower. Out of these, 12.2 per cent sprays were done with recommended insecticides, 71.9 per cent with non recommended insecticides and 15.8 per cent with non recommended mixtures. Spinosad 48 SC and chlorantraniliprole 18.5 SL, being non recommended, were used to the tune of 28 per cent, while, endosulfan (6.3%) lead in recommended insecticides. Cypermethrin and fenvalerate were the most frequently used mixtures.

Tandi *et al.* (2014) studied the perception on pesticide usage and practices in Buea Cameroon. They conducted survey on small-scale tomato cultivators'. Through a standardized

questionnaire, interviews, field observations and an analytical ranking game were used to describe the pesticide use of 93 tomato growing farmers. It was observed that many farmers (47.6%) used pyrethroid and organophosphorus insecticides and identified these chemicals as the most effective in pest control. Most farmers (83.8%) used knapsack sprayers to apply pesticides, with 76.3 per cent using no or partial personal protective equipment (PPE). Most farmers (85 %) reported at least one symptom of acute pesticide poisoning following spraying.

Banerjee *et al.* (2014) studied the pesticide use pattern among 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%), imidacloprid (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.

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 was used by most farmers both as

an insecticide and nematicide 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 were using synthetic pesticide formulations as crop protection to combat various pests and insects. The widely used insecticides were chlorpyrifos, monocrotophos, cypermethrin, quinalphos, fungicides including copper oxide, bavistin and mancozeb. Glyphosate and paraquat were used under herbicides group. Survey results further revealed that, multiple formulations of pesticides were used for a single crop.

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 azadiractin (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 chlorpyrifos, triazophos and quinalphos in/on chilli

Insecticides are being used for protecting the crops from pests. The pest problem in chilli is so acute that without the use of plant protection chemicals, no produce can be harvested. Some chemicals do not pose any health hazards in the harvested produce while some others leave toxic residues at the time of harvest. Hence, knowledge on the amount of insecticidal residues left in green chilli is estimated for the proper selection of insecticides and the time required for harvesting chilli from the time of application of chemicals. The residual toxicity of various insecticides has been reported by various workers on chilli crop.

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 mg kg⁻¹ (89.6%) 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.

Reddy *et al.* (2007 a) studied the dissipation of fipronil and profenofos on chilli by spraying at 15 days interval, starting

from 45 days after transplanting. Results revealed that initial deposits of fipronil and profenofos after last spray were 0.20 and 0.36 mg kg⁻¹, which dissipated to 0.01 and 0.02 mg kg⁻¹ by 30 days amounting to the loss of 94.0 and 92.4 per cent, respectively. Half-life values for fipronil and profenofos were 16.8 and 41.0 days, respectively. Waiting period (T_{tol}) of 5 and 19 days has been suggested. The residues in dried chilli were below detectable level (BDL).

Studies on the dissipation of dimethoate, ethion and oxydemeton-methyl on chilli revealed 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 and on the 10th day 87.92 per cent of the residue gets dissipated and 96.72 per cent of the residue get dissipated on the 15th days. The residues were below detectable level on the 20th day of spraying and the LOQ for this method was 0.01 mg kg⁻¹ (Varghese *et al.*, 2011)

Waghulde *et al.* (2011) studied the dissipation of endosulfan, chlorpyrifos, dimethoate and malathion on chilli and okra fruits. Results revealed that half life of residues in chilli and okra varied from 3.22 to 5.49 and 3.68 to 6.92 days, respectively and waiting period from 9.38 to 18.08 and 14.54 to 20.9 days, respectively.

Mathew *et al.* (2012) studied the dissipation of combination mixture (spirotetramat 120 + imidacloprid 120) – 240 w/v SC on chilli at two doses of 120+120 and 240+240 g a.i.ha⁻¹ by applying thrice at 10 days interval starting from fruit setting stage.

The results revealed that the mean initial deposit of spirotetramat in green chilli was 1.2 to 1.75 mg kg⁻¹ for lower and higher dose, respectively, dissipated and reached below quantification level within 15 and 20 days. The half life values were 2.01 and 3.09 days for both the treatments. The mean initial deposits of imidacloprid in green chilli was 2.53 and 3.15 mg kg⁻¹ for lower and higher dose, respectively dissipated and reached below quantification limit within 30 and 35 days. The half life values were 5.82 and 5.77 day for both the treatments.

Jyot *et al.* (2013) studied the dissipation of chlorpyrifos and cypermethrin on chilli with three applications of a combination formulation of Nurelle-D 505 (chlorpyrifos 50 % + cypermethrin 5 %) at 1 and 2 L ha⁻¹ at an interval of 15 days. Half-life periods for chlorpyrifos were found to be 4.43 and 2.01 days, whereas for cypermethrin these values were observed to be 2.51 and 2.64 days at single and double the application rates respectively. It also observed that residues of chlorpyrifos dissipated to more than 80 per cent after 10 days at both the doses. However, residues of cypermethrin dissipated to the extent of more than 70 per cent in 7 days. Soil samples collected after 15 days of the last application did not show the presence of chlorpyrifos and cypermethrin at their respective determination limit of 0.01 mg kg⁻¹.

Sharma and Parihar (2013) studied the dissipation and persistence of dimethoate and ethion on chilli (*Capsicum annuum L.*) after spraying twice with dimethoate 30 EC @ 300 and 600 g a.i. ha⁻¹ and ethion 50 EC @ 500 and 1000 g a. i. ha⁻¹ at 45 days after transplanting and second spray at 15 days there after. Initial

residues of dimethoate on chilli were 3.12 and 5.16 mg kg⁻¹ and the half life values were 1.74 and 1.51 days, respectively at 300 and 600 g a.i. ha⁻¹ and the respective waiting periods were 3.29 and 4.50 days. In case of ethion, initial deposit were 2.40 and 4.84 mg kg⁻¹ and half life values were 1.81 and 2.32 days at 500 and 1000 g a. i. ha⁻¹, respectively.

Dissipation studies of neonicotinoid insecticides, revealed that residues of imidacloprid persisted up to 7 days, whereas the acetamiprid persisted up to 15 days of spraying. The half-life values of acetamiprid and imidacloprid were 2.27 and 2.08 days, respectively. Waiting period of 7.18 and 11.26 days for acetamiprid and imidacloprid was suggested in chilli (Varghese *et al.*, 2014).

Singh *et al.* (2015) studied the dissipation pattern of triazophos on capsicum following two applications of triazophos (Truzo 40 EC) at 500 and 1000 g a.i. ha⁻¹, Mean initial deposits were found to be 3.61 and 6.26 mg kg⁻¹, respectively. These residues dissipated below the limit of quantification (LOQ) of 0.05 mg kg⁻¹ in 10 and 15 days and half-life values were 2.31 and 2.14 days at recommended and double the recommended doses, respectively.

2.4 Residues of insecticides in cropped soil

Studies on persistence of chlorpyrifos and fenprothrin pesticides in soil revealed that chlorpyrifos and fenprothrin were stable upto 2 months in soil i.e. degradation was not observed in the parent compound of both the pesticides (Akhtar *et al.*, 2004)

Li *et al.* (2005) determined the degradation dynamics and final residues of triazophos in litchi and soil by single application of

triazophos at a dose of 500 times. The results revealed that the initial residues in litchi flesh and skin were 0.04-0.07 and 4.05-4.77 mg kg⁻¹, respectively and the half life values were 6.8 and 8.2 days, respectively. The initial residues and the half life in soil were 0.13-0.18 mg kg⁻¹ and 7.4 days, respectively.

Ngan *et al.* (2005) studied the fate of chlorothalonil, chlorpyrifos and profenophos in sandy loam soil under tropical condition. The results revealed that residues of chlorothalonil, chlorpyrifos and profenophos in soil were in the range of <0.01-0.08 mg kg⁻¹, < 0.01-0.06 mg kg⁻¹ and < 0.01-0.02 mg kg⁻¹, respectively. All three pesticides dissipated rapidly, with DT₅₀ of less than two days.

Kumari *et al.* (2008) studied the status of insecticide contamination in soil. cypermethrin (0.001–0.035 µg g⁻¹) and fenvalerate (0.001–0.022 µg g⁻¹) among synthetic pyrethroids and chlorpyrifos (0.002–0.172 µg g⁻¹), malathion (0.002–0.008 µg g⁻¹), quinalphos (0.001–0.010 µg g⁻¹) among organophosphates were estimated.

Wei *et al.* (2008) studied the dissipation rates in wheat crops and soil. They reported that maximum residues of triazophos in wheat grain, stems and leaves and soil were 1.865, 44.506 and 0.973 mg kg⁻¹, respectively. It was further revealed that the mean half life of triazophos in wheat plants (grain, stems and leaves) was 5.22 days with a dissipation rate of 90 per cent over 14 days. The half life in soil was 7.93 days with a dissipation rate of 90 per cent over 21 days.

