# RESIDUE DYNAMICS OF CHLORPYRIFOS, CYPERMETHRIN AND PROFENOFOS ON CAULIFLOWER

*Thesis*

**by**


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**(H-2019-02-M)**


**submitted to**

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

**in**

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

**of**

**MASTER OF SCIENCE (AGRICULTURE) ENTOMOLOGY**

**DEPARTMENT OF ENTOMOLOGY**
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# CERTIFICATE – I

This is to certify that the thesis titled **"Residue dynamics of chlorpyrifos, cypermethrin and profenofos on cauliflower"** submitted in partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE (AGRICULTURE) ENTOMOLOGY** in the discipline of **PLANT PROTECTION** to Dr. Yashwant Singh Parmar University of Horticulture and Forestry, (Nauni) Solan (HP) -173 230 is a bonafide research work carried out by **Ms. DIVYA BHARTI (H-2019-02-M)** daughter of Mr. Rahul Sharma under my supervision and that no part of this thesis has been submitted for any other degree or diploma.

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

**Place: Nauni, Solan**
**Date:**

**(Dr. Sapna Katna)**
**Chairperson**
**Advisory Committee**

## CERTIFICATE - II

This is to certify that the thesis titled, **"Residue dynamics of chlorpyrifos, cypermethrin and profenofos on cauliflower"**, submitted by **Ms. DIVYA BHARTI (H-2019-02-M)** daughter of Mr. Rahul Sharma to Dr. Yashwant Singh Parmar University of Horticulture and Forestry, Nauni, Solan (HP)- 173 230, India in partial fulfilment of the requirements for the degree of **MASTER OF SCIENCE (AGRICULTURE) ENTOMOLOGY** in the discipline of **PLANT PROTECTION** has been approved by the Advisory Committee after an oral examination of the student in collaboration with an External Examiner.

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*Acknowledge all of your small victories. They will eventually add up to something great*

***-Kara Goucher***

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**Place:- Nauni, Solan**
**Date:-** **(DIVYA BHARTI)**

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# LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| *et al*. | : | etalia (Co-workers) |
| % | : | Percent |
| / or -1 | : | Per or per unit |
| @ | : | At the rate |
| < | : | Less than |
| > | : | More than |
| °C | : | Degree Celsius |
| µg | : | Microgram ($10^{-6}$ g) |
| µl | : | Microlitre |
| µm | : | Micrometer |
| µv | : | Microvolt |
| a.i. | : | Active ingredient |
| ADI | : | Acceptable daily intake |
| b | : | Slope of regression equation |
| BDL | : | Below determination limit |
| CIBRC | : | Central Insecticides Board and Registration Committee |
| cm | : | Centimetre |
| DRR | : | Double recommended rate |
| E | : | East direction |
| EC | : | Emulsifiable concentrate |
| EPA | : | Environmental protection agency |
| FAO | : | Food and Agriculture Organization |
| Fig. | : | Figure |
| FSSAI | : | Food Safety and Standards Authority of India |
| FYM | : | Farm Yard Manure |
| g | : | Gram |
| GC | : | Gas chromatography |
| ECD | : | Electron capture detector |
| FPD | : | Flame photometric detector |
| ha | : | Hectare |
| i.e. | : | Id Est (that is) |
| kg | : | Kilogram |
| L | : | Litre |
| $LD_{50}$ | : | Lethal dose |
| LOD | : | Limit of determination |

| | | |
|---|---|---|
| LOQ | : | Limit of quantification |
| $m^3$ | : | Cubic meter |
| mm | : | Millimetre |
| mg | : | Milligram |
| min | : | Minutes |
| ml | : | Millilitre |
| mol | : | Mole |
| MPRNL | : | Monitoring of Pesticide Residues at National Level |
| MRL | : | Maximum residue limit |
| MT | : | Metric tonnes |
| N | : | North direction |
| ND | : | Not detected |
| PHI | : | Pre harvest interval |
| ppm | : | Parts per million |
| PRL | : | Pesticide Residue Laboratory |
| PSA | : | Primary Secondary Amines |
| $R^2$ | : | Correlation coefficient |
| RBD | : | Randomized block design |
| rpm | : | Rotations per minute |
| RR | : | Recommended rate |
| SC | : | Suspension concentrate |
| SD | : | Standard deviation |
| $T_{1/2}$ or $RL_{50}$ | : | Half-Life |
| UV | : | Ultraviolet |
| viz. | : | Namely |
| WHO | : | World Health Organization |
| w/v | : | Weight by volume |

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# *Chapter-1*

# INTRODUCTION

Food is the basic necessity of life and vegetables are one of the most important component of food. India holds the second position in the production of vegetables after China (48 per cent) with a global share of 14 per cent. They are considered as the cheap source of energy, rich source of essential biochemicals and nutrients such as carbohydrates, proteins, vitamins, carotene, iron, calcium, ascorbic acid and palpable concentration of trace minerals; hence they fulfil the requirements of our balanced diet (Chandra *et al.,* 2015). Higher intakes of vegetables are beneficial for the maintenance of human health or prevention of diseases such as cancer, cardiovascular diseases and obesity (Walia *et al*., 2010). They not only help us by providing a balanced diet, but can also improve farm economy, conserve natural resources and alongside improve farmers income, thus cultivation of vegetables can play a indispensable role to maintain the sustainability and profitability of Indian agriculture. In India, vegetables are grown on an area of 103.16 lacs hectares with an annual production of 1894.64 lacs MT and corresponding figures for Himachal Pradesh are 90.94 thousand hectares and 1856.80 thousand MT (Anonymous, 2020).

Cauliflower (*Brassica oleracea var. botrytis* L.*)* belonging to the family brassicaceae is one of the most important winter vegetable which is grown for its edible curds throughout the country and give better return over investment to the farmers. It is available year-round, although especially plentiful in the spring and fall (Rumeza and Hanit, 2006). It is high in protein, fiber, folacin, potassium, vitamin C whereas low in calories, fat and cholesterol. In India, the area under cauliflower cultivation is around 458 thousand hectares with an annual production of 8840 thousand MT. In Himachal Pradesh it covers an area of 5.56 thousand hectares with 131.01 thousand MT annual production (Anonymous, 2018). Intensive cultivation of cauliflower in main season as well as in off season has resulted in high pest infestation. Some of the important insect pests of cauliflower are diamondback moth (*Plutella xylostella*); cabbage caterpillar (*Pieris brassicae*); aphids (*Brevicoryne brassicae*); head caterpillar (*Hellula undalis*) and flea beetle (*Phyllotreta cruciferae*) (Chaudhuri *et al*., 2001). Among these, diamondback moth (*Plutella xylostella* L.) is the most notorious pest on cruciferous vegetables causing 52 percent loss in marketable produce and farmers apply pesticides 8 to 10 times to effectively control this pest (Reddy *et al*., 2017a).

The population of the world is increasing day by day; hence there is a need to produce 60 per cent more food for the over increasing world population by 2050 (FAO, 2012). To ensure this demand, control of insect-pests and diseases plays a key role in order to increase the production. The crop losses in the world would have been estimated around 40 per cent, if pesticides were not used in agriculture. Pesticides are the chemical substances which are generally utilized to manage agricultural pests, such as fungi, insects and weeds, in order to increase crop productivity. They are the most important component of integrated pest management, however, among the wide ranges of chemical pesticides, the insecticides usage account for 73 per cent in India (Patil and Katti, 2012). They are characterized by pronounced persistence against chemical/biological degradation, high environmental mobility, strong tendency for bioaccumulation in human and animal tissues and significant impacts on human health and the environment, even at extremely low concentrations (Liu *et al*., 2009). It is well recognized that the pesticides treated crops lead to harmful residues in the produce due to indiscriminate application of non-approved pesticides over a longer period of time and hence, increasing risks among the consumers. Pesticide residues have been found in both raw and fresh processed produce (Keikotlhaile *et al*., 2010) and therefore, rigorous safety assessments are undertaken to make sure that a particular insecticide recommended against insect-pests of a crop do not leave harmful residues in the crop.

Pesticide formulations are approved to be used against insect pests of crop only if used at right dose, right time, right interval and also there is no alarm about pesticide residues. Different insecticides are recommended by Central Insecticides Board and Registration Committee (CIBRC) against insect-pests of various crops and farmers found these chemicals effective in controlling the target pests. However, the recommended use of these insecticides vis-à-vis their effectiveness on wide range of pests, provoke the farmers to use them against pests of other crops also, on which they are not recommended, thus leaving harmful residues on treated crop at harvest. An extensive study conducted under the project 'Monitoring of Pesticide Residues at National Level' (MPRNL) revealed that residues of some insecticides viz. chlorpyrifos, cypermethrin and profenofos have been surfacing in cauliflower crop, although they are not recommended or approved against the insects-pests of cauliflower, throughout the country.

Food safety is an area of growing concern worldwide on account of its direct bearing on human health. Contamination of vegetables with pesticide residues has been reported by several researchers (Madan *et al*., 1996; Kumari *et al*., 2003). Processing of food at domestic and industrial level would offer a suitable means to tackle the current scenario of unsafe food (Kaushik *et al*., 2009). Food processing treatments such as washing, peeling, canning or cooking lead to a significant reduction of pesticide residues. Washing of vegetables is the most traditional and the preliminary unit operation applied to remove dirt and debris from vegetables prior to consumption. There have been various reports suggesting use of different simple household processes in dislodging pesticide residues from food commodities thus making them safe for human consumption (Chavarri *et al*., 2005; Aktar *et al*., 2009).

With the addition of data on persistence behaviour of chlorpyrifos, cypermethrin and profenofos on cauliflower, the farmers can be advised to follow proper waiting period for respective insecticide application. Hence, to review the persistence and to study effects of various decontamination treatments on these reported insecticides on cauliflower crop grown under open field conditions, the present investigation was carried out in localized condition of Solan district with following main objectives:

**Objectives**

i) To study the persistence of chlorpyrifos, cypermethrin and profenofos in/on cauliflower

ii) To study the pesticide residues in cauliflower cropped soil

iii) To study the effects of decontamination treatments on the residue status of chlorpyrifos, cypermethrin and profenofos in cauliflower

## *Chapter-2*

# REVIEW OF LITERATURE

This chapter contains the relevant literature pertaining to the present study entitled "**Residue dynamics of chlorpyrifos, cypermethrin and profenofos on cauliflower".** Insecticide application is one of the management options that can substantially reduce yield losses associated with insect pests infestation. However, indiscriminate use of insecticides has led to insecticide resistance, pest resurgence, secondary pest outbreak and environmental pollution besides upsetting the natural ecosystem. Now it is realized that many pesticide residues in agricultural produce cause health hazards (Patil *et al*., 2019). It is important to standardize simple cost effective methods to eliminate pesticide residues from the food commodities. The present study was designed to aid in decisions on the type of action that would be most appropriate for minimizing human exposure in treated crop. The available literature is reviewed under different headings as follows:

**1. Chlorpyrifos**

i) General information of chlorpyrifos
ii) Persistence of chlorpyrifos on crops
iii) Persistence of chlorpyrifos in soil
iv) Decontamination of chlorpyrifos

**2. Cypermethrin**

i) General information of cypermethrin
ii) Persistence of cypermethrin on crops
iii) Persistence of cypermethrin in soil
iv) Decontamination of cypermethrin

**3. Profenofos**

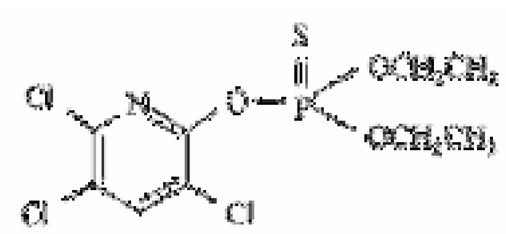
i) General information of profenofos
ii) Persistence of profenofos on crops
iii) Persistence of profenofos in soil
iv) Decontamination of profenofos

## 1. CHLORPYRIFOS

### 1.1 GENERAL INFORMATION OF CHLORPYRIFOS

Chlorpyrifos has a broad range of insecticidal activity and is effective by contact, ingestion and vapour action. It was introduced in 1965 by The Dow Chemical Co. under the code number ‘DOWCO 179’ and the trade marks ‘Dursban’ and ‘Lorsban’. It is non-systemic contact insecticide which is effective against household insects and crop pests.

#### 1.1.1 Chemical designation



| | |
|---|---|
| Common name | Chlorpyrifos |
| Trade name | Lorsban, Dursban, Wankrip, Tricel, Lethal, Durmet |
| IUPAC name | O, O-diethyl O - (3, 5, 6 – trichloro – 2 - pyridyl) - phosphorothioate |
| Molecular formula | $C_9H_{11}Cl_3NO_3PS$ |
| Molecular weight | 350.62 g $mol^{-1}$ |
| Formulation | Emulsifiable concentrate, granules, wettable powder |
| Application mode | Soil incorporation, crop foliar spray, chemigation |

#### 1.1.2 Physicochemical properties

The technical chlorpyrifos is a colourless to white crystal, with a mild mercaptan odour similar to the smell of sulfur compounds found in rotten eggs, onions, garlic and skunks, melting point 42.5-43$^0$C, Hg and vapour pressure 1.87 x $10^{-5}$ mmHg at 25$^0$C and Henry's constant 4.2 x $10^{-6}$ atm·$m^3$/mol at 25 °C. The technical product is about 94 per cent pure (Racke, 1993).

#### 1.1.3 Solubility and Stability

The solubility of chlorpyrifos at 35$^0$C is 2 mg/l water. It is also miscible with most organic solvents like ethyl acetate, acetonitrile, toluene and methanol (Tomlin, 2006). It is stable under normal storage conditions. The rate of hydrolysis in water increases with pH and temperature, the presence of copper and possibly other chelating metals. It is compatible with non-alkaline pesticides but is corrosive to copper and brass (Tomlin, 2006).

### 1.1.4 Metabolism

During exposure to UV light or to sunlight, chlorpyrifos underwent hydrolysis in the presence of water to liberate 3, 5, 6-trichloro-2-pyridinol, which further decomposed to diols and triols and ultimately cleavage of the ring to fragmentary products (Worthing, 1987). Hydrolysis in water occurs least readily at about pH 6 and very readily above pH 8.

### 1.1.5 Toxicology

According to Gallo *et al*. (1991), the acute oral $LD_{50}$ values for rats was 135-163 mg $kg^{-1}$ and for rabbits 1000-2000 mg $kg^{-1}$. The acute dermal $LD_{50}$, for rabbits was less than 2000 mg $kg^{-1}$. It was rapidly detoxified in the animal body. It was toxic to shrimps and fish. The acceptable daily intake (ADI) of chlorpyrifos for humans was 0.01 mg $kg^{-1}$.

### 1.1.6 Uses

Chlorpyrifos is used against broad array of insects and mites, primarily as a contact insecticide. It is used for control of Coleoptera, Diptera and Lepidoptera in soil or on foliage in a wide range of crops including cereals, vegetables, cotton, tobacco, sunflower, peanuts, potato, soya bean, beet, banana, fig, vines, pome fruits, stone fruits, citrus, strawberries, glasshouse and outdoor ornamentals, mushrooms and in forestry (Tomlin, 2006). It is also effective in controlling of household pests, mosquitoes (wrigglers and adults), ectoparasites on cattle and sheep (Solomon *et al*., 2014).

## 1.2 PERSISTENCE OF CHLORPYRIFOS ON CROPS

Raina and Raina (2008) recorded the average initial deposits of chlorpyrifos @ 0.56-0.86 and 1.29-1.43 mg $kg^{-1}$ on cauliflower curds at 500 g a.i. $ha^{-1}$ and 1000 g a.i. $ha^{-1}$ dose which dissipated below the MRL of 0.05 mg $kg^{-1}$ in 5.0-6.3 and 7.1-7.3 days with half-life values varied from 1.4-1.5 days and 1.5-1.6 days, respectively for two consecutive years. Gupta *et al*. (2015) also reported the average initial deposits of 0.604 and 0.805 μg $g^{-1}$ after the application of chlorpyrifos at single dose (400 g a.i. $ha^{-1}$) and double dose (800 g a.i. $ha^{-1}$), respectively on cabbage with half-life values ranged between 0.68-0.76 days and safe waiting period of 1 day at respective doses.

On okra fruits, the initial build-up residues of chlorpyrifos were 2.225 and 4.021 mg $kg^{-1}$ at 300 and 600 g a.i./ha, respectively. The half-life values were found to be 1.61–1.83 days and safe waiting period determined were 12.6 and 15.87 days at respective doses

(Moudgil, 2015). In another study, persistence behavior of chlorpyrifos in chilli was evaluated by Kumari and Chauhan (2015) following application of formulation of 20 EC @ 160 (single dose) and 320 g a.i.ha$^{-1}$ (double dose) at fruiting stage. The initial deposits of residues on the chilli fruits were observed to be 0.397 and 1.021 mg kg$^{-1}$ with the half-life period of 6.02 and 5.67 days at single and double dose, respectively. Similarly, Raut (2016) observed the mean initial residues 0.85 and 1.70 mg kg$^{-1}$ in chilli which reached to BDL on 10$^{th}$ and 15$^{th}$ day at recommended (300 g a.i./ha) and double the recommended dose (600 g a.i./ha), respectively. The half-life periods and pre-harvest intervals for chlorpyrifos were 2.05-2.74 and 7 days at respective doses.

Shukla *et al.* (2016) evaluated that the application of chlorpyrifos on capsicum @ 300 g a.i. ha$^{-1}$ resulted in initial deposits of 0.28 mg kg$^{-1}$ and 0.22 mg kg$^{-1}$ which reached to BDL in 20 days with the half-life values of 3.14 and 5.7 days in greenhouse and open field conditions, respectively. In the same direction, Ramadan *et al.* (2016) also evaluated the residual levels and dissipation behavior of chlorpyrifos in tomato (*Solanum lycopersicum* L.) fruits under Egyptian field condition and recorded the initial deposits of 4.280 mg kg$^{-1}$ when applied at 1140 g a.i. ha$^{-1}$ with half-life value and PHI of 2.5 and 15 days, respectively.

Persistence of chlorpyrifos and cypermethrin was studied by Banshtu and Patyal (2017a) on cauliflower after application of their individual as well as ready-mix formulations. Results revealed that the chlorpyrifos and cypermethrin residues in curds reached BDL in 10 and 7 days when applied at recommended rate (500 and 50 g a.i. ha$^{-1}$) and in 15 and 10 days when applied at double the recommended rate (1000 and 100 g a.i ha$^{-1}$), respectively. The initial deposits of chlorpyrifos were reduced to their half in 1.25-1.50 days and cypermethrin deposits became half in 1.38-1.69 days. Similarly, chlorpyrifos at two different doses of @ 300 g a.i/ha (standard dose) and 600 g a.i/ha (double dose) for persistence studies on brinjal crop had an initial deposits of 1.092 and 1.982 mg kg$^{-1}$ with a half-life values of 1.55 and 2.15 days and the waiting periods were observed to be 3.81 and 7.13 days at the respective doses (Brar *et al*., 2018). A residue study of chlorpyrifos in black pepper showed that residue value ranged between < 10 µg kg$^{-1}$ to 392.07 µg kg$^{-1}$ with the mean half-life of 1.41 days and waiting period of 13 days (Yap and Jarroop, 2018).

Katna *et al*. (2018) reported the initial deposits of 3.083 and 6.017 mg kg$^{-1}$ with a half-life of 1.86 and 2.29 days after the application of chlorpyrifos single dose (600 g a.i ha$^{-1}$) and double dose (1200 g a.i ha$^{-1}$), respectively on French beans. Residues declined below the limit of quantitation (LOQ) of 0.05 mg $kg^{-1}$ after 15 days of application of double dose of chlorpyrifos in green beans however, at the time of harvest in dry bean seeds and a waiting period of 5 days was suggested.

## 1.3 PERSISTENCE OF CHLORPYRIFOS IN SOIL

Fang *et al.* (2006) studied the dissipation of chlorpyrifos in pakchoi (*Brassica chinensis*) vegetated soil in a greenhouse and field conditions. The dissipation half-lives at the recommended dose were 0.6-1.2 days in a greenhouse and 0.4-1.0 days in a field, the corresponding values at double dose were 1.2-2.1 days in a greenhouse and 0.5-1.3 days in a field.

Gupta *et al*. (2011) observed no chlorpyrifos residues in 0 day sampled soil at single dose and detected residues (0.012 mg $kg^{-1}$) at double dose which persisted up to 3 days on tomato crop after the application of Action 505 EC (chlorpyrifos 50 per cent + cypermethrin 5 per cent) @ 0.8 and 1.6 L $ha^{-1}$. Persistence of chlorpyrifos in okra soil was studied by Samriti *et al*. (2012) following the application of pre-mix formulation of insecticides Action 505EC (chlorpyrifos 50 per cent + cypermethrin 5 per cent) at single (275 g a.i. $ha^{-1}$) and double dose (550 g a.i. $ha^{-1}$). The average initial deposits of chlorpyrifos in okra soil were 0.15 mg $kg^{-1}$ and 0.36 mg $kg^{-1}$ with the half-life ($t_{1/2}$) periods of 0.6 and 1.9 days for single and double dose, respectively. In soil, residues of chlopyrifos persisted up to 5 and 7 days in single and double dose, respectively.

The average initial deposits of chlorpyrifos in tomato cropped soil were 0.029 and 0.053 mg $kg^{-1}$ with the half-life period of 3.25 and 2.77 days after the application of single dose (400 g a.i. $ha^{-1}$) and double dose (800 g a.i. $ha^{-1}$), respectively (Rani *et al*., 2013). Moudgil (2015) observed that the initial deposits of chlorpyrifos were 0.584 mg $kg^{-1}$ at single dose (300 g a.i./ha) and 0.903 mg $kg^{-1}$ at double dose (600 g a.i./ha) in okra cropped soil which reduced to half in less than 2 days at both the doses. In another study, Raut (2016) found that the residues of chlorpyrifos were below detection limit in chilli cropped soil at harvest when applied @ 300 and 600 g a.i. $ha^{-1}$. Similarly, Ahlawat *et al*. (2017) revealed that the residues of chlorpyrifos 20 EC @ 300 g a.i. $ha^{-1}$ were below the limit of determination in tomato and green pea cropped soil at harvest.

## 1.4 DECONTAMINATION OF CHLORPYRIFOS

Mukherjee *et al*. (2006) studied the effects of various decontamination processes on the residues of the chlorpyrifos in cauliflower curds. The results indicated that washing reduced the residues of chlorpyrifos by 27.9 per cent and cooking by 41.4 per cent. Similarly, Satpathy *et al*. (2012) monitored the effects of household processing on removal of chlorpyrifos residues in tomato, okra, bean, eggplant, cauliflower and capsicum. In all the vegetables, washing with different household chemicals (NaCl @ 0.9 per cent, $NaHCO_3$ @ 0.1 per cent, acetic acid @ 0.1 per cent and $KMnO_4$ @ 0.001 per cent) reduced the residues by 20-89 per cent and boiling reduced the residues by 52-100 per cent.