Aktar *et al.* (2008) studied the degradation dynamics and persistence of quinalphos and methomyl in okra fruits and cropped soil by applying four sprays at 15 days interval at the recommended and double the recommended dose (i.e. 500 and 1,000 g a.i. ha⁻¹). Results revealed that residues of both insecticides in soil persisted for 6–8 days depending on dose. The half-life in soil were found to be 1.07–1.20 days for Quinalphos and 0.97–1.25 days for Methomyl.

Gilani *et al.* (2010) studied chlorpyrifos degradation in soil and reported that chlorpyrifos remained stable in soil for one year.

Gupta *et al.* (2011) studied the dissipation of cypermethrin, chlorpyrifos and profenofos in tomato fruits and soil by application of two premix formulations of insecticides *viz.* Rokat 44 EC (profenofos 40% + cypermethrin 5%) and Action 505 EC (chlorpyrifos 50%+ cypermethrin 5%) at recommended (0.8-1.0 L ha⁻¹) and double dose (1.6-2.0 L ha⁻¹). In all the treatments, residues persisted beyond 7 days in tomato fruits. In case of Rokat 44 EC, residues of cypermethrin on fruits dissipated with half life of 2.0-3.6 days, whereas residues of profenofos dissipated with the half life of 2.2-5.4 days. In case of Action 505 EC, residues of chlorpyrifos and cypermethrin dissipated from fruits with the half life values of 2.9-3.3 and 2.5-4.8 days, respectively. In soil, residues of profenofos persisted for 7-15 days, whereas residues of chlorpyrifos and cypermethrin persisted for 0-7 days only.

Gaur *et al.* (2011) studied the residues of pesticides in soil and reported that chlorpyrifos, phosphomidon, quinalphos, ethion

and monocrotophos were the most frequently detected pesticides. Phosphamidon (10.47 ng g^{-1}) and chlorpyriphos (8.86 ng g^{-1}) concentrations were the highest followed by monocrotophos (3.45 ng g^{-1}), quinalphos (3.26 ng g^{-1}) and ethion (3.23 ng g^{-1} .)

Akan *et al.* (2013) determined the concentrations of some organophosphate pesticide residues (dichlorvos, diazinon, chlorpyriphos and fenitrothion) in different depth of soil samples from Alau Dam Agricultural site, Borno State, Nigeria. Results revealed that the concentration of these pesticides for 0-10 cm depth ranged from 57.98 to $232.98 \mu\text{g g}^{-1}$, 78.92 to $264.98 \mu\text{g g}^{-1}$ at 11-20 cm depth and 88.98 to $287.89 \mu\text{g g}^{-1}$ at 21-30 cm depth. The lowest value of $57.98 \mu\text{g g}^{-1}$ was observed at depth of 0-10 cm, while the highest concentration of $287.89 \mu\text{g g}^{-1}$ was observed at depth of 21-31 cm.

Mohapatra and Deepa (2013) studied the persistence and dissipation of quinalphos in cauliflower and soil under semi arid conditions of Karnataka. They reported that initial residues of quinalphos on cauliflower after applications at 2 concentrations, i.e. recommended and double the recommended dose ($500 \text{ g a.i. ha}^{-1}$ of $1,000 \text{ g a.i. ha}^{-1}$) were 1.19 and 1.84 mg kg^{-1} . The residues persisted up to 15 days from both the treatments. The residues of quinalphos dissipated from both treatments with half-life of 4.8 and 5.3 days. Analysis of soil samples was carried out on the 15th day of sampling and residues were found to be 0.01 and 0.04 mg kg^{-1} .

2.5 Residues of insecticides on other vegetables and fruits.

Raj *et al.* (1999) studied the dissipation of triazophos from brinjal and okra fruits following its application at 350 and 700 g a.i.ha⁻¹. The results revealed that initial residues of triazophos in okra were found to be 2.54 and 6.61 µg g⁻¹ with a half-life of 1 day. Whereas initial residues in brinjal were found to be 0.16 and 0.21 µg g⁻¹ with half life of 1 and 2 day for the lower and the higher doses, respectively. The residues persisted up to 10 days on okra and up to 15 days on brinjal

Khan *et al.* (1999) studied the dissipation of dichlorvos and dimethoate residues in okra. The results revealed that the initial deposits of 2.07 and 2.93 mg kg⁻¹ of dichlorvos and dimethoate, dissipated to 0.04 mg kg⁻¹ (98.97 %) and 0.31 mg kg⁻¹ (89.42%), respectively, after spraying five times at an interval of 10 days. Waiting periods (T_{tol}) suggested for dichlorvos and dimethoate were 2.34 and 2.19 days, respectively.

Hassan *et al.* (2005) investigated the residual persistence of chlorpyrifos, imidacloprid and acephate in brinjal fruit. The results revealed that residues of the aforesaid insecticides on the three sampling periods i.e. 3 hrs, 3 day and 7 day ranged from 0.075-0.039, 0.038-0.015 and 0.067-0.040 ppm, respectively. The quantity of insecticide residues was negligible in the brinjal fruit. This leads to conclusion that it was safe to recommend brinjal fruit for human consumption after 3 days of spraying.

Parasnath *et al.* (2005) studied the persistence and dissipation of ready mix Polytrin C 44 EC (profenophos 40 % + cypermethrin 4%) and Spark 36 EC (triazophos 35% + deltamethrin

1%) applied @ 1 L ha⁻¹ in okra crop. Results revealed that deposits of triazophos were 1.52 µg g⁻¹ ± 0.0008 on zero day. The residues dissipated by 37.6 per cent with average deposits of 0.95 µg g⁻¹ ± 0.002 on the first day which further dissipated by 72.1 per cent leaving residues 0.42 µg g⁻¹ ± 0.003 on third day and 77.0 per cent degradation on fifth day showing average deposits of 0.35 µg g⁻¹ ± 0.003. Finally, on 7th day, the residues dissipated to the tune of 86.2 per cent leaving deposits of 0.21 µg g⁻¹ ± 0.003. Half-life period of triazophos was 2.55 days.

Raina and Raina (2008) studied the dissipation of chlorpyrifos after applying chlorpyrifos at recommended and double the recommended dose (i.e. 500 and 1000 g a.i. ha⁻¹.) on cauliflower. Results revealed that the average initial deposits varied from 0.56 to 0.86 and from 1.29 to 1.43 mg kg⁻¹, for lower and higher doses, respectively. The residue half-life of chlorpyrifos varied from 1.4-1.5 and 1.5-1.6 days for lower and higher doses, respectively. The residues reached below the MRL of 0.05 mg kg⁻¹, in 5.0-6.3 and 7.1-7.3 days at normal and double dose, respectively.

Aktar *et al.* (2010) studied risk assessment and decontamination of quinalphos under different culinary processes in cabbage for two consecutive seasons. Results revealed that the initial deposits (3 hr 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 deposits were dissipated within 48 hour 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.

Samriti *et al.* (2011) studied the persistence and effect of processing on reduction of chlorpyrifos residues in okra fruits with the application of chlorpyrifos (Radar 20 EC) at 200 g a.i. ha⁻¹ and 400 g a.i. ha⁻¹. The results revealed that the average initial deposits of chlorpyrifos at single and double dose were 0.07 and 0.13 mg kg⁻¹, respectively. Residues decreased very fast and on first day reached to 0.02-0.05 mg kg⁻¹ showing thereby 65.67 and 63.56 per cent dissipation at single and double dose, respectively. Residues on 7th and 15th day of application reached below detection limit (BDL) of 0.010 mg kg⁻¹ in single and double dose, respectively.

Pathan *et al.* (2012) studied the dissipation of quinalphos in brinjal and soil when sprayed at its recommended dose (375 g a.i. ha⁻¹) and double the recommended dose (750 g a.i. ha⁻¹). They suggested 6 and 9 days waiting period for recommended and double the recommended dose (i.e. 375 and 750 g a.i. ha⁻¹). No residues were detected in soil in treated plots at both the treatment levels 30 days after the spray of insecticide to the crop.

Parmar *et al.* (2012) studied the dissipation and decontamination of some pesticides in okra. Results revealed that the average initial deposit of deltamethrin, alphamethrin, deltamethrin (in combination), triazophos, ethion, cypermethrin and profenophos on okra 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 %), 0.010 (60.00 %), 0.015 (0.015 %), 0.013 (94.88 %), 0.020 (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.

Samriti *et al.* (2012) studied the persistence of chlorpyrifos in okra fruits and soil following the application of pre-mix formulation of insecticides Action 505 EC (chlorpyrifos 50% cypermethrin 5%) at single (275 g a.i. ha⁻¹) and double dose (550 g a.i. ha⁻¹). It was revealed that average initial deposits of chlorpyrifos on okra were observed to be 0.07 and 0.15 mg kg⁻¹ at single and double dose, respectively, which dissipated to 92 per cent after 10 days for both the doses. Residues of soil under okra crop were found to be 0.15 mg kg⁻¹ at the single and 0.36 mg kg⁻¹ at the double dose. The residues persisted up to 3 days at single and 5 days at double dose. The half-life (t_{1/2}) periods of chlorpyrifos on okra and soil were observed to be 0.6 days and 1.9 days for single and double dose, respectively. Residues of chlorpyrifos reached below detectable level (BDL) of 0.01mg kg⁻¹ in okra fruits after 7th days at single dose and in 15 days in double dose.