Liang *et al*. (2012) revealed that washing with tap water, saline water (2 per cent), acetic acid (2 per cent) and baking soda (5 per cent) dislodged the chlorpyrifos residues in cucumber by 62.90, 66.70, 65.40 and 85.20 per cent, respectively. Similarly, the average initial deposits of chlorpyrifos (4.449 mg $kg^{-1}$) in tomato sampled after 2 hrs were dislodged by 58.50-83.20 per cent as a result of different decontamination processes viz; tap water washing, lemon water washing, bio wash, cooking, tamarind water washing (2 per cent), saline water washing (2 per cent), washing with sodium bicarbonate (0.1 per cent) and 4 per cent acetic acid (Harinathareddy *et al*., 2014). In another experiment, Chandra *et al.* (2015) investigated the effects of household processing on removal of chlorpyrifos and cypermethrin residues in brinjal and okra which included washing with water, 2.0 per cent NaCl, 1.0 per cent $NaHCO_3$, 0.5 per cent acetic acid and boiling in water. The results concluded that the residues in brinjal reduced by 29.5-99.2 and 30.2-92.1 per cent, whereas, residues in okra reduced by 24.5-98.9 and 27.2-92.2 per cent in case of chlorpyrifos and cypermethrin, respectively, out of which maximum reduction in residues (99.7 per cent) was observed in boiling as compared to washing. Harinathareddy *et al*. (2015) revealed that washing of grapes with tap water dislodged the residues of chlorpyrifos to 28.00 per cent and subsequent washing with 2 per cent salt solution reduced chlorpyrifos residues to 23.5 per cent.

Nowowi *et al*. (2016) conducted studies in order to investigate the effectiveness of several cleaning solutions in removing chlorpyrifos residues in cauliflower (*Brassica oleracea*) and observed that tamarind juice solution had the greatest removal effect in comparison to other cleaning solutions with 93.04 per cent removal rate followed by filtered flour solution (17.03 per cent) and vinegar solution (11.42 per cent) however, tap water and soda-salt solution had no removal effect in removing chlorpyrifos in cauliflower.

Muralikrishna *et al*. (2016) reported that dipping of amaranthus (*Amaranthus tricolor* L.) in 1 per cent veggie wash for 20 minutes followed by three further washings plus cooking was most effective in removal of chlorpyrifos 20 EC residues (83 per cent) followed by 1 per cent veggie wash for 20 minutes (78 per cent), 1 per cent veggie wash for 10 minutes plus cooking (76 per cent) and 2 per cent vinegar (74 per cent). In another study, N Vinay (2018) determined the effects of various culinary processes on the residues of chlorpyrifos in onion among which microwave cooking after tap water washing was found most effective in providing relief to the tune of 95.98-100 per cent followed by open pan cooking after tap water washing (78.62-100 per cent), tamarind water washing (52.88-100 per cent), saline water washing (43.34-100 per cent), lukewarm water washing (33.17- 56.31 per cent) and tap water washing (21.06-32.72 per cent). Similarly, Brar *et al*. (2018) found that washing of brinjal fruits with tap water, 2 per cent NaCl and lukewarm water was effective in removing chlorpyrifos residues to the extent of 36.17, 45.74 and 48.63 per cent, respectively, however, cooking (open pan and microwave) was found to be most effective (up to 70.06 per cent) in removing insecticide residues.

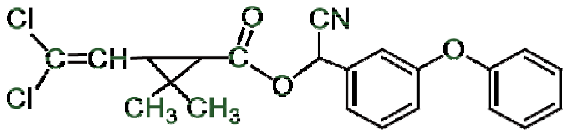
Hassanzadeh and Bahramifar (2019) subjected cucumber fruits to different household processes which resulted in 27–100 per cent reduction of chlorpyrifos residues by washing and 53-100 per cent reduction by peeling which was found most effective. Similarly, Singh *et al*. (2019) revealed that when the chlorpyrifos (300 g a.i. $ha^{-1}$) treated cucumber fruits collected at 1, 3 and 5 days were washed with running tap water for 2 minutes, the residues reduced to 0.458, 0.225 and 0.064 mg $kg^{-1}$, respectively and the per cent relief obtained to the tune of 30.23, 31.79 and 30.07, respectively, however, peeling was found most effective which provided upto 91.36 per cent relief from chlorpyrifos residues.

## 2. CYPERMETHRIN

### 2.1 GENERAL INFORMATION OF CYPERMETHRIN

Synthetic pyrethroids are a group of compounds which are environmentally safe because of their effectiveness at low dosages and low mammalian toxicity. Cypermethrin is one insecticide of this series which is non-systemic with contact and stomach action and also exhibits anti-feeding action. It is compatible with many pesticides and may be found in formulations with profenofos, chlorpyrifos and endosulfan. It has been developed by Shell International Chemical Co. Ltd in 1975 under the code number ‘WL 43 467’ and the trade mark ‘Ripcord’ (Cox, 1996).

### 2.1.1 Chemical designation



| | |
|---|---|
| Common name | Cypermethrin |
| Trade name | Ammo, Cymbush, Demon, Cyperguard, Challenger, Ripcord, Imperator, Avicide, Folcord, Kafil Super |
| IUPAC name | Cyano(3-phenoxyphenyl)methyl3-(2,2- dichloroethenyl)- 2,2-dimethylcyclopropanecarboxylate |
| Molecular formula | $C_{22}H_{19}C_{l2}NO_3$ |
| Molecular weight | 416.3 g mol$^{-1}$ |
| Formulation | Emulsifiable concentrate, oil-base concentrate, wettable powder |
| Application mode | Crop foliar spray in water |

### 2.1.2 Physicochemical properties

The technical product is a viscous yellowish brown semi-solid mass, which is liquid at $60^0$C, vapour pressure 3.8 x $10^{-8}$ mmHg at $70^0$C. Cypermethrin being a mixture of 8 isomers including alpha, beta, theta and zeta. Alpha-cypermethrin is a mixture of two of the four cis isomers present to approximately 25 per cent in cypermethrin i.e., (1R, cis)S and (1S, cis)R which produce 90 per cent of the insecticidal activity.

### 2.1.3 Solubility and Stability

Water solublility of cypermethrin is 0.01-0.2 mg/litre at $21^0$C. It is also soluble in various organic solvents like acetone, hexane, ethanol, cyclohexane, xylene and chloroform (WHO, 1990). It is more stable in acid than alkaline media, with optimum stability at pH 4 (WHO, 1990).

### 2.1.4 Metabolism

Alpha-cypermethrin is metabolized by cleavage of its ester bond. In the rat, the henoxybenzyl alcohol portion of the molecule is hydroxylated and conjugated with sulfate; the cyclopropane carboxylic acid portion is also conjugated (probably as a glucuronide) prior to urinary excretion. Studies with liver microsomes from rats, rabbits and man have demonstrated that esteric hydrolysis and oxidative pathways can occur in all three species but esteric hydrolysis is the more prominent pathway for liver preparations from rabbit and man (Cox, 1996).

### 2.1.5 Toxicology

The acute oral $LD_{50}$ for rats is 303-4123 mg/kg (depending on the carrier and conditions used), whereas, the dermal $LD_{50}$ for rabbits is >2400 mg/kg. It is a slight skin irritant, a mild eye irritant and can cause skin sensitization. It is toxic for fish, aquatic arthropods and honey-bees in laboratory tests but in practical usage, no serious adverse effects have been noticed because of the low rates of application and lack of persistence in the environment (Worthing, 1987). The acceptable daily intake (ADI) of cypermethrin for humans is 0.05 mg/kg.

### 2.1.6 Uses

Cypermethrin is considered to be a moderately toxic pesticide. It is mostly used to control wide range of insects belonging to orders especially Lepidoptera, Coleoptera, Diptera and Hemiptera infesting fruits (including citrus), vines, vegetables, cereals, cotton, coffee, cocoa, oilseeds and ornamentals. Cypermethrin, one of a handful of light-stable synthetic pyrethroids, is registered to control cockroaches, fleas and other indoor pests at home, restaurants, hospitals, schools and food-processing plants (Roy Choudhury, 2017).

## 2.2 PERSISTENCE OF CYPERMETHRIN ON CROPS

Duara *et al.* (2003) evaluated residues of cypermethrin on brinjal following single application at 22.5, 45 and 75 g a.i./ha. The initial deposits of cypermethrin were 0.31, 0.58 and 0.93 µg $g^{-1}$ with the half-life values of 3.30, 3.39 and 3.16 days at respective doses and reached below MRL at $7^{th}$ day. In another experiment, Deen *et al*. (2009) determined the residues of cypermethrin @ 60 g a.i. $ha^{-1}$ on okra crop and recorded the initial deposits of 0.53 µg $g^{-1}$ with the half-life period of 3.3 days and safe waiting period of 4.7 days, whereas, residue levels reached below MRL value in 9 days. Another study was conducted by Paneru *et al*. (2012) to evaluate the residue levels of cypermethrin (Super killer 10% EC) @ 1.5 ml/L on cauliflower and reported residues of 0.45, 0.40, 0.37 and 0.32 ppm on 1,3,7 and 15 days after spraying, respectively.

Jaswal (2015) studied the dissipation behaviour of cypermethrin (@ 50 and 100 g a.i. $ha^{-1}$) and profenofos (@ 500 and 1000 g a.i. $ha^{-1}$) in chilli fruits. The initial deposits of cypermethrin and profenofos recorded as 0.353 and 1.197 mg $kg^{-1}$ at single dose and 0.523 and 2.251 mg $kg^{-1}$ at double dose, respectively. The residues of profenofos reduced to half in less than 2 days, whereas in cypermethrin it took 2.2-2.3 days with the safe waiting periods of 7.7 and 10.3 days for cypermethrin and profenofos, respectively. Similarly, Singh *et al.* (2015) conducted the study to observe the persistence pattern of cypermethrin in chilli fruits following three applications of cypermethrin (Super fighter 25 EC) at 50 and 100 g a.i. $ha^{-1}$ at 10 days interval. The average initial deposits of cypermethrin in chilli fruits were 1.46 and 3.11 mg $kg^{-1}$ with the half-life periods of 4.43 and 4.70 days at recommended and double the recommended dosages, respectively, however, residues of cypermethrin declined below its limit of quantification of 0.05 mg $kg^{-1}$ after 25 days at both the dosages.

Rahman *et al.* (2015) evaluated that the residues of cypermethrin determined from eggplant fruit samples sprayed @ 1 ml/L were above MRL upto 3 days after application (0.762 ppm) while in case of 2 ml/L, fruit samples had residues above MRL upto 5 days after spraying (0.753 ppm), whereas, the safe waiting periods were 3 and 5 days at respective dosages.

Banshtu and Patyal (2016) observed that the cypermethrin (Challenger 25 EC) residues reached below detectable limit in 7 and 10 days when applied at recommended rate (@ 50 g a.i./ha) and double the recommended rate (100 g a.i./ha), respectively on cauliflower curds, however, it became half in 1.38–1.69 days. In another study, Nahar *et al.* (2016) studied the dissipation of cypermethrin in cauliflower and found residues @ 6.7±1.8 mg $kg^{-1}$ at 0 and 0.12±0.01 mg $kg^{-1}$ at 15 days after application, respectively. The residues of cypermethrin were found below MRL at 7 days.

Mayannavar *et al.* (2017) studied the persistence of cypermethrin @ 50 and 100 g a.i./ha on okra crop applied twice at an interval of 10 days at fruit initiation stage. The initial residues of cypermethrin dissipated with half-life of 2.38 and 2 days at recommended and double the recommended dose, respectively, whereas, the pre-harvest interval of 5 days was suggested at the LOQ of 0.05 mg/kg for cypermethrin for safe consumption of okra fruits.

Gogikar *et al*. (2017a) conducted field experiments during kharif 2014 and 2015 with curry leaf variety Suwasini to study the dissipation pattern of cypermethrin 10 EC @ 50 g a. i./ha (550 ml/ha) by giving two sprays first at vegetative stage and second 10 days later. Results showed that the initial deposits of cypermethrin 13.09 mg $kg^{-1}$ dissipated to 0.28 mg kg$^{-1}$ and the residues reached to BDL in 10 days. Amir *et al*. (2017) in their studies reported residues of chlorpyrifos, cypermethrin and profenofos from different cauliflower samples collected from District Faisalabad ranging from 0.003 to 0.314 mg kg$^{-1}$, 0.039 to 0.334 mg kg$^{-1}$ and 0.006 to 0.875 mg kg$^{-1}$, respectively.

Patil *et al.* (2019) studied the persistence of cypermethrin 5 EC (55.5 ml a.i./ha) in chilli fruits and revealed the initial deposit and half-life period of 0.55 µg g$^{-1}$ and 2.6 days, respectively. Similarly, experiments were conducted by Anuradha and Bhuvaneswari (2020) for two consecutive years to study the dissipation pattern of cypermethrin at 50 and 100 g a.i. ha$^{-1}$ on curry leaf. The initial deposits of cypermethrin at recommended dose and double the recommended dose were 2.99 and 3.83 µg g$^{-1}$ which dissipated to 0.16 and 0.21 mg kg$^{-1}$, respectively and reached BDL at 30$^{th}$ days after application in both the doses.

## 2.3 PERSISTENCE OF CYPERMETHRIN IN SOIL

Jyot *et al.* (2013) applied combination formulation of chlorpyrifos 50 per cent and cypermethrin 5 per cent (Nurelle-D 505) at recommended dosage (1 L ha$^{-1}$) and double dosage (2 L ha$^{-1}$) three times at an interval of 15 days on chilli fruits and reported that the soil samples did not show the presence of chlorpyrifos and cypermethrin after 15 days of the last application at the determination limit of 0.01 mg kg$^{-1}$. In another study, Jaswal (2015) observed 0.081 mg kg$^{-1}$ cypermethrin and 0.561 mg kg$^{-1}$ profenofos residues in chilli cropped soil after application at single dose @ 0.111 mg kg$^{-1}$ and at double dose @ 1.102 mg kg$^{-1}$, respectively. Similarly, Mohapatra (2014) carried out an experiment to study the residue dynamics of chlorpyrifos and cypermethrin in/on pomegranate (*Punica granatum* L.) cropped soil. The results concluded that the chlorpyrifos residues were 0.21 and 0.46 mg kg$^{-1}$ and cypermethrin residues were 0.15 and 0.36 mg kg$^{-1}$, respectively which reached below LOQ at harvest in both the test insecticides.

Rahman *et al.* (2015) reported that the cypermethrin residues determined from eggplant cropped soil sprayed @ 1 ml/L were above MRL upto 5 days after spraying (0.608 ppm) while in case of 2 ml/L, soil samples had residues above MRL upto 7 days after spraying (0.768 ppm). Mayannavar *et al.* (2017) studied the persistence of cypermethrin @ 50 and 100 g a.i./ha on okra cropped soil when applied twice at an interval of 10 days at fruit initiation stage and observed that the residues of cypermethrin in soil at harvest (30$^{th}$ day after application) were below detection limit at both the doses.

Banshtu and Patyal (2017b) studied the persistence pattern of profenofos and cypermethrin in cauliflower field soil when applied at recommended rate (400 and 40 g a.i. $ha^{-1}$) and double recommended rate (800 and 80 g a.i. $ha^{-1}$), respectively and found that the residues of both the insecticides persisted in soil upto 10 days only.

## 2.4 DECONTAMINATION OF CYPERMETHRIN

Walia *et al*. (2010) observed that the removal of cypermethrin residues was more in grilling (50.12 per cent), followed by cooking in oil (45.2 per cent), cooking in water (41.4 per cent) and microwave cooking (40.89 per cent), whereas, minimum effects were observed in washing with water.

Chowdhury *et al*. (2013) conducted decontamination studies of cypermethrin residues in tomato using rice bran. Tomato samples were spiked with 0.45 mg/kg of cypermethrin and the results concluded that rubbing with rice bran paste for 10 min removed residues upto 97.56±0.22 per cent, whereas, residues were not detected in tomato samples treated for 15 minutes. Tomer *et al*. (2014) also studied that washing with 5 per cent $NaHCO_3$ and 2 per cent $KMnO_4$ solution resulted in 89.53 and 56.88 per cent removal of cypermethrin residues from okra fruits.

The effects of household processing on removal of acephate, cypermethrin and profenofos residues in chilli were investigated in a study conducted by Jaswal (2015). It was observed that the tap water washing, lukewarm water washing, vinegar water washing and tamarind water washing of chilli fruits were effective in removing residues upto 45.06, 48.92, 53.80 and 54.10 per cent, respectively. The results revealed that the saline water washing was found most effective (upto 59.05 per cent) in dislodging insecticide residues. In another experiment, decontamination of cypermethrin and deltamethrin was studied by Patel *et al.* (2016) in/on brinjal fruits where washing the fruits with tap water as well as cooking for 10 minutes was found most effective process and resulted in BDL of both cypermethrin and deltamethrin residues in brinjal fruits. Priyadarshini *et al*. (2017) observed reduction in residues of chlorpyrifos, cypermethrin and profenofos in curry leaves by using various decontamination treatments like tap water washing (43.37, 58.36 and 57.64 per cent), sodium bicarbonate dipping (35.28, 19.21 and 17.63 per cent), acetic acid dipping (22.26, 44.53 and 50.08 per cent) and washing with salt solution (6.97, 37.93 and 42.98 per cent), respectively.

Banshtu and Patyal (2018) carried out experiments to evaluate the effect of different decontamination processes on reduction of chlorpyrifos and cypermethrin residues in cauliflower curds such as washing of zero day contaminated curd samples provided 37.41 per cent and 40.10 per cent relief, cooking degraded residues up to 36.58-58.95 per cent and 45.45-66.31 per cent, washing plus cooking removed residues up to 70 per cent as compared to other processes and proved to be the best technique in removing the residues, washing of curds with 2 per cent NaOH solution reduced the residues up to 60.97- 69.03 per cent and 62.50-69.20 per cent, whereas washing with 0.05 per cent HCl solution reduced the residues up to 58.53-65.06 per cent and 63.44-66.97 per cent, respectively.

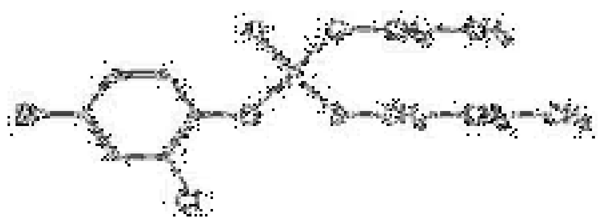
The efficiency of washing solutions (citric acid, acetic acid, garlic extract and ginger extract) along with tap water in spinach was investigated for cypermethrin residues dissolution by Hussnain *et al*., 2021. The results showed that the highest reduction in cypermethrin residues were 0.017±0.014 mg $kg^{-1}$ (83 per cent) by 10 per cent acetic acid followed by 0.037±0.048 mg $kg^{-1}$ (81 per cent) with 10 per cent ginger extract while the lowest reduction in residues were 0.468 ± 0.016 mg $kg^{-1}$ (38 per cent) by 5 per cent citric acid, respectively. Mahugija *et al*. (2021) studied the effect of washing on the removal of chlorpyrifos, cypermethrin and profenofos residues in tomatoes and resulted in reduction upto 73.2 per cent, 70.2 per cent and 47.4 per cent, respectively.

## 3. PROFENOFOS

### 3.1 GENERAL INFORMATION OF PROFENOFOS

Profenofos is a broad spectrum organophosphorus insecticide and acaricide with moderate mammalian toxicity and brief to moderate persistence. It is not only a contact and stomach insecticide but also has an excellent translaminar action. It was developed by Ciba-Geigy AG in 1975 under the code number ‘CGA 15 324’ and trade mark ‘Curacron’ (Kegley *et al*., 2010).

#### 3.1.1 Chemical designation



| | |
|---|---|
| Common name | Profenofos |
| Trade name | Curacron, Profex, Profos, Carina |
| IUPAC name | O-(4-bromo-2-chlorophenyl)-O-ethyl-S-propylphosphorothioate |
| Molecular formula | $C_{11}H_{15}Br\ ClO_3PS$ |
| Molecular weight | 373.6 g $mol^{-1}$ |
| Formulation | Emulsifiable concentrate |
| Application mode | Crop plant spray |

### 3.1.2 Physicochemical properties

Profenofos is a pale yellow liquid having garlic like odour. Its melting point is $2.85^0C$, boiling point $110^0C \times 10^{-3}$ mmHg and vapour pressure $1.78 \times 10^{-5}$ mmHg at $20^0C$. The technical product is about 94 per cent pure.

### 3.1.3 Solubility and Stability

The solubility of profenofos at $20^0C$ is 20 mg/l. It is also miscible with most organic solvents like ethyl acetate, acetonitrile, toluene and methanol (Tomlin, 2006). It is stable under neutral and slightly acid conditions and unstable in alkaline conditions (Tomlin, 2006).

### 3.1.4 Metabolism

Profenofos is biotransformed by a major pathway involving side chain depropylation, desulfuration, and phenyl-ester bond cleavage to 4-bromo-2- chlorophenol and by a minor pathway involving side chain O-dethylation and subsequent phenyl-ester bond cleavage to the above phenol. Both pathways culminated in conjugation with glucuronic and sulfuric acids (Kegley *et al*., 2010).

### 3.1.5 Toxicology

According to Gallo *et al*. (1991), the acute oral $LD_{50}$ values for rats is 358 mg/kg. Profenofos is low in toxicity when applied to the skin. The acute dermal $LD_{50}$ in rats is less than 3300 mg/kg. It is highly toxic to birds and fish. The acceptable daily intake (ADI) of profenofos for humans is 0.01 mg/kg.

### 3.1.6 Uses

Profenofos is a non-systemic broad spectrum insecticide used to control a wide range of agricultural and horticultural crop pests such as aphids, boll weevils, fruit flies etc. It is mainly used as acaricide due to presence of active sulphur compound. Profenofos is also used against various household pests like houseflies, cockroaches, mosquitoes, animal ectoparasites and human head and body lice.