Chandra *et al.* (2014 a) studied the persistence pattern of chlorpyrifos, cypermethrin and monocrotophos applied at the dose of 100, 200 and 300 g a.i. ha⁻¹ respectively, on brinjal. The results revealed that the average initial residues were in the range of 0.362-0.876, 0.340-0.858 and 0.388-0.891 mg kg⁻¹ of chlorpyrifos, cypermethrin and monocrotophos, respectively. The residues of pesticide fall below detection limit in 13-17, 11-15 and 13-17 days of chlorpyrifos, cypermethrin and monocrotophos, respectively.

Chandra *et al.* (2014 b) studied the persistence pattern of chlorpyrifos, cypermethrin and monocrotophos applied at the dose

of 100, 200 and 300 g a.i. ha⁻¹ respectively, on okra. The results revealed that the average initial residues were in the range of 0.389-0.874, 0.378-0.862 and 0.391-0.891 mg kg⁻¹ of chlorpyrifos, cypermethrin and monocrotophos, respectively. The residues of pesticide fall below detection limit in 15, 17 and 19 days of chlorpyrifos, cypermethrin and monocrotophos, respectively.

3. MATERIAL AND METHODS

Investigations were carried out to study the insecticide usage pattern and dissipation of chlorpyrifos, triazophos and quinalphos in chilli fruits and harvest time residues in cropped soil. Field experiment were conducted during *Kharif-2015* at the Instructional Farm of Post Graduate Institute, M.P.K.V., Rahuri. The dissipation of insecticides was studied at Pesticide Residue Laboratory, 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 Chilli seed

The seeds of chilli variety Phule Jyoti were obtained from Agriculture Technology and Information Center (ATIC) at the central campus of M.P.K.V., Rahuri.

3.1.2 Insecticides.

In this experiment, seven treatments including untreated were maintained. Chlorpyrifos, triazophos and quinalphos are not registered in India for usage on chilli hence no Pre Harvest Interval (PHI) are recommended. However, the pest management practices of farmers revealed, they are commonly used for management of insect pests in chilli. The test insecticides were procured from local market. Particulars of evaluated insecticides *viz.*, common name, chemical name, trade name, formulation and manufacturer of product/source are presented in Table 1. The treatment details *viz.*,

name of insecticides, its formulation, dose in g a.i. ha⁻¹ and concentration of spray solution are given in Table 2.

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Table.1. Particulars of insecticides sprayed on chilli crop for residue studies.

Common Name	Chemical Name	Trade Name	Formulation	Source
Quinalphos	0,0- diethyl 0- quinoxalin-2-yl phosphorothioate	Ekalux	25 EC	M/s. Syngenta India Ltd., Amar Paradigim, S.No. 110/11/3 Bener Road, Pune, 411045.
Triazophos	0,0-diethyl 0-1-phynyl-1,2,4-triazol-3-yl phosphorothioate	Triazocel	40 EC	M/s. Excel cropcare Ltd. Reg. Office 184-87, S. V., Road, Jogeshwari (East), Mumbai,400102
Chlorpyriphos	0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl)-phosphoroyhioate	Teevra	20 EC	M/s. Mahindra & Mahindra Ltd. Agribusiness, Gate No.4 ,Aakurli Road, Kandiwali (East) Mumbai, 400101.

Table 2: Treatment details for field trial on chilli crop

Treatment No.	Common Name	Formulation	Dose (g a.i. ha⁻¹)	Spray Concentration (ml lit⁻¹)
T ₁	Triazophos	40 EC	500*	1.12
T ₂	Triazophos	40 EC	1000**	2.25
T ₃	Chlorpyrifos	20 EC	300*	1.35
T ₄	Chlorpyrifos	20 EC	600**	2.7
T ₅	Quinalphos	25 EC	250*	0.9
T ₆	Quinalphos	25 EC	500**	1.8
T ₇	Control	Water spray		

*Recommended Dose ** Double Recommended Dose

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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, (M.S.)
- 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 (M. S.)
- e. Toluene (Analytical Reagent grade), Avantor Performance Materials India Limited, Thane, (M.S)
- f. η -Hexane (HPLC grade), Thermo Fisher Scientific India Pvt. Ltd., Mumbai (M. S.)
- g. Pesticides: Certified Reference Materials of triazophos, chlorpyrifos and quinalphos insecticide with purity 98.9 %, 99.7 % and 99.7 %, respectively were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany)

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 (Shimadzu QP 2010 plus)
- b. Gas Chromatography equipped with FPD (Shimadzu-GC 2010)

3.1.6 Appliance

Manually operated knapsack sprayer (Aspee make) with hollow cone nozzle was used for spraying insecticide on chilli crop.

3.2 Methods

3.2.1. Survey of pesticide usage pattern

A detailed survey on insecticide usage pattern in chilli crop was undertaken using the format of questionnaire (Appendix-I) with the farmers of Ahmednagar district of Maharashtra.

Considering the area under cultivation of chilli, Rahuri (Ahmednagar) locations were selected. The information of insecticide use pattern was collected from 25 farmers from selected location. A format of questionnaire was prepared and used for the collection of information by interviewing the individual farmers.

3.2.2 Field experiment

3.2.2.1 Raising of chilli crop

The experiment was laid out at instructional farm of Post Graduate Institute, MPKV, Rahuri, District-Ahmednagar, Maharashtra state. Chilli seedlings were grown on raised beds by sowing disease free seeds of variety Phule Jyoti. Seedlings were ready for transplanting on 30 days after sowing. Land for planting the experiment was ploughed once and latter given two harrowings. The layout of the experiment was done by preparing ridges and furrows. All the cultural practices were carried out as per recommendation. For the control of sucking pests, a blanket spray of nimbicidine @ 2ml lit⁻¹ was given on a month old crop. Other experimental details are given below.

Treatments	7
Replications	3
Plot size	3.6 m × 3.6 m
Spacing	60 cm × 30 cm
Variety	Phule Jyoti
Date of sowing	20 June, 2015
Date of transplanting	28 July, 2015
Time of application	Fruit initiation stage
Number of application	Two at 10 days interval
Date of application	21 st October, 2015, 30 th October, 2015

3.2.2.2 Application of insecticides

The spraying was done manually by hand operated knapsack sprayer fitted with hallow cone nozzle. Two foliar sprays of

each insecticide were given at an interval of 10 days. First spray was given at 50 per cent flowering stage. Quantity of spray fluid required per plot was calculated by spraying untreated 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 insecticide to another during spraying. All sprayings were done during morning hours to avoid drift due to heavy winds from one treatment plot to other.

3.2.3 Residue analysis:

3.2.3.1 Standard Preparation

An accurately weighed 10 mg of an individual analytical grade pesticide was dissolved in 10 ml volumetric flask using toluene to prepare the standard stock solution of 1000 mg kg⁻¹. Standard stock solution of each insecticide was serially diluted to obtain intermediate lower concentration of 100 mg kg⁻¹. They were stored in a refrigerator at -2°C. From intermediate standards, working standards of triazophos and quinalphos at concentration of 0.05, 0.10, 0.25, 0.40, and 0.50 mg kg⁻¹ and concentration of 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00 mg kg⁻¹ of chlorpyrifos were prepared by suitably diluting the stock solution in n-hexane and acetonitrile and used as standard check in analysis, linearity and recovery studies.

3.2.3.2 Method validation

Method validation is the process used to confirm that the analytical procedure employed for a specific test is suitable for

its intended use. Results from method validation can be used to judge the quality, reliability and consistency of analytical results; it is an integral part of any good analytical practice. Limit of detection (LOD), Limit of quantification (LOQ), Linearity and recovery studies were performed in order to validate the method.

3.2.3.2.1 Limit of Detection (LOD) and Limit of Quantification (LOQ)

The limit of detection (LOD) of triazophos, chlorpyriphos and quinalphos 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 (LOQ) determined as 3 times of LOD.

3.2.3.2.2 Linearity study

Five linear concentrations *i.e.* 0.05 mg kg⁻¹, 0.10 mg kg⁻¹, 0.25 mg kg⁻¹, 0.40 mg kg⁻¹, and 0.50 mg kg⁻¹ of triazophos and quinalphos working standard whereas, six linear concentrations *i.e.* 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00 of chlorpyriphos were injected 3 times and the linearity lines were drawn.