## 3.2 PERSISTENCE OF PROFENOFOS ON CROPS

Reddy *et al*. (2007) studied the dissipation of profenofos (@ 0.1 per cent a.i./ha) on chillies by applying four sprays each at 15 days interval and the initial deposits after last spray in green chillies were recorded to be 0.36 mg $kg^{-1}$, which dissipated to 0.02 mg $kg^{-1}$ by 30 days amounting to the loss of 92.4 per cent, respectively with half-life value and waiting period of 41 days and 19 days, respectively, whereas, the residues in dried red chillies (collected at harvest) were below detectable level. Similarly, Singh (2013) studied the persistence of profenofos in capsicum and reported the initial deposits of 1.403 mg $kg^{-1}$ at single dose and 2.720 mg $kg^{-1}$ at double dose, respectively which reduced to half in 2-2.6 days with the safe waiting period of 9.6 days.

Raveendranath *et al.* (2014) carried out studies on persistence of profenofos 50 EC on cucumber when applied @ 500 g a.i./ha and the samples were collected at regular intervals of 0, 1, 3, 5, 7, 10 and 15 days after second spray. The initial deposits of profenofos recorded were 7.20 ppm with the half-life period of 3.65 days. In another study, Reddy *et al.* (2014) evaluated the persistence of profenofos residues in cabbage during kharif 2012 and showed the initial deposits of 2.75 mg $kg^{-1}$ which dissipated to below detectable level in 15 days. The MRL for profenofos was 0.2 mg $kg^{-1}$ while the safe waiting period was 4 day.

In order to recommend the maximum residual limits and pre harvest intervals for ensuring food safety, Rao *et al.* (2015) studied the dissipation dynamics of profenofos and cypermethrin on tomato crop when sprayed twice at the rate of 500 and 50 g a.i. $ha^{-1}$, respectively. Initial deposits of profenofos (1.698 mg $kg^{-1}$) and cypermethrin (0.158 mg $kg^{-1}$) dissipated to BDL by $10^{th}$ and 5th day, respectively. MRLs of 4 mg $kg^{-1}$ and 0.4 mg $kg^{-1}$ were recommended for profenofos and cypermethrin, respectively and PHI of 1 day was recommended for food safety.

Bansode *et al.* (2017) while studying the persistence of profenofos @ 500 g a.i./ha in okra crop concluded that the residues dissipated with half life of 1.59 days. Similarly, the persistence of profenofos residues in brinjal fruits was studied by Brar *et al.* (2017) after spraying the crop twice at 10 days interval at recommended rate (RR) and double recommended rate (DRR). The initial deposits of profenofos residues were 1.966 and 2.460 mg $kg^{-1}$ at 500 and 1000 g a.i./ha and dissipated to half in 1.5 and 1.9 days. A waiting period of 8 days was suggested for profenofos on brinjal. The dissipation pattern of profenofos 50 EC (1000 g a.i. $ha^{-1}$) on cabbage crop revealed the initial deposits of 0.99 mg $kg^{-1}$ recorded at 0 day (2 hours after last spray) which dissipated to 0.85, 0.82, 0.16 and 0.07 mg $kg^{-1}$ by 1, 3, 5 and 7 days after last spray, respectively and below determination level by 10th day (Reddy *et al*., 2017b).

Persistence of profenofos and cypermethrin was studied by Banshtu and Patyal (2017b) on cauliflower curds after application of their individual as well as ready-mix formulations. Profenofos and cypermethrin when applied at recommended rates @ 400 g and 40 g a.i./ha reached below the limit of determination in 10 and 5 days, whereas, in 15 and 7 days when applied at double the recommended rates @ 800 g and 80 g a.i./ha, respectively. The initial deposits of profenofos were reduced to their half in 1.78–2.21 days and cypermethrin deposits became half in 1.06–1.42 days. The safe waiting period of one day was suggested at recommended and double the recommended rates on cauliflower curds.

Naik *et al*. (2020) conducted the field study to investigate the dissipation kinetics of profenofos 50 per cent EC at 500 and 1000 g a.i.$ha^{-1}$ in pigeonpea pods and recorded the initial deposits of 20.28 and 41.64 µg $g^{-1}$ which dissipated to the level of 0.78 and 1.98 µg $g^{-1}$ accounting to the loss of 96.15 and 95.58 per cent with the half-life values of 5.18 and 5.93 days at single and double dose, respectively.

### 3.3 PERSISTENCE OF PROFENOFOS IN SOIL

Ahmed *et al.* (2009) found average initial deposits of profenofos in tomato cropped soil as 11.71±1.0 mg $kg^{-1}$ which dissipated after 14 days of application and found below the limit of detection. In another study, Singh (2013) found initial deposits of profenofos as 0.913 mg $kg^{-1}$ at single dose and 1.796 mg $kg^{-1}$ at double dose, respectively in capsicum cropped soil, whereas, Patel (2014) revealed an initial profenofos deposits of 5.24 µg $g^{-1}$ in clayey loam soil and 5.92 µg $g^{-1}$ in sandy loam soil which dissipated significantly over the time.

Negi (2015) observed the initial deposits of 0.500 mg $kg^{-1}$ at single dose and 1.003 mg $kg^{-1}$ at double dose for profenofos in okra cropped soil. The persistence pattern of profenofos residues in brinjal cropped soil was studied by Brar *et al.* (2017) after spraying the crop twice at 10 days interval at recommended rate and double the recommended rate and found residues of profenofos persisted in soil for 5-10 days only.

### 3.4 DECONTAMINATION OF PROFENOFOS

Singh (2013) studied the effect of culinary processes on insecticide residues of profenofos in capsicum fruits and found that the tap water washing, saline water washing and lukewarm water washing were effective in removing residues upto 45.9, 54.09 and 61.29 percent, respectively, whereas, the results concluded that cooking (open pan and microwave) was found most effective (upto 73.77 per cent) in dislodging insecticide residues. Similarly, Negi (2015) found that the washing of okra fruits by tap water, saline water and lukewarm water were effective in removing the residues of profenofos upto 41.87, 50.00 and 58.13 per cent, respectively.

Dhiman and Hiremath (2014) found that the tap water washing reduced the chlorpyrifos, cypermethrin and profenofos residues to 67.162, 6.991 and 54.354 per cent, respectively while, washing with boiled water lead to respective reduction of residues to 55.019, 29.841 and 97.379 percent in cauliflower curds.

Kelageri *et al*. (2015) studied risk mitigation methods for removal of profenofos residues from tomato for food safety. Among various decontamination methods tested, veggy wash (acetic acid glacial+ baking soda+ lemon juice+ water) was very effective in removing residues to an extent of 75.84 per cent followed by 4 per cent acetic acid solution (71.22 per cent) and tap water washing was found least effective (37.60 per cent) in removing profenofos residues from tomato.

Banshtu *et al.* (2018) evaluated the effect of various decontamination processes on reduction of profenofos and chlorpyrifos residues in cauliflower curds after application of Profex 50EC @ 0.8 ml per L and Lethal 20EC @ 2.50 ml per L twice at 15 days interval. The results revealed that the washing of zero day contaminated curd samples provided 26.06-67.09 per cent and 35.44-67.18 per cent relief, cooking degraded residues up to 37.17-67.57 per cent and 36.00-56.80 per cent, while washing plus cooking removed residues up to 70 per cent as compared to other processes and proved to be the best technique in removing the residues, washing of curds with 2 per cent NaOH solution reduced residues up to 67.09-70.30 per cent and 40.00-67.18 per cent, whereas, washing with 0.05 per cent HCl solution removed residues up to 63.48-65.52 per cent and 44.00-61.17 per cent in case of profenofos and chlorpyrifos, respectively.

Kyi *et al*. (2020) studied the effect of household processing methods on the removal of profenofos residues in mustard greens and concluded that the high amount of residues were found in the control group (93.45 mg/kg) followed by washing of the mustard greens with tap water (30 mg/kg), or after washing and subsequent dipping in a 1 per cent salt solution (25.26 mg/kg) of sample had pesticide residues below maximum residue levels which was found more effective than washing of mustard greens with tap water only. In another study, Srivastava *et al*. (2021) evaluated the efficacy of different decontamination processes in reducing the pesticide mixture load of six insecticides (quinalphos, profenofos, ethion, lambda-cyhalothrin, imidacloprid, and acetamiprid) from chilli (*Capsicum annuum* L.) and samples were subjected to decontamination processes after 48 hours of pesticide mixture spray. The results revealed that solutions of 1 and 5 per cent NaCl and 5 per cent $CH_3COOH$ were found efficient decontaminants in removal of quinalphos, profenofos, ethion, and lambda-cyhalothrin residues from chili upto 90 per cent, whereas, the solutions of 5 per cent $NaHCO_3$ and 0.01 per cent $KMnO_4$ were found effective only in removing lambda-cyhalothrin residues from the chili crop, but for all other insecticides the decontamination was not much pronounced.

# *Chapter-3*

# MATERIALS AND METHODS

The present investigation entitled **"Residue dynamics of chlorpyrifos, cypermethrin and profenofos on cauliflower"** was carried out in the Department of Entomology, Dr. Y. S. Parmar University of Horticulture and Forestry, Nauni, Solan (H.P.) during the year 2020-2021. The supervised field trial was carried out at the experimental farm following all good agricultural practices as per standard package of practices recommended by the university (Anonymous, 2014) and the residues of respective insecticides were estimated in the Pesticide Residue Laboratory (PRL) of the department. The experimental details related to study sites, materials used, methodology adopted for the studies and observations recorded are presented in this chapter under different heads.

3.1 Location
3.2 Crop raising
3.3 Treatments
3.4 Laboratory materials
3.5 Cleaning of glassware
3.6 Preparation of stock solutions
3.7 Insecticide persistence study
3.8 Decontamination studies
3.9 Recovery studies
3.10 Dissipation studies

## 3.1 LOCATION

The experimental site is located at Nauni, district Solan, Himachal Pradesh, at an elevation of about 1200 meters above mean sea level, lying between 30°50'30" to 30°52'0" N latitude and 77°8'30" to 77°11'30" E longitude. Agro-climatically, the location falls under zone-II mid-hills. The climate is sub-temperate, having annual rainfall between 1100-1300 mm, most of which occurs during monsoon (June-August).

## 3.2 RAISING OF CROP

The cauliflower (*Brassica oleracea var. botrytis* L.) crop variety Pusa snowball K-1 was raised at the experimental farm as per the package of practices of the university. Seeds were purchased from the seed sale centre of IARI Regional Station Katrain, Kullu valley. Before sowing the seeds, field was ploughed and sufficient quantity of well decomposed FYM and fertilizers were added into the soil. Seeds were sown @ 500-625 g/ha on 16th September 2020 and the seedlings were transplanted on 27th October 2020 at a spacing of 60×45 cm (Plate 1a.) in the main field. The experiment was laid out in Randomized Block Design (RBD) with 9 treatments including untreated control replicated thrice with individual plot size of 3×2 m spacing with bunds all round and irrigation channels in between the replications (Plate 1b.).

### 3.2.1 Climatic conditions

**Table 3.1 Climatic parameters during experimental period of cauliflower crop**

| | |
|---|---|
| Average Maximum temperature (º C) | 25.40 |
| Average Minimum temperature (º C) | 7.28 |
| Average Relative Humidity (%) | 52.50 |
| Rainfall (mm) | 55.73 |

**Source:** Meteorological Observatory, Department of Environmental Science, Dr. Y.S. Parmar University of Horticulture and Forestry, Nauni, Solan (H.P.) 173230

## 3.3 TREATMENTS

Insecticides presented in Table 3.2 were studied for persistence and decontamination in cauliflower.

**Table 3.2 Details of different treatments of insecticides used:**

| Treatments | Insecticides | | Dosage (g a.i./ha) | Source Company |
|---|---|---|---|---|
| | Common Name | Trade Name | | |
| $T_0$ | Untreated control | - | - | - |
| $T_1$ | Chlorpyrifos (X) (20%EC) | SA- Safaban | 300 | Saraswati Agro Life Science (India) Pvt. Ltd. |
| $T_2$ | Chlorpyrifos (2X) (20%EC) | | 600 | |
| $T_3$ | Cypermethrin (X) (25% EC) | Challenger 25 | 50 | Tropical Agrosystem (India) Pvt. Ltd. |
| $T_4$ | Cypermethrin (2X) (25% EC) | | 100 | |
| $T_5$ | Profenofos (X) (50%EC) | Curacron | 500 | Syngenta India Limited |
| $T_6$ | Profenofos (2X) (50%EC) | | 1000 | |
| $T_7$ | Chlorpyrifos (20%EC) + Cypermethrin (25% EC) + Profenofos (50%EC) (X) | - | 300+50+500 | - |
| $T_8$ | Chlorpyrifos (20%EC) + Cypermethrin (25% EC) + Profenofos (50%EC) (2X) | - | 600 + 100 + 1000 | - |

Treatments ($T_0$ to $T_6$) were studied for persistence in cauliflower curds and soil whereas treatments $T_0$, $T_7$ and $T_8$ were evaluated for decontamination studies. The measured quantities of test insecticides were mixed with small quantity of water and subsequently

**<u>Plate 1a</u>. Field after transplanting of cauliflower seedlings**

**<u>Plate 1b</u>. View of the experimental field**

remaining quantity of water added to it to make up the final spray volume required for the plot. The spray fluid was evenly mixed with a stick before spraying (Plate 2).

The insecticides mentioned in the Table 3.2 were sprayed on cauliflower crop at the curd formation stage with each insecticide dose ($T_1$ to $T_6$) sprayed twice at an interval of 10 days for persistence studies whereas single spray was given in $T_7$ and $T_8$ for decontamination studies. The first and second spray applications were done on 28$^{th}$ January and 7$^{th}$ February 2021, respectively for persistence studies while single spray of $T_7$ and $T_8$ for decontamination studies was given on 15$^{th}$ February with a knapsack sprayer fitted with a triple action nozzle. Spray was done during a clear sky day, when there was minimum wind and all necessary precautions were taken to avoid the chances of drifting of spray fluid to adjacent plots. Care was also taken that lower concentration was sprayed first, followed by higher concentration. The sprayer as well as measuring cylinder was washed thoroughly after their use in order to avoid the carryover of insecticide from one treatment to another.

## 3.4 LABORATORY MATERIALS

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

### 3.4.1 Chemicals

1. Acetone ($C_3H_6O$), Genetix Biotech Asia Pvt. Ltd. Nazafgarh Road, New Delhi
2. Acetonitrile ($CH_3CN$), Genetix Biotech Asia Pvt. Ltd. Nazafgarh Road, New Delhi
3. Magnesium Sulphate ($MgSO_4$), Merck Specialities Pvt. Ltd. Worli, Mumbai
4. n-hexane ($C_6H_{14}$), HPLC Grade, Genetix Biotech Asia Pvt. Ltd. Nazafgarh Road, New Delhi
5. Potassium dichromate ($K_2Cr_2O_7$), Merck Specialities Pvt. Ltd. Worli, Mumbai
6. Primary Secondary Amines (PSA), Agilent Technology, USA
7. Reference standards, Dr. Ehrenstorfer, Augsburg, Germany
8. Sodium Chloride (NaCl), Merck Specialities Pvt. Ltd. Worli, Mumbai
9. Sodium Sulphate ($Na_2SO_4$), Merck Specialities Pvt. Ltd. Worli, Mumbai
10. Sulphuric acid ($H_2SO_4$), Merck Specialities Pvt. Ltd. Worli, Mumbai
11. Teepol, Merck Specialities Pvt. Ltd. Worli, Mumbai

### 3.4.2 Glassware and plastic wares

1. Beakers of 50 and 100 ml capacity, Borosil Glassworks Ltd., Delhi
2. Capillary glass column, DB–5, Agilent Technologies, USA

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

### 3.4.3 Instruments

1. Auto Pipettes (1 and 5 ml): Tarson Products Pvt. Ltd., Subhash Road, Kolkata
2. Centrifuge: Eppendorf India Ltd., Chandigarh
3. Electronic balance: Mettler Toledo India Pvt. Ltd., Mumbai
4. Agilent 7890B Gas chromatograph with ECD: M/s Agilent Technologies India Pvt. Ltd.
5. Gas chromatograph with FPD: Shimadzu Corporation, Japan
6. Low volume high speed homogenizer: Heidolph, Germany
7. High volume homogenizer: Heidolph, Germany
8. Phillips mixer grinder: Phillips India Ltd., Nalagarh, Baddi, HP.
9. Refrigerator: Godrej India Ltd., Mumbai
10. Rotospin mixer: Tarson Products Pvt. Ltd., Subhash Road, Kolkata
11. Spinex test tube shaker: Tarson Products Pvt. Ltd., Subhash Road, Kolkata
12. Turboevaporator: Turbo Vap® LV, Caliper Life Service
13. Sonicator: PCI India Pvt. Ltd. Biwandi, Mumbai

### 3.4.4 Gases

Nitrogen, Hydrogen and Zero air of 99.99% purity: M/s Linde India Ltd., Mumbai.

## 3.5 CLEANING OF GLASSWARES

The EPA (1980) procedure for cleaning of glassware was adopted to eliminate any kind of contamination. The glassware was soaked in hot water followed by rinsing with organic solvent in order to remove the contamination. The deep penetrant and oxidizing agent, chromic acid 20 per cent [potassium dichromate (20 g) in sulphuric acid (100 ml) w/v]

**Plate 2. Scheduled spraying of test insecticides in/on cauliflower crop**

was used to remove traces of organic contaminants. The glassware was dipped in chromic acid for 4-5 hours and thereafter, the same was washed under running tap water to remove the chromic acid. The glassware was further washed with soap solution and tap water, rinsed with distilled water and finally with acetone to flush out the traces of organic contaminants.

### 3.6 PREPARATION OF STOCK SOLUTIONS

Certified reference material (CRMs) of insecticide standards (Dr. Ehrenstorfer, Augsburg, Germany) under study were used to prepare the respective stock solutions of 400 ppm each by applying the formula:

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

Where,

Wt = Weight of the CRM (g)

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

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

$$C_1V_1 = C_2V_2$$

Where,

$C_1$ = Concentration of unknown solution

$V_1$ = Volume of unknown solution

$C_2$ = Concentration of known solution

$V_2$ = Volume of known solution

Similarly, lower concentrations *viz.,* 0.01, 0.05, 0.1, 0.25, 0.5, 1.0 mg $kg^{-1}$ etc. were prepared with n-hexane for analysis in GC.

### 3.7 INSECTICIDE PERSISTENCE STUDY

The persistence of chlorpyrifos, cypermethrin and profenofos was studied in cauliflower curds and its cropped soil. After second foliar application of each insecticide on cauliflower field at recommended dose (X) and double the recommended dose (2X) along with untreated control, two kg of curd samples were collected from each replication at an interval of 0, 1, 3, 5, 7, 10 days or till the residues reached below detectable level (BDL) and soil sample (1 kg) were collected at 20 days after last spray and analysed for residues of chlorpyrifos, cypermethrin and profenofos. The persistence data were subjected to statistical analysis using Hoskins (1961) method.

### 3.7.1 Sampling

#### 3.7.1.1 Fruits

Cauliflower curd samples (2 kg) were collected from each replication at an interval of 0 (2 hours after spray), 1, 3, 5, 7 and 10 days, after second spray and 2 kg curd samples were also collected from control plot which was sprayed with water only. The samples were packed in polyethylene bags, labelled well and brought to laboratory for residue analysis.

#### 3.7.1.2 Soil

Soil samples (1 kg) from the sprayed field were drawn from each replication after 20 days of last spray for analysis. During soil sampling, samples collected randomly from 5-6 sites from a depth of 0-5 cm were quartered and sub-quartered, mixed and then a representative sample (1 kg) from each treatment and control plot were collected. The samples were spread over plastic sheets and allowed to shade dry at room temperature in the laboratory. The air dried samples were desegregated manually using a pestle and a marble mortar, passed through a No. 20 mm brass soil sieve and mixed thoroughly to achieve homogeneity.

### 3.7.2 Principle of QuEChERS technique

Cauliflower curds and soil samples were analysed by QuEChERS technique. QuEChERS stands for quick, easy, cheap, effective, rugged and safe technique for residue analysis. In this technique, samples were extracted with acetonitrile and in the extract sodium chloride was added in order to reduce the amount of polar interferences and then after centrifugation, the supernatant was added to anhydrous sodium sulphate for the removal of water from the organic extract. The extract was then cleaned up with dispersive solid-phase by using magnesium sulphate anhydrous and primary secondary amine (PSA). Addition of magnesium sulphate anhydrous was done to remove water from organic phase and that of PSA to remove sugars, fatty acids, organic acids, lipids and some pigments.

### 3.7.3 Cauliflower curd analysis

Cauliflower curds were chopped into small pieces, homogenized in high volume homogenizer and analyzed by QuEChERS technique (Dubey *et al*., 2018).

#### 3.7.3.1 Extraction

Out of cauliflower curds homogenized sample, 15 g representative sample was taken in 50 ml polypropylene centrifuge tube containing 30 ml acetonitrile and homogenized at 15,000 rpm for 3 minutes by using low volume high speed homogenizer. Anhydrous sodium chloride (3 g) was added into the tube, shaken at 50 rpm for 5 minutes with Rotospin shaker and then centrifuged at 3000 rpm for 3 minutes. Upper layer fraction of 18 ml was transferred to another 50 ml polypropylene centrifuge tube containing 9 g anhydrous sodium sulphate and was shaken for 5 minutes at 50 rpm.

#### 3.7.3.2 Dispersive Solid Phase Cleanup

Anhydrous magnesium sulphate (1150 mg) and PSA (400 mg) were taken in 15 ml polypropylene centrifuge tube. The tube was capped and shaken for one minute on Spinix test tube shaker. 11ml fraction from 18 ml extract was added into the centrifuge tube, shaken for one minute at 50 rpm in Rotospin shaker and then centrifuged at 3000 rpm for 5 minutes. The 6 ml fraction was transferred to the 30 ml turbo glass tube and evaporated in turbo evaporator to dryness at 45°C in the presence of air current. The residues were dissolved in 3 ml n-hexane and injected 1µl into gas chromatograph (GC-ECD and GC-FPD) for estimation of chlorpyrifos, cypermethrin and profenofos.

### 3.7.4 Soil Analysis

Soil samples were analyzed by another QuEChERS technique, modified for analysis of soil (Asensio-Ramos *et al*., 2010).

#### 3.7.4.1 Extraction

A representative 10 g sieved ground dry soil sample was taken in a 50 ml polypropylene centrifuge tube, to which 20 ml acetonitrile was added and allowed for shaking up to 1 minute using a Rotospin shaker.