3.2.3.2.3 Recovery studies

The analytical method for estimation of residues of triazophos, chlorpyriphos and quinalphos in chilli fruits as well as soil has been validated by conducting recovery studies using chilli fruits and soil samples from control samples. 10 gram each of control samples of chilli fruits and soil was taken in separate 50 ml centrifuge tubes in three replicates each were spiked separately with

chlorpyrifos, triazophos and quinalphos 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 insecticide in the samples. The extraction and cleanup was followed as described under 3.2.3.5. Per cent recovery was calculated by using following formula.

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

3.2.3.3 Sample collection

The chilli fruit samples (1kg) were collected at random from each replicate of the treated and control plots separately at regular time interval of 0 (2 hrs after spraying), 1, 3, 5, 7, 10 and 15 days after the second spray. Whereas soil samples were collected at final harvest. The collected samples (chilli and soil) were brought to the laboratory in polythene bags till their transfer to the Pesticide Residue Laboratory and processed immediately. Homogenized samples were kept at -20 °C in deep freezer until used for analysis. The dates of collection of chilli and soil samples are mentioned below.

Substrate	Interval between last application and sampling	Date of sample collection
Chilli Fruits	0 day	30.10.2015
	1 day	31.10.2015
	3 day	02.11.2015
	5 day	05.11.2015
	7 day	07.11.2015
	10 day	10.11.2015
	15 day	15.11.2015
Soil	30 day	30.11.2015

3.2.3.4 Sample preparation

The chilli samples were extracted and cleaned up using QuEChERS method (Anastassiades *et al.*, 2003).

3.2.3.5 Extraction and clean up of chilli fruits for triazophos, chlorpyrifos and quinalphos

The entire laboratory sample (1 kg) was crushed thoroughly in a mixer and 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. 2 ml supernatant was transferred to the 15 ml tube containing 50 mg PSA. The content was vortexed for 30 second and then cetrifuged for 2 min at

2500 rpm. The supernatant was filtered through 0.2 micron filter and GC-MS analysis was carried out in Pesticide Residue Laboratory, AINP on pesticide Residues, Department of Entomology, MPKV, Rahuri.

3.2.3.6 Extraction and clean up for cropped soil for triazophos, chlorpyriphos and quinalphos

A representative 10 gm soil sample was taken in 50 ml polypropylene tube. In this acetonitrile 20 ml was added and shaken vigorously for 1 minute. 4 gm MgSO₄ and 1 gm NaCl was added and centrifuge at 3300 rpm for 5 minute. Transferred 10 ml supernatant to the 15 ml polypropylene tube containing 1.5 g MgSO₄ and 0.25 gm PSA was shaken on vortex for few minute, sonicate for 1 minute, and then centrifuge again for 10 minute at 4400 rpm. Then 4 ml aliquot of supernatant was taken and evaporate to dryness. Finally, the dry residue was redissolved (make up) with 1 ml of cyclohexane. Quantitative analysis was performed on GC-FPD.

3.2.3.7 Residue Determination

Residue estimation of triazophos, chlorpyriphos and quinalphos was performed using GC-FPD and GC-MS, respectively. 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.

$$\text{Residues (mg kg}^{-1}\text{)} = \frac{\text{Area of sample}}{\text{Area of standard}} \times \frac{\text{ul of sample injected}}{\text{ul of standard injected}} \times \frac{\text{conc. of standard (ppm)}}{\text{wt .of sample}} \times \text{Final vol (ml)}$$

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

3.2.3.7.1 GC-MS analysis:

The analysis of samples for quinalphos residues was carried out with Shimadzu make GCMS-QP-2010 with auto injector. Shimadzu GCMS solution software was used as the data analysis system. The operating parameters of the instrument were given as follows.

Column Type	VF-5MS,30m × 0.25 μm × 0.25 mm	
Oven Programming	@ 11 ^o C/min	80 ^o C..... 1 min hold 140 ^o C 3 min hold 225 ^o C 5 min hold 280 ^o C 7 min hold
Detector	Interface Temperature	285 ^o C
	Ion source Temperature	250 ^o C
	Mass Range M/Z	40 - 400 ^o C.
Injector	Injector Temperature	250 ^o C
	Injection Volume	1 μl
	Injection Mode	Splitless
	Column flow	1.5 ml min ⁻¹
Carrier gas	Helium (99.999%)	
Retention time Approx.	Quinalphos 10.61 min	

3.2.3.7.2 GC-FPD Conditions:

The analysis of samples for triazophos and chlorpyriphos residues was carried out with GC-FPD (Shimadzu GC-2010 with auto injector). Shimadzu GC solution software was used as the data analysis system. The operating parameters of the instrument given as follows.

Column	DB-1, 30m x 0.25 μ m x 0.25 mm
Column Temperature	170 ^o C 3 min hold @ 6.5 ^o C/min 220 ^o C 2 min hold @ 10 ^o C/min 280 ^o C 6 min hold
Injector Temperature	250 ^o C
Column Temperature	170 ^o C
Detector Temperature	300 ^o C
Injection Volume	1 μ l
Column flow	0.96 ml min ⁻¹
Hydrogen Flow	90 ml min ⁻¹
Air Flow	120 ml min ⁻¹
Retention time Approx	Chlorpyriphos 11.97 min Triazophos 16.49 min

3.2.3.8 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. RESULTS AND DISCUSSION

The present investigation on the “Persistence of triazophos, chlorpyrifos and quinalphos in/on chilli and cropped soil” were undertaken at the Department of Entomology, MPKV, Rahuri during 2015-2016. Results are presented in this chapter.

4.1 Survey on pesticide usage pattern on chilli

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

Survey reports revealed that share of conventional insecticides was highest (61%) followed by novel insecticides (35%) and biopesticides (4%). Majority of the farmers generally used combination of insecticides. The data on quantity of insecticide used in respect of chilli (Table 3 & Fig 1) revealed that total consumption of conventional insecticide was 9.57 kg a.i ha⁻¹ and share of conventional insecticide was 60.60 per cent. whereas, total consumption of novel insecticides was 34.93 per cent @ 5.52 kg a.i ha⁻¹, and share of biopesticides was 4.43 per cent i.e @ 0.699 kg a.i ha⁻¹ in chilli crop.

Survey on pesticide usage pattern on chilli explicated wide range of insecticide use by the farmers in chilli growing areas. Farmers relied upon conventional insecticides, novel insecticides, and biopesticides. The usage of pesticides largely depend on the incidence of pest and diseases of the location. Farmers used

organophosphates and neonicotinoids for the control of sucking pests and organophosphates and synthetic pyrethroids for the lepidopteran pest control. The quantity of organophosphate insecticides used was 5.87 kg a.i ha⁻¹ for the control of insect pest in chilli. Among the insecticide groups, per cent share of organophosphate, organochlorines, carbamate and synthetic pyrethroid was 37.17, 6.90, 3.48 and 13.04 per cent, respectively. Whereas, novel insecticides *viz.*, Neonicotinoid, Oxadizines, Avermectin, Spinosyn, Diamide, Fiprole and IGR were 10.36, 4.56, 7.85, 6.97, 3.80, 0.32 and 1.10 per cent, respectively. Among these insecticides, quinalphos, acephate, chlorpyrifos, profenofos, imidacloprid, thiamethoxam, emamectin benzoate, indoxacarb, spinosad and chlorantraniliprole 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⁻¹ year⁻¹ synthetic insecticides against *S. litura*. Organophosphates, carbamates, synthetic pyrethroids and oxadiazines were used @ 2.231, 0.400, 0.767 and 0.036 kg a.i. ha⁻¹, respectively.

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

As regards the frequency of spraying, majority of farmers (55 %) adopted 7 to 9 sprays during cropping season, whereas only 5 per cent farmers gave more than 10 sprays in one season (Table 4 and Fig. 2).

The application of insecticides frequently at short intervals as observed in present investigation is in agreement with

Odhiambo *et al.* (2014) 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 of the farmers (87%) did not know about safe waiting period. Further, only 25 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 20 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 of insecticides in Ahmednagar district during cropping season

Sr. No.	Insecticide category	Insecticide group	Quantity of insecticides (kg a. i./ha/season)	Per cent share
			Rahuri	
1	Conventional insecticides	Organophospate	5.870	37.18
		Organochlorine	1.090	6.90
		Carbamate	0.550	3.48
		Synthetic pyrethroid	2.060	13.04
Total (A)			9.57	60.60
2	Novel insecticides	Neonicotinoid	1.636	10.36
		Oxadiazine	0.72	4.56
		Avermectin	1.240	7.85
		Spinosyn	1.101	6.97
		Diamide	0.599	3.8
		Fiprole	0.05	0.33
		IGR	0.175	1.10
Total (B)			5.52	34.97
3	Biopesticide	Neem based formulation	0.699	4.43
Total (C)			0.699	4.43
Total (A+B+C)			15.79	100

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

Sr. No.	Variables	Response of farmers (%)
1.	i) Conventional insecticides (Cypermethrin, quinalphos, Chlorpyrifos, profenofos)	62
	ii) Novel insecticides (Imidacloprid, acetamiprid, emamectine benzoate)	32
	iii) Biopesticides (Neem oil and Azadirachtin)	6
2.	Spraying interval followed by farmers	
	1) 1-3 times	16
	2) 4-6 times	24
	3) 7-10 times	55
	4) > 10 times	5
3.	Awareness about natural enemies	0
4.	Awareness about recommended dose of pesticides	20
5.	Knowledge of safe waiting period	13
6.	Awareness about the harmful effect of pesticide residues	8

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4.2 Dissipation of triazophos, chlorpyrifos, quinalphos and cropped soil

Dissipation of triazophos, chlorpyrifos and quinalphos was determined by conducting a supervised field trial during 2015-16, at the Instructional Farm of Post Graduate Institute, MPKV, Rahuri. Two sprays of insecticides were given at an interval of ten days, first being at the fruit initiation stage. The fruits were collected at zero, one, three, five, seven, ten and fifteen days after second application and subjected to QuEChERS method of analysis to determine residues as explained under section 3.4 of the chapter 3 (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 chilli samples.

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

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4.2.1.1 Limit of Detection (LOD) and Limit of Quantification (LOQ)

The limit of detection (LOD) of the tested pesticides was 0.01 mg kg⁻¹ and resulted by considering a signal-to-noise ratio of compound with reference to the background noise obtained for the blank sample. The limits of quantification (LOQ) determined as the lowest concentration in chilli 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 triazophos and quinalphos and 0.01 mg kg⁻¹ for chlorpyriphos.

4.2.1.2 Linearity

Five linear concentrations *i.e.* 0.05 mg kg⁻¹, 0.10 mg kg⁻¹, 0.25 mg kg⁻¹, 0.40 mg kg⁻¹, and 0.50 mg kg⁻¹ of triazophos and quinalphos working standard whereas, six linear concentration *i.e.* 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00 of chlorpyriphos were injected 3 times and the linearity lines were drawn. The response was linear over the range tested and R² values were 0.999, 0.994 and 0.998 for triazophos, chlorpyriphos and quinalphos, respectively as given in Fig. 1.

These results indicated that the GC-MS and GC-FPD analysis is a valid method for residue determination of the tested insecticides in chilli 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 chilli fruits and soil fortified with three concentrations *i.e.*, 0.05, 0.25 and 0.50 mg kg⁻¹ of triazophos and quinalphos and 0.01, 0.05 and 0.50 mg kg⁻¹ of chlorpyriphos. The extraction and clean-up were performed as described earlier (3.2.3.5.). Recoveries of three tested insecticides 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 results of recovery studies of triazophos carried out at the levels of 0.05, 0.25 and 0.50 mg kg⁻¹ (Table 5) on chilli fruits and soil were between 94.50, 95.36, 93.40 per cent and 88.13, 85.10, 94.46 per cent, respectively.

For chlorpyriphos, the recovery studies were carried out at the levels of 0.01, 0.05 and 0.1 mg kg⁻¹ (Table 6) on chilli fruits and soil. The values were between 94.16, 92.10, 93.86 per cent and 96.50, 93.53, 91.23 per cent, respectively.

For quinalphos, results of recovery studies carried out at the levels of 0.05, 0.25 and 0.50 mg kg⁻¹ (Table 7) on chilli fruits and soil were between 94.50, 105.5, 96.73 per cent and 84.65, 86.56, 86.56 per cent, respectively.

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These results indicated that the QuEChERS method is a valid method for residue determination of the tested insecticides in chilli fruits and soil.

The analytical method employed for the extraction and clean up of chilli fruit 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 (RSD) below 20 per cent is accurate and precise.

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Table 5. Recovery of triazophos in chilli fruits and soil

Substrate	Fortification Level (mg kg ⁻¹)	Recovery (%)			
		R-I	R-II	R-III	Mean
Chilli fruits	0.05	94.40	89.60	84.40	94.50 (±5.00)
	0.25	96.00	96.40	93.70	95.36 (±1.46)
	0.50	93.90	92.00	94.30	93.40 (±1.23)
Soil	0.05	92.70	88.40	83.30	88.13 (±4.71)
	0.25	92.50	96.80	93.00	85.10 (±2.35)
	0.50	94.70	93.40	95.30	94.46 (±0.97)

Table 6. Recovery of chlorpyriphos in chilli fruits and soil

Substrate	Fortification Level (mg kg ⁻¹)	Recovery (%)			
		R-I	R-II	R-III	Mean
Chilli fruits	0.01	95.90	89.10	97.50	94.16 (±4.46)
	0.05	92.10	88.60	95.60	92.10 (±3.5)
	0.10	95.90	94.40	91.30	93.86 (±2.35)
Soil	0.01	97.70	96.10	95.70	96.50 (±1.06)
	0.05	96.00	89.40	95.20	93.53 (±3.60)
	0.10	94.70	90.50	88.50	91.23 (±3.14)

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Table 7. Recovery of quinalphos in chilli fruits and soil

Substrate	Fortification Level (mg kg ⁻¹)	Recovery (%)			
		R-I	R-II	R-III	Mean
Chilli fruits	0.05	86.80	97.70	99.0	94.50 (±6.7)
	0.25	109.0	100.6	107.0	105.5 (±4.39)
	0.50	98.70	86.40	105.1	96.73 (±9.50)
Soil	0.05	81.13	86.53	86.31	84.65 (±3.06)
	0.25	94.08	95.72	96.98	86.56 (±1.45)
	0.50	84.93	80.81	93.96	86.56 (±6.73)

4.3 Residues of insecticides in chilli fruits and soil

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

4.3.1 Persistence and dissipation of triazophos in/on chilli fruits

Dissipation of insecticide 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 insecticide in chilli fruits with time.

In case of triazophos 40 EC @ 500 and 1000 g a.i. ha⁻¹, initial deposits were recorded as 1.12 and 2.34 mg kg⁻¹ and were found to be below detection limit (BDL) on 10th and 15th day, respectively. The half-life (RL₅₀) values of triazophos for chilli were 1.72 and 1.99 days, respectively (Table 8). The residues dissipated to 95.53 and 91.02 per cent at both the dosage of application (Table 9).

Similar type of study was also conducted by Kumar *et al.* (2000) where the initial deposits of triazophos on chilli were found to be 0.43 mg kg⁻¹ at the recommended dose. The residues dissipated to more than 70 per cent at 15 days. Singh and Kapoor (1998) reported that residues dissipated about 94 per cent after 6 days of last spray of triazophos in brinjal fruit at both the doses. Vijayalakshmi, *et al.* (2000) reported initial deposits of 0.68 and 1.39 mg kg⁻¹ at lower and high doses of triazophos on okra. The rate of dissipation was found to be rapid up to the 5th day and dissipated about 93 per cent. Raj *et al.* (1999) reported half-life of 1 and 2 days for the lower and higher dose of triazophos on brinjal. All these reports support to the present findings. However, Singh *et al.* (2015) reported higher initial deposits of triazophos *i.e.* 3.61 and 6.26 mg kg⁻¹. The residues of triazophos dissipated after seventh day after last spray at both doses. Residues were found to be below detectable limit at ten and fifteen days, respectively. Half-life of triazophos on capsicum was observed to be 2.31 and 2.14 days, respectively.

Table 8. Persistence of triazophos residues at different intervals in chilli fruits and soil

Interval between last application and sample collection	Residues (mg kg ⁻¹)											
	Control				Triazophos @ 500 g a.i. ha ⁻¹				Triazophos @ 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	1.11	1.09	1.16	1.12 (+0.04)	2.31	2.38	2.32	2.34 (+0.04)
1 day	ND	ND	ND	ND	0.68	0.73	0.64	0.68 (+0.05)	1.70	1.43	1.52	1.55 (±0.14)
3 day	ND	ND	ND	ND	0.36	0.38	0.36	0.37 (+0.01)	1.00	1.04	0.96	1.00 (±0.04)
5 day	ND	ND	ND	ND	0.25	0.28	0.23	0.25 (+0.03)	0.46	0.42	0.48	0.46 (±0.03)
7 day	ND	ND	ND	ND	0.05	0.06	0.05	0.05	0.23	0.22	0.20	0.21 (±0.02)
10 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	0.07	0.06	0.07	0.07 (±0.01)
15 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Soil at harvest	ND	ND	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL
RL 50 (days)	-				1.72				1.99			

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

Table 9. Per cent dissipation of triazophos in chilli fruit.