#### 3.7.4.2 Dispersive solid phase cleanup

Add 4 g of anhydrous magnesium sulphate and 1 g of sodium chloride and centrifuged at 3300 rpm for 5 minutes. After centrifugation, 10 ml of supernatant was taken in another centrifuge tube of 15 ml containing 1.5 g of magnesium sulphate and 0.25 g of

PSA, thereafter allowed for 3 minutes shaking. After shaking, the tube was sonicated for 1 minute and then centrifuged for 10 minute at 4400 rpm. From this tube, 4 ml aliquot of the supernatant was taken in a turbo tube and evaporated to dryness in presence of air current at 45°C. The dried residues were dissolved in 2 ml of n-hexane for injection (1µl) into gas chromatograph (GC-ECD and GC-FPD) for estimation of chlorpyrifos, cypermethrin and profenofos.

### 3.7.5 Determination of residues

#### 3.7.5.1 Parameters of GC-ECD for cypermethrin residue analysis:

| | |
|---|---|
| Instrument | Agilent 7890B |
| Detector | Electron capture detector (ECD) |
| Oven temperature | Initial temperature 80ºC for 3 minutes, raised to 150ºC at the rate of 30º C $min^{-1}$ with a hold time of 2 min, further raised to 205ºC at the rate of 3ºC $min^{-1}$ and finally raised to 260ºC for 22 minutes @ 10ºC $min^{-1}$ |
| Injection port temperature | 250ºC |
| Detector temperature | 300ºC |
| Carrier gas | Nitrogen |
| Gas Flow Rate | 1 ml $min^{-1}$ |
| Column | DB-5, 30m long, 0.25mm ID and 0.25µm film thickness |

#### 3.7.5.2 Parameters of GC-FPD for chlorpyrifos and profenofos residue analysis:

| | |
|---|---|
| Instrument | SHIMADZU-2010 |
| Detector | Flame Photometric Detector (FPD) |
| Oven temperature | Initial temperature 170ºC held for 5 minutes and then increased to 250ºC @ 20ºC $min^{-1}$ and held for 10 minutes and finally raised to 280ºC @ 4ºC $min^{-1}$ and hold for 7 minutes |
| Injection port temperature | 250ºC |
| Detector temperature | 300ºC |
| Carrier gas | Nitrogen, Hydrogen and zero air |
| Gas flow rate | Nitrogen - 1 ml $min^{-1}$<br>Hydrogen - 80.0 ml $min^{-1}$<br>Zero air - 120.0 ml $min^{-1}$ |
| Column | Capillary glass column, DB-5 (30m long, 0.25mm ID and 0.25µm film thickness) |

**Table 3.3 Retention time and Limit of Quantification (LOQ) of insecticides**

| Name of Insecticide | Retention Time (minutes) | Limit of Quantification (mg/kg) |
|---|---|---|
| Chlorpyrifos | 24.852 | 0.01 |
| Cypermethrin | 39.335 | 0.05 |
| Profenofos | 28.902 | 0.05 |

## 3.8 DECONTAMINATION STUDIES

The pesticides namely chlorpyrifos, cypermethrin and profenofos were pre-mixed as per the dosages mentioned in the Table 3.2 and mixture was sprayed at curd development stage of the crop. Representative curd samples from each treatment (single and double dose of mixture spray) collected after 48 hours of spray were used to undertake the decontamination studies. The following decontamination treatments were used:

### 3.8.1 Running tap water washing

1 kg curds from each treatment were rubbed and washed under running tap water for 1 minute and then dried in shade.

### 3.8.2 Lukewarm water washing

1 kg curds from each treatment were dipped in 4 litres of lukewarm water (45-50°C) for 10 minutes with 15 rpm.

### 3.8.3 Saline water dipping

1 kg curds from each treatment were dipped in 4 litres of 1 per cent NaCl aqueous solution for 10 minutes with 15 rpm.

### 3.8.4 Sodium bicarbonate solution dipping

1 kg curds from each treatment were dipped in 4 litres of 5 per cent $NaHCO_3$ aqueous solution for 10 minutes with 15 rpm.

### 3.8.5 Acetic acid solution dipping

1 kg curds from each treatment were dipped in 4 litres of 2 per cent acetic acid aqueous solution for 10 minutes with 15 rpm.

### 3.8.6 Potassium permanganate solution dipping

1 kg curds from each treatment were dipped in 4 litres of 0.01% $KMnO_4$ aqueous solution for 10 minutes with 15 rpm.

### 3.8.7 Veggie Clean solution dipping

1 kg curds from each treatment were dipped in 4 litres of Veggie Clean (from Marico) aqueous solution for 10 minutes with 15 rpm.

### 3.8.8 Nimwash solution dipping

1 kg curds from each treatment were dipped in 4 litres of Nimwash (from ITC) aqueous solution for 10 minutes with 15 rpm.

### 3.8.9 Arka Herbiwash solution dipping

1 kg curds from each treatment were dipped in 4 litres of Arka herbiwash aqueous solution for 10 minutes with 15 rpm.

### 3.8.10 Control

1 kg curds from each treatment were not washed or treated.

The curd samples processed with the above mentioned decontamination treatments were dried for 20-30 minutes on filter paper at room temperature and analysed for residue estimation by employing QuEChERS method as described above. The per cent relief was calculated as follows:

$$\text{Per cent relief (\%)} = 100 - \frac{\text{Residues in processed sample (mg/kg)}}{\text{Residues in unprocessed sample (mg/kg)}} \times 100$$

## 3.9 RECOVERY STUDIES

The recovery was determined by spiking the untreated cauliflower curds and soil samples with chlorpyrifos at 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$ levels and with cypermethrin and profenofos at 0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$ levels, respectively. Fortified samples were processed as per the procedure described for analysis of sample and linearity was checked. The per cent recovery was calculated as follows:

$$\text{Per cent recovery (\%)} = \frac{\text{Amount recovered (mg/kg)}}{\text{Amount added (mg/kg)}} \times 100$$

As per SANTE guidelines, acceptance criteria for recovery should range between 80–120 per cent (SANTE, 2019).

## 3.10 DISSIPATION STUDIES

### 3.10.1 Calculation of Residue Half Life ($RL_{50}$) Values

The $RL_{50}$ values were calculated as per Hoskins (1961) formula, which is as follows:

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

Where,

| | | |
|---|---|---|
| $t_{1/2}$ | = | half-life value ($RL_{50}$) in days |
| $k_1 = b$ | = | slope of regression equation of the log residues determined in mg/kg or ppm (y) on the time elapsed in days (x) |

### 3.10.2 Calculation for safe waiting period

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

Where,

| | | |
|---|---|---|
| $T_{si}$ | = | time taken in days by the insecticide to reach tolerance limit |
| $\log k_2$ | = | log of initial deposit |
| log tol | = | log of proposed tolerance limit |
| $k_1$ | = | b = slope of regression equation |

### 3.10.3 Residues dissipation rate

The per cent dissipation of the residue over the initial deposit was calculated for various sampling intervals as per the following mathematical formula:

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

# *Chapter-4*

# RESULTS AND DISCUSSION

The present investigation was carried out in order to assess the "**Residue dynamics of chlorpyrifos, cypermethrin and profenofos on cauliflower".** All the test insecticides viz. chlorpyrifos, cypermethrin and profenofos were analysed for their residue dynamics on treated cauliflower curd and cropped soil during cropping season 2021. Various decontamination treatments were also studied to analyse their potential in lowering the levels of insecticide residues from treated cauliflower curds. The experimental results, thus obtained have been described for each insecticide under the following heads:

**4.1 Recovery studies**

**4.2 Insecticide persistence studies**

**4.3 Statistical constants of insecticides**

**4.4 Decontamination studies**

## 4.1 RECOVERY STUDIES

### 4.1.1 Efficiency of analytical method

#### 4.1.1.1 Fruits

##### 4.1.1.1.1 Linearity of chlorpyrifos

To establish the linearity of chlorpyrifos, correlation coefficient ($R^2$) was worked out by running the standards of various concentrations *viz.,* 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$ in GC–FPD and plotting the linearity graph. The Fig. 4.1 shows the linear response of chlorpyrifos in GC–FPD with correlation coefficient of 0.999.

##### 4.1.1.1.2 Recovery of chlorpyrifos from fortified cauliflower curds

The analytical method was evaluated for its efficiency by conducting recovery studies of chlorpyrifos in cauliflower curd and cropped soil. The recovery of chlorpyrifos was observed to be above 90 per cent at all levels of fortification. A scrutiny of Table 4.1 shows that the recovery of chlorpyrifos from fortified cauliflower curd at six different fortification levels *viz*., 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$ was 93.00, 94.00, 92.00, 97.92, 97.40 and 97.28 per cent, respectively. The average recovery of chlorpyrifos from cauliflower curds varied between 92.00 – 97.92 per cent which is in the range of 80-120 per cent as per the acceptance criteria of SANTE (2019).

Similar to these results, Banshtu *et al*. (2018) in their study recovered 90.00 – 94.10 per cent chlorpyrifos from fortified samples of cauliflower curds at five different fortification levels (0.01, 0.05, 0.10, 0.50 and 1.00 mg $kg^{-1}$) which is well supportive to our findings. Aktar *et al*. (2009) reported the mean per cent recovery of chlopyrifos in cabbage at 0.25, 0.5 and 1.00 µg $g^{-1}$ spiking concentration levels in the range of 93.00 to 98.00 per cent with an average of 95.67 per cent. Chlorpyrifos when fortified at 0.01, 0.10 and 0.25 mg $kg^{-1}$ in tomato gave recovery percentages of 87.40, 90.84 and 92.20, respectively (Rani *et al.,* 2013). Hwang *et al*. (2018) recorded 90.2 – 92.3 per cent of average recovery at two different fortification levels (0.2 and 1.0 mg $kg^{-1}$) for chlorpyrifos from fortified lettuce. The mean recovery value of 88.30 and 91.27 percent at the fortification level of 0.05 and 0.10 mg $kg^{-1}$ for chlorpyrifos in hot pepper samples was recorded by Sushil *et al*. (2018). Singh *et al*. (2019) delineated a per cent recovery of 95.40- 101.00 in cucumber fruits at fortification level ranging between 0.05-1.00 mg $kg^{-1}$. Wani *et al.* (2019) calculated the mean per cent recovery of chlorpyrifos in green pea samples to be 86.2, 83.2 and 98.6 per cent at 0.05, 0.01 and 0.5 mg $kg^{-1}$ levels of fortification.