Interval between last application and sample collection	Triazophos			
	@ 500 g a.i. ha ⁻¹		@ 1000 g a.i. ha ⁻¹	
	Mean Residues (mg kg ⁻¹)	Dissipation (%)	Mean Residues (mg kg ⁻¹)	Dissipation (%)
0 day (2 hr)	1.12	-	2.34	-
1 day	0.68	39.28	1.55	33.76
3 day	0.37	66.96	1.00	57.26
5 day	0.25	77.67	0.46	80.34
7 day	0.05	95.53	0.21	91.02
10 day	BDL	-	BDL	-
15 day	BDL	-	BDL	-

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4.3.2 Persistence and dissipation of chlorpyrifos in/on chilli fruits

As regards application of chlorpyrifos 20 EC @ 300 and 600 g a.i. ha⁻¹, initial deposits were recorded as 0.85 and 1.70 mg kg⁻¹ at 300 and 600 g a.i ha⁻¹, respectively. The chlorpyrifos residues were below detection limit (BDL) on tenth and fifteenth day, respectively. The residual half-life (RL₅₀) values recorded were 2.05 and 2.74 days, respectively (Table 10). The residues of chlorpyrifos dissipated to 98.82 and 98.23 per cent on 10th and 15th day at both the doses, respectively (Table 11). These findings are in agreement with those of Jyot *et al.* (2013) who reported the mean initial deposits of 0.59 and 2.02 mg kg⁻¹ of chlorpyrifos on green chilli fruits, at recommended and double the recommended dose. More than 75 per cent of these residues got dissipated within a week at both doses. These initial residues were dissipated to 84.75 and 88.61 per cent at both the doses after 10 days of last application of the insecticide. Raina and Raina (2008) reported the average initial deposits of chlorpyrifos on cauliflower varied from 0.56 to 0.86 and 0.86 to 1.43 mg kg⁻¹, respectively, for two consecutive years. The persistence of chlorpyrifos till nine days was recorded. Cent per cent dissipation of chlorpyrifos on 10th and 15th day after application on okra fruits at single and double dose respectively, were recorded by Samriti *et al.* (2011). All these reports lend support to the present findings.

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Table 10. Persistence of chlorpyrifos residues at different intervals in chili fruits and soil

Interval between last application and sample collection	Residues (mg kg ⁻¹)											
	Control				Chlorpyrifos @ 300 g a.i. ha ⁻¹				Chlorpyrifos @ 600 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	0.87	0.89	0.81	0.85 (±0.04)	1.69	1.70	1.72	1.70 (±0.02)
1 day	ND	ND	ND	ND	0.62	0.60	0.59	0.60 (±0.02)	1.00	1.09	1.04	1.04 (±0.05)
3 day	ND	ND	ND	ND	0.27	0.26	0.29	0.27 (±0.02)	0.56	0.57	0.60	0.58 (±0.02)
5 day	ND	ND	ND	ND	0.19	0.21	0.19	0.20 (±0.01)	0.31	0.31	0.28	0.30 (±0.02)
7 day	ND	ND	ND	ND	0.08	0.08	0.06	0.07 (±0.01)	0.19	0.21	0.19	0.20 (±0.01)
10 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	0.013	0.13	0.15	0.14 (±0.09)
15 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	0.04	0.03	0.03	0.03 (±0.01)
Soil at harvest	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
RL 50 (days)	-				2.05				2.74			

* ND-Not Detected BDL= Below Detection Limit LOQ 0.01 mg kg⁻¹

Table 11. Per cent dissipation of chlorpyrifos in chilli fruits

Interval between last application and sample collection	Chlorpyrifos			
	@ 300 g a.i. ha ⁻¹		@ 600 g a.i. ha ⁻¹	
	Mean Residues (mg kg ⁻¹)	Dissipation (%)	Mean Residues (mg kg ⁻¹)	Dissipation (%)
0 day (2 hr)	0.85	-	1.70	-
1 day	0.60	29.41	1.04	38.82
3 day	0.27	68.23	0.58	65.88
5 day	0.20	76.47	0.30	82.35
7 day	0.07	91.76	0.20	88.23
10 day	0.01	98.82	0.14	91.76
15 day	BDL	-	0.03	98.23

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4.3.3 Persistence and dissipation of quinalphos in/on chilli fruits

In case of quinalphos 25 EC @ 250 and 500 g a.i. ha⁻¹, the initial deposits were recorded as 0.96 and 1.83 mg kg⁻¹. Residues reached below detectable limit (BDL) on tenth and fifteenth days respectively, at both rates of application. The residual half-life (RL₅₀) values were 1.99 and 2.07 days, respectively (Table 12). More than 90.62 and 96.17 per cent quinalphos residues dissipated after seventh and tenth day (Table 13).

Aktar *et al.* (2010) reported that more than 60 per cent of the initial deposits of quinalphos on cabbage were dissipated within 48 hours, except double the recommended dose. The half-life values were found to be 1.27-1.38 for cabbage heads. These reports lend support to present finding.

Pathan *et al.* (2012) reported half life value of 2 days for lower dose and 3 days for higher dose, following the application of quinalphos 25 EC in/on brinjal fruit and soil. Hence, 6 and 9 days waiting period was suggested for recommended and double the recommended dose, respectively. However, higher initial deposits (i.e. 3.20 and 7.50) of quinalphos were detected on okra after application at recommended and double the recommended dose (i.e. 500 and 1000 g a.i. ha⁻¹) as reported by Aktar *et al.*, (2008).

Table 12. Persistence of quinalphos residues at different intervals in chilli fruits and soil

Interval between last application and sample collection	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	1.12	0.92	0.84	0.96 (±0.14)	1.94	1.74	1.80	1.83 (±0.10)
1 day	ND	ND	ND	ND	0.66	0.77	0.71	0.71 (±5.25)	1.36	1.26	1.27	1.29 (±0.06)
3 day	ND	ND	ND	ND	0.49	0.42	0.50	0.47 (±0.04)	0.77	0.80	0.85	0.81 (±0.04)
5 day	ND	ND	ND	ND	0.15	0.16	0.18	0.16 (±0.02)	0.35	0.35	0.33	0.34 (±0.01)
7 day	ND	ND	ND	ND	0.09	0.08	0.11	0.09 (±0.02)	0.16	0.16	0.17	0.16 (±0.01)
10 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	0.07	0.07	0.07	0.07
15 day	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Soil at harvest	ND	ND	ND	ND	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
RL 50 (days)	-				1.99				2.07			

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

Table 13. Dissipation pattern of quinalphos in chilli fruit

Interval between last application and sample collection	Quinalphos			
	@ 250 g a.i. ha ⁻¹		@ 500 g a.i. ha ⁻¹	
	Mean Residues (mg kg ⁻¹)	Dissipation (%)	Mean Residues (mg kg ⁻¹)	Dissipation (%)
0 day (2 hr)	0.96	-	1.83	-
1 day	0.71	26.04	1.29	29.50
3 day	0.47	51.04	0.81	55.73
5 day	0.16	83.33	0.34	81.42
7 day	0.09	90.62	0.16	91.25
10 day	BDL	-	0.07	96.17
15 day	BDL	-	BDL	

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4.3.4 Persistence of triazophos, chlorpyrifos and quinalphos in cropped soil

Analysis of soil samples for the residues of triazophos, chlorpyrifos and quinalphos was carried out on the 15th 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 insecticides (*i.e.*, triazophos, chlorpyrifos and quinalphos) in soil at harvest were found to be below detection limit (BDL) in both the doses.

Jyot *et al.* (2013) studied chlorpyrifos residues in soil and reported that soil samples collected after 15 days of the last application did not show the presence of chlorpyrifos at determination limit of 0.01 mg kg⁻¹. These reports lend support to the present finding. According to Gupta *et al.* (2011) residues of chlorpyrifos in soil persisted for 0-7 days only. However, Wei *et al.* (2008) reported the half-life of triazophos in soil as 7.93 days with a dissipation rate of 90 per cent over 21 days. Low residues in soil suggest that this pesticide may be otherwise environmentally safe.

The residues of quinalphos were not detected in soil samples on 30 days after spraying of insecticide as reported by Pathan *et al.*, (2012). Mohapatra and Deepa (2013) reported that residues of quinalphos in soil on 15th day of sampling were found to be 0.01 and 0.04 mg kg⁻¹. However, according to Aktar *et al.* (2008) the residues of quinalphos persisted in soil for 6-8 days depending on dose.

The use of pesticides has become indispensable in present agriculture to control insect pests. Survey reports

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revealed that farmers give 7 to 9 applications of insecticides in/on chilli 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 chilli 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 triazophos persisted upto seven and ten days on chilli at recommended and double the recommended doses, respectively. Persistence of chlorpyrifos and quinalphos was for seven and fifteen days and seven and ten days, respectively.

Half-life (RL_{50}) values calculated for triazophos on chilli were 1.72 and 1.99 days, for recommended and double the recommended dose, respectively. Considering this, Pre Harvest Interval (PHI) of seven days can be suggested for triazophos for safe consumption of chilli fruits.

Half-life (RL_{50}) recorded for chlorpyrifos in/on chilli were 2.05 and 2.74 days for single and double dose, respectively. As there is no MRL available for chlorpyrifos in chilli, 0.01mg kg^{-1} may be taken as a default MRL. On the basis of this, Pre Harvest Interval (PHI) of seven days can be suggested for chlorpyrifos.

As regards quinalphos, half-life values calculated were 1.99 and 2.07 days for single and double doses, respectively. There is no prescribed MRL for quinalphos in chilli and hence 0.05 mg kg^{-1} may be taken as default MRL. On this basis, Pre

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Harvest Interval of seven days may be suggested for quinalphos for safe consumption of chilli fruits.

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5. SUMMARY AND CONCLUSION

5.1 Summary

5.1.1 Pesticide usage pattern in chilli

During survey, the pesticide usage pattern in chilli indicated that the farmers from selected location of Ahmednagar District of Maharashtra relied mostly on chemical pesticides to control the pest and diseases of chilli. Survey report revealed that farmers used different chemical insecticides most frequently *viz.*, profenophos, chlorpyriphos, cypermethrin, triazophos and spinosad.

Majority of the farmers sprayed at an interval of 7-9 days giving maximum 6-8 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 insecticide.

None of the farmers were aware of natural enemies whereas, only 8 per cent were aware about effect of pesticide residues in/on food and safe waiting periods for harvesting. Few farmers (20 %) knew about recommended dose of insecticide. Most of the farmers used non recommended insecticides with higher doses.

5.2 Dissipation of triazophos, chlorpyriphos and quinalphos in /on chilli fruits and cropped soil

5.2.1 Recovery studies

In case of triazophos, chlorpyriphos and quinalphos in /on chilli fruits and soil, the mean recovery per cent ranged from 85.10 to 95.36, 91.23 to 96.50 and 84.65 to 105.53 per cent

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respectively, which was within the acceptable range of 70-120 per cent.

5.2.2 Persistence and dissipation studies of triazophos, chlorpyrifos and quinalphos

The mean initial residues of triazophos 40 EC @ 500 and 1000 g a.i ha⁻¹ in chilli fruits were found to be 1.12 and 2.34 mg kg⁻¹ which dissipated to BDL on 10th and 15th day after 2nd spray. The half life values were 1.72 and 1.99 days. The residues of triazophos were found to be BDL in soil at harvest at both doses, respectively.

As regards chlorpyrifos 20 EC @ 300 and 600 g a.i.ha⁻¹, the initial residues of 0.85 and 1.70 mg kg⁻¹ reached BDL at 10th and 15th day after 2nd spray. The half-life values calculated were 2.05 and 2.74 days for both the doses, respectively. The residues of chlorpyrifos were found to be BDL in soil at harvest.

As in respect of quinalphos 25 EC @ 250 and 500 g a.i.ha⁻¹, the initial residues of 0.96 and 1.83 mg kg⁻¹ reached BDL at 10th and 15th day after 2nd spray. The half-life values calculated were of 1.99 and 2.07 days. The residues of quinalphos were found to be BDL in soil at harvest.

5.2. Conclusion

Pesticides are toxic substances and 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 triazophos, chlorpyrifos and quinalphos in chilli. Pre harvest Intervals of seven days, be observed for triazophos, chlorpyrifos and quinalphos respectively, if these insecticides are recommended on chilli.

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6. LITERATURE CITED

- Afari-Sefa, V., Asare-Bediako, E., Kenyon, L. and Micah, J. A. 2015. Pesticide use practices and perceptions of vegetable farmers in the Cocoa Belts of the Ashanti and Western Region of Ghana. *Adv. Crop. Sci. Tech.*, 3(3):174.
- Akan, J. C., Jafiya, L., Mohammed, Z. and Abdulrahman F. I. 2013. Organophosphorus pesticide residues in vegetables and soil samples from alau dam and gongulong agricultural areas, Borno State, Nigeria. *Int. J. Environ. Monit. Anal.* 1(2): 58-64.
- Akhtar, S., Gilani, S. T. S. and Hasan, N. 2004. Persistence of chlorpyrifos and fenprothrin alone and in combination with fertilizers in soil and their effect on soil microbes. *Pak. J. Bot.*, 36(4): 863-870.
- Aktar, W., Sengupta, D., Purkait, S. and Chawdhury, A. 2008. Degradation, dynamics and persistence of quinalphos and methomyl in/on okra (*Ablemoschus esculentus*) fruits and cropped soil. *Bull. Environ. Contam. Toxicol.* 80:74-77.
- Aktar, W., Sengupta, D., Purkait, S. and Chawdhury, A. 2010. Risk assessment and decontamination of quinalphos under different culinary processes in/on cabbage. *Environ. Asses.*, 163:369-377.
- Al-Sayed, R., Ramlawi, A. and Salah, A. 2011. A national survey on the use of agricultural pesticides in Palestine. (special issue: Palestine.). *Int. J. Environ. Studies*, 68 (4): 519-529.

- Anastassiades, M., Lehotay, S. J., Stajnbaher, D. and Schenck, F. J. 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid phase extraction" for the determination of pesticides residue in produce. *J. AOAC Int.*, 86:412-431.
- Anonymous, 2010. Government of India. Ministry of Agriculture, Post Harvest Profile of Technical Report; pp. 1-80.
- Anonymous, 2014. Indian Horticulture Database. National Horticulture Board, pp: 16-17.
- Banerjee, I., Tripathi, S. K. Sinha Roy, A. and Sengupta, P. 2014. Pesticide use pattern among farmers in rural district of West Bengal, India. *J. Nat. Sci. Biol. Med.*, 5(2):313-316.
- Borjan, M., Robson, M. G., Hamilton, G., Brown, C. and Mayer, R. 2006. Trends indicated by the New Jersey pesticide use survey. *Outlooks on Pest Mgmt.*, 17(4): 157-163.
- Chandi, R. S., Chandi, A. K., Singh, G. and Suri, K. S. 2012. Insecticide use pattern on cole crops in Punjab. *J. Insect Sci.*, 25 (2): 210-213.
- Chandra, S., Mahindrakar, A. N., Fugare, M. K., and Shinde, L. P. 2014 a. Studies on pattern of pesticides on brinjal. *Inter. J. Curr. Res. Chem. Pharma Sci.*, 1(7):88-91.
- Chandra, S., Kumar, M., Mahindrakar, A. N. and Shinde, L. P. 2014 b. Persistence pattern of chlorpyrifos, cypermethrin and monocrotophos in okra. *Inter. J. Adv. Res.*, 2 (12): 738-743.
- Devi, I. 2010. Pesticides in agriculture: A boon or a curse. A case study of Kerala. *Economic and Political Weekly*, 14(26 & 27): 199-207.

- Deviprasad, A. G., Radha, S. and Manonmani, H. K. 2015. Pesticide use pattern in four districts of Karnataka: A survey. *J. Environ. Sci. Toxicol Food tech.* 9(10): 48-51.
- Epstein, L. and Bassein, S. 2003. Patterns of pesticide use in California and the implications for strategies for reduction of pesticides. *Ann. Rev. Phytopathol.*, 41: 351-375.
- Gaur, R., Goel, G., Mishra, M., Singh, S. K., Dev, P., Kumar, S and Sharma, C. S 2011. Residues of pesticides and herbicides in soils from agriculture areas of Delhi region, India. *J. Environ. Earth Sci.*, 1(2):1-8.
- Gilani, S. T. S., Ageen, M., Shah, H. and Raza, S. 2010. Chlorpyriphos degradation in soil and its effect on soil microorganisms. *J. Animal Plant Sci.*, 20(2): 99-102.
- Gupta, S., Gajbhiye, V. T., Sharma, R. K and Gupta, R. K. 2011. Dissipation of cypermethrin, chlorpyriphos and profenofos in tomato fruits and soil following application of pre-mix formulations. *Environ. Monit. Asses.*, 174(1-4):337-345.
- Hassan, M. U., Ahmed, F., Mohammed, S., Iqbal, M. F. and Mohammed, T. 2005. Residual persistence of chlorpyriphos, imidachlopride and acephate in brinjal fruit. *Pak. Entomol.*, 27(1): 53-55.
- Huber, 2007. Validation of Analytical Methods. In "Validation and Quantitation in Analytical Laboratories" 2nd Edition Published by Informa Healthcare USA, Inc. 52 Vanderbilt Avenue New York. Ny 100/Y, pp 125.
- Jyot, G., Mandal, K., Battu, R. S. and Singh, B. 2013. Estimation of chlorpyriphos and cypermethrin residues in chilli (*Capsicum annumm* L.) by gas-liquid chromatography. *Environ. Monit. Asses.*, 185:5703-5714

- Khan, M. A., Rao, S. V. and Reddy, D. J. 1999. Dissipation of dichlorvos and dimethoate residues in okra fruits. Pestic. Res. J., 11(1):204-206.
- Kumar, K. P., Reddy, D. J., Babu, T. R. and Narendranath, V. V. 2000. Dissipation and decontamination of triazophos and acephate residues in chilli (*Capsicum annuum* Linn). Pestic. Res. J. 12:26-29.
- Kumari, B., Madan, V. K. and Kathpal, T. S. 2008. Status of insecticide contamination of soil and water in Haryana, India. Environ. Monit. Asses., 136:239-244.
- Li, X. S., Lu, Z. X., Lin, M. Z. and Huang, H. Y. 2005. Degradation dynamics of triazophos residues in lychee and soil. Southwest China J. Agric. Sci., 18(6):758-763.
- Lindsay, D. G. 1997. Pesticide residues in food: The need for fairer cost-benefit. Analy. Pestic. Outlook, 8: 6-10.
- Magdoleen Ali Ahmed Saeed, 2007. Seasonal Variation of pesticide residues in some salad vegetables in Khartoum State-Sudan. Thesis submitted to Department of food science and technology Faculty of Agriculture University of Khartoum.
- Mahalingappa, P. B., Reddy, K. D., Reddy, K. N. and Subbaratnam, G. V. 2006. Dissipation of ethion and chlorpyrifos residues in/on chilli (*Capsicum annuum* L.). Pestic. Res. J., 18(1): 72-73.
- Mathew, T. B., Beevi, S. N., George, T., Nair, K. P., Rajith, R. and Kumar, N. P. 2012. Persistence and dissipation of combination (spirotetramat+imidacloprid) on chilli (*Capsicum annuum* L.) Pestic. Res. J., 24(2):151-154.

- Mohapatra, S. and Deepa, M. 2013. Persistence and dissipation of quinalphos in/on cauliflower and soil under the semi arid climatic condition of Karnataka, India. Bull. Environ. Contam. Toxicol., 90(4):489-493.
- Mukherjee, U. and Singh, H. N. 2005. Pesticide use pattern on cabbage and cauliflower against diamondback moth, *Plutella xylostella* Curt in Varanasi (Uttar Pradesh). J. Res., Birsa Agricultural University; 17(1):69-75.
- Muzlon, N. and Mumford, John. 2005. Insecticide use in cabbage pest management in the Cameron Highlands, Malaysia. Int. J. Trop. Insect Sci., 34(2):88-97.
- Ngan C. K., Cheah, U. B., Wan Abdullah, W. Y., Lim, K. P. and Ismail, B. S. 2005. Fate of chlorthalonil, chlorpyrifos and profenofos in a vegetable farm in Cameron highland, Malaysia. Water, Air, and Soil Pollution: Focus, 5:125-136.
- Nyakundi, W. O., Magoma, G., Ochora, J. and Nyende, A. B. 2011. A survey of pesticide use and application pattern among farmers in Rift Valley Central Provinca, Kenya. J. Entomol. Acarol. Res., 10(2): 161-166.
- Odhiambo, J. A. O., Winfred, S. K. Gbeworryo and Danial, O. O. 2014. Insecticide use pattern and residue levels in cabbage (*Brassica oleracea var. Capitata L.*) within selected farms in Southern Ghana. JENRM 1(1): 44-55.
- Parasnath, Kumari, B., Yadav, P. R. and Kathpal, T. S. 2005. Persistence and dissipation of ready mix formulations of insecticides in/on okra fruits. Environ. Monit. Asses., 107:173-179.

- Parmar, K. D., Korat, D. M., Shah, P. G. and Singh, S. 2012. Dissipation and decontamination of some pesticides in/ on okra. *Pesti. Res. J.*, 24(1): 42-46.
- Pathan, A. R. K., Parihar, N. S. and Sharma, B. N. 2012. Dissipation study of quinalphos (25 EC) in/on brinjal and soil. *Bull. Environ. Contam. Toxicol.*, 88:894-896.
- Patil. S. K. 2012. Assesment of insecticide resistance in *Spodoptera litura* (Fabricus) in western Maharashtra. Thesis submitted to MPKV, Rahuri, India.
- Plianbangchang, P., Jetiyanon, K. and Wittaya-areekul, S. 2009. Pesticide use patterns among small-scale farmer: A case study from phitsanulok, Thailand. *Southeast Asian J. Trop. Med. Public Health*, 40(2):401-410.
- Raina, A. K. and Raina, M. 2008. Dissipation of chlorpyriphos on cauliflower (*Brassica oleracea L. var. botrytis.*). *Pestic. Res. J.*, 20: 263-265.
- Raj, M. F., Shah, P. G., Patel, B. K., Patel, B. A. and Patel, J. A. 1999. Dissipation of triazophos in brinjal and okra fruits. *Pestic. Res. J.*, 11(1):102-105.
- Rao, C. S., Bour, T. B. and Reddy, K. N. 2005. Pesticide residues: Impact on Indian Agriculture Exports in WTO era. Proceeding of the National Symposium on Pesticide Residues and Their Risk Assesment, January 20-21, pp. 54-57.
- Reddy, K. D., Reddy, K. N. and Mahalingappa, P. B. 2007a. Dissipation of fipronil and profenophos residues in chillies (*Capsicum annuum L.*). *Pesti. Res. J.*, 19(1):106-107.

- Reddy, K. N., Satyanarayana, S. and Reddy, K. D. 2007b. Persistence of some insecticides in chillies. *Pesti. Res. J.*, 19:234-236.
- Samriti, Chauhan, R. and Kumari, B. 2011. Persistence and effect of processing on reduction of chlorpyriphos residues in okra fruits, *Bull. Environ. Contam. Toxicol.*, 87: 198-201.
- Samriti, Chauhan, R. and Kumari, B. 2012. Persistence of chlorpyriphos in okra fruits and soil. *Toxicol. Environ.Chem.*, 94 (9):1726-1734.
- Sanap, M. M. and Nawale, R. N. 1986. Relative efficacy of modern pesticide for the control of mites on chilli. *Pesticides*, 20 (1):31-33.
- SANCO. 2011. Method Validation and quality control procedures for pesticide residue analysis in food and feed. Document No. 12459/2011 8:15.
- Sharma, B. N. and Parihar, N. S. 2013. Dissipation and persistence of dimethoate and ethionne residues in/on chilli, *Capsicum annuum* (L.) *Pesti. Res. J.*, 25(1):80-82.
- Shetty, P. K., Murugan, M., Hiremath, M. B. and Sreeja, K.G. 2010. Farmers' education and perception on pesticide use and crop economies in Indian agriculture. *J. Experimental Sci.*, 1(1): 03-08.
- Singh, N. and Kapoor, S. K. 1998. Dissipation of triazophos residues on brinjal fruits (*Solanum melongena* L.). *Pestology*, 22:27-32.
- Singh, Y., Mandal, K., and Singh, B. 2015. Dissipation pattern and risk assesmant studies of triazophos residues on

- capsicum (*Capsicum annuum L.*) using GLC-FPD and GC-MS. Environ. Monit. Asses., 187:637-642.
- Tandi, T. E., Wook, C. J., Shendeh, T. T., Eko, E. A. and Afoh, C. O. 2014. Small-Scale Tomato Cultivators' Perception on Pesticides Usage and Practices in Buea Cameroon. Health, 6: 2945-2958.
- Tyagi, H., Gautam, T. and Prashar, P. 2015. Survey of pesticide use patterns and farmers perceptions: A case study from cauliflower and tomato cultivating areas of district Faridabad, Haryana, India. Inter. J. MediPharm Res., 1(3): 139-146.
- Varghese, T. S., Mathew T. B., George T., Beevi N. S. and Xavier G. 2014. Persistence and dissipation of neonicotinoid insecticides on chilli fruits. Quality Assurance and Safety of Crops & Foods. 7(4):487-491.
- Varghese, T. S., Thomas, B. M., Thomas, G., Naseema Beevi, S. and George X. 2011. Dissipation study of dimethoate, ethion and oxydemeton methyl in chilli. Pestic. Res. J., 23(1): 68-73.
- Vijayalakshmi, K., Jayakumar, R. and Kuttalam, S. 2000. Dissipation of triazophos residues in/on bhendi. Pestology, 24:32-34.
- Waghulde, P. N., Khatik, M. K., Patil, V. T. and Patil P. R. 2011. Persistence and dissipation of pesticide in chilli and okra at North Maharashtra Region. Pestic. Res. J., 23(1):23-26.
- Wei, Li, Shao-Ping Qiu. and Yi-Jun Wu. 2008. Triazophos residues and dissipation rates in wheat crops and soil. Ecotoxic. Envirol. Saf., 69(2):312-316.

Willam, J. N., Huub, J. G., Peter, K. and Pay, D. 2006. Farmer's perception and pesticides in vegetables production in Ghana. Pest Manag. Sci., 62: 356-365.

Yen, I. C., Bekele, I. and Kalloo, C. 1999. Use pattern and residual levels of organophosphate pesticides on vegetables in Trinidad, West Indies. J. AOAC Int., 82(4): 991-995.

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