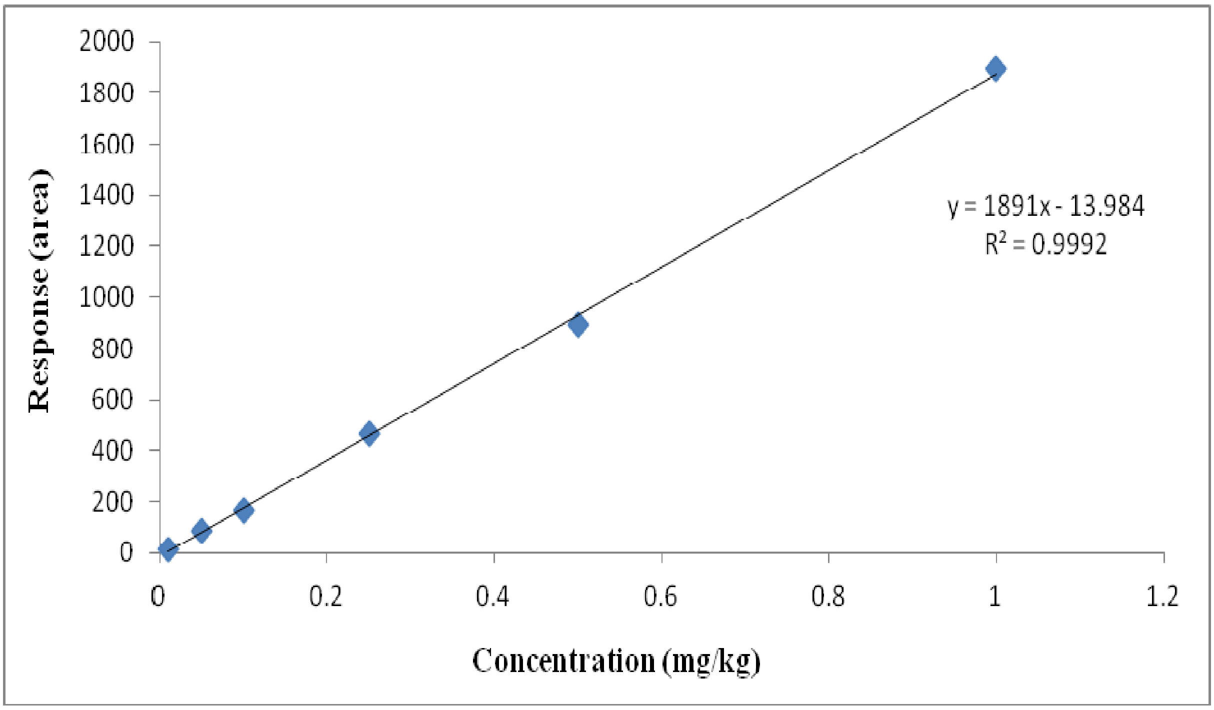



**Fig 4.1 Linearity of chlorpyrifos in cauliflower**

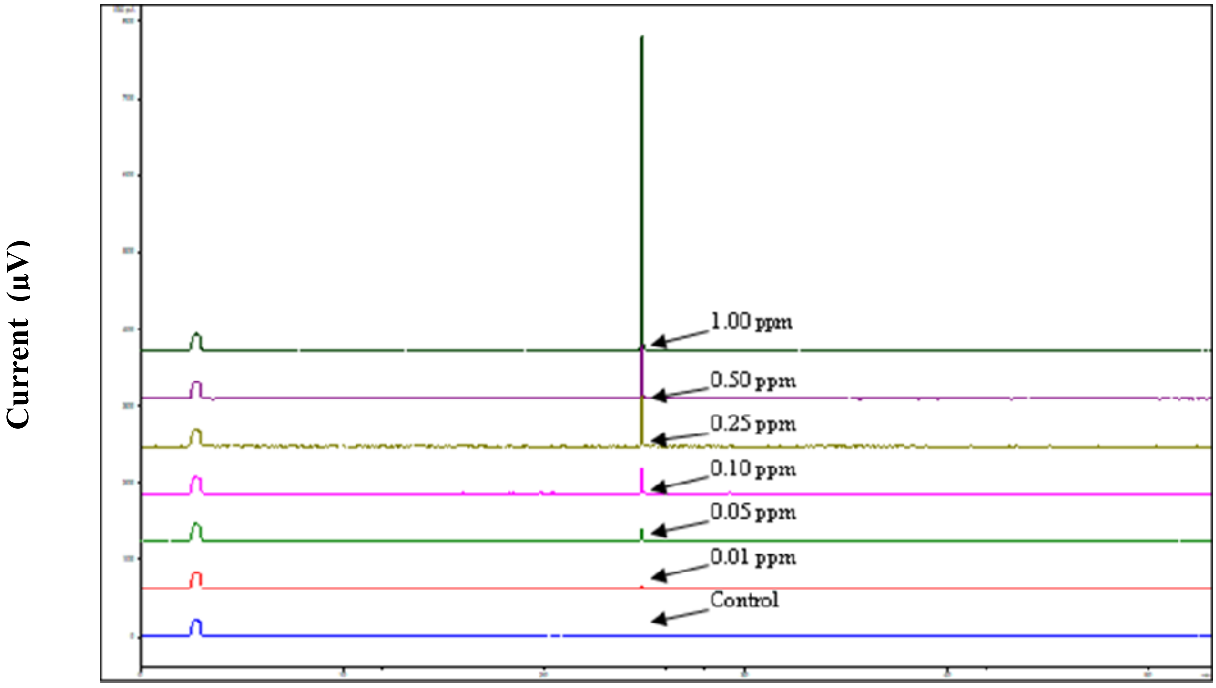



**Fig 4.2 Overlay chromatogram of response of different concentrations of chlorpyrifos in cauliflower**

**Table 4.1 Recovery of chlorpyrifos from fortified cauliflower curds**

| Fortification levels (mg kg$^{-1}$) | Recovery (mg kg$^{-1}$) | | | | | | Average recovery (%) |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | Mean amount recovered ± SD | |
| 0.01 | 0.009 | 0.009 | 0.01 | 0.008 | 0.011 | 0.009 ±0.0009 | 93.00 |
| 0.05 | 0.046 | 0.053 | 0.049 | 0.042 | 0.045 | 0.047 ±0.0042 | 94.00 |
| 0.10 | 0.091 | 0.104 | 0.085 | 0.081 | 0.099 | 0.092 ±0.0095 | 92.00 |
| 0.25 | 0.223 | 0.267 | 0.244 | 0.216 | 0.274 | 0.245 ±0.0257 | 97.92 |
| 0.50 | 0.481 | 0.462 | 0.492 | 0.542 | 0.458 | 0.487 ±0.0337 | 97.40 |
| 1.00 | 1.113 | 1.001 | 0.960 | 0.982 | 0.862 | 0.973 ±0.0934 | 97.28 |

#### 4.1.1.1.3 Linearity of cypermethrin

To establish the linearity of cypermethrin, calibration curve was plotted by running the standards of various concentrations *viz.,* 0.05, 0.10, 0.25, 0.50 and 1.00 mg kg$^{-1}$ in GC–ECD and working out its correlation coefficient ($R^2$). Fig 4.3 shows the linear response of cypermethrin in GC–ECD with correlation coefficient of 0.999.

#### 4.1.1.1.4 Recovery of cypermethrin from fortified cauliflower curds

The recovery of cypermethrin was assessed by spiking the extract of cauliflower curds at five fortification levels viz., 0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$. As evident from the data presented in Table 4.2, recoveries of cypermethrin from fortified cauliflower curds at different fortification levels *viz*., 0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$ were 97.20, 93.20, 100.40, 97.20 and 94.42 per cent, respectively. The average recovery of cypermethrin from spiked cauliflower curds came out between 93.20– 100.40 per cent.

The results of present findings showed a close resemblance to those obtained by Banshtu and Patyal (2018) where the recovery of cypermethrin obtained from cauliflower curds was reported 90.00 - 92.00 per cent at different (0.05, 0.10, 0.50 and 1.00 mg $kg^{-1}$) fortification levels. The average recovery of cypermethrin from tomato fruits fortified at three different concentration levels (0.05, 0.10 and 0.50 mg $kg^{-1}$) found to range between 88.00 and 96.26 per cent (Cherukuri *et al*., 2015). The recovery percentage was 97.73, 104.04 and 92.68 per cent in brinjal when spiked with cypermethrin at 0.01, 0.05 and 0.10 mg $kg^{-1}$ fortification levels, respectively (Patel *et al*., 2016). Similarly, the mean recovery of cypermethrin at the fortification levels of 0.05, 0.25 and 0.50 mg $kg^{-1}$ in/on okra fruits were 83.76, 93.36 and 83.66 per cent, respectively as reported by Mayannavar *et al*. (2017). Priyadarshini *et al*. (2017) reported recovery of cypermethrin from samples of curry leaves with fortification levels of 0.05, 0.25 and 0.50 mg $kg^{-1}$ with a range between 97.60-115.33 per cent. Anuradha and Bhuvaneshwari (2020) fortified curry leaf samples with cypermethrin at 0.10, 0.50 and 1.00 µg $g^{-1}$ and recovered 97.00, 93.00 and 84.67 per cent, respectively.

**Table 4.2 Recovery of cypermethrin from fortified cauliflower curds**

| Fortification levels (mg $kg^{-1}$) | Recovery (mg $kg^{-1}$) | | | | | | Average recovery (%) |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | Mean amount recovered ± SD | |
| 0.05 | 0.051 | 0.048 | 0.049 | 0.042 | 0.053 | 0.049 ±0.0042 | 97.20 |
| 0.10 | 0.097 | 0.101 | 0.088 | 0.082 | 0.098 | 0.093 ±0.0079 | 93.20 |
| 0.25 | 0.273 | 0.248 | 0.254 | 0.224 | 0.256 | 0.251 ±0.0177 | 100.40 |
| 0.50 | 0.543 | 0.445 | 0.501 | 0.513 | 0.428 | 0.486 ±0.0481 | 97.20 |
| 1.00 | 0.985 | 1.045 | 0.914 | 0.876 | 0.901 | 0.944 ±0.0694 | 94.42 |

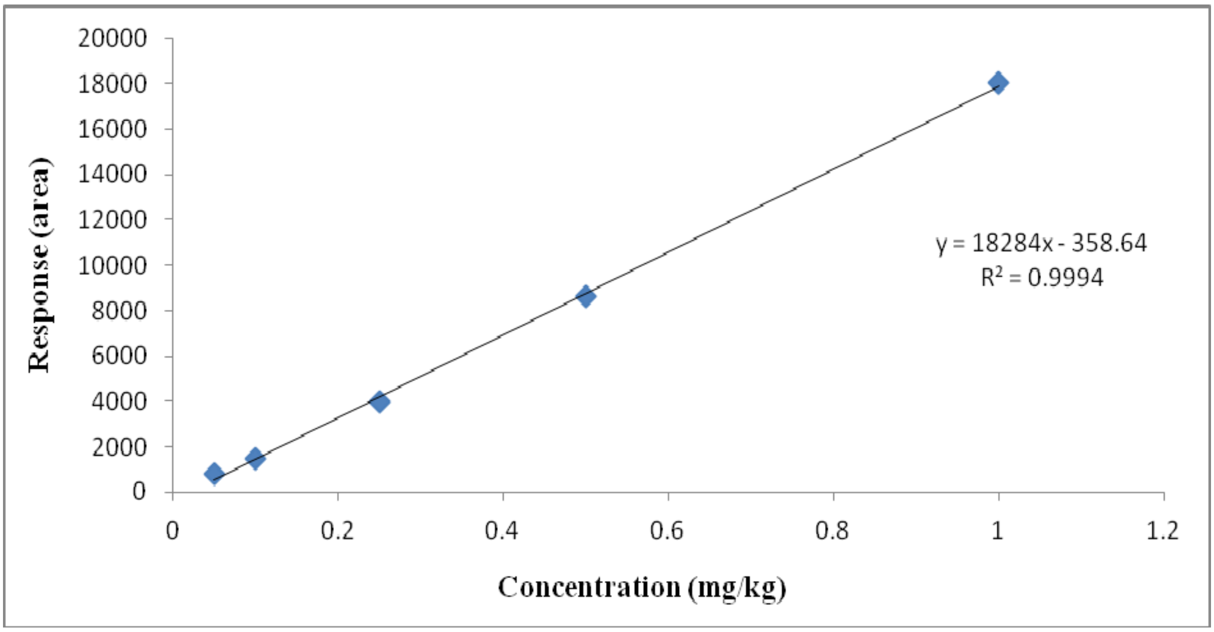



**Fig. 4.3 Linearity of cypermethrin in cauliflower**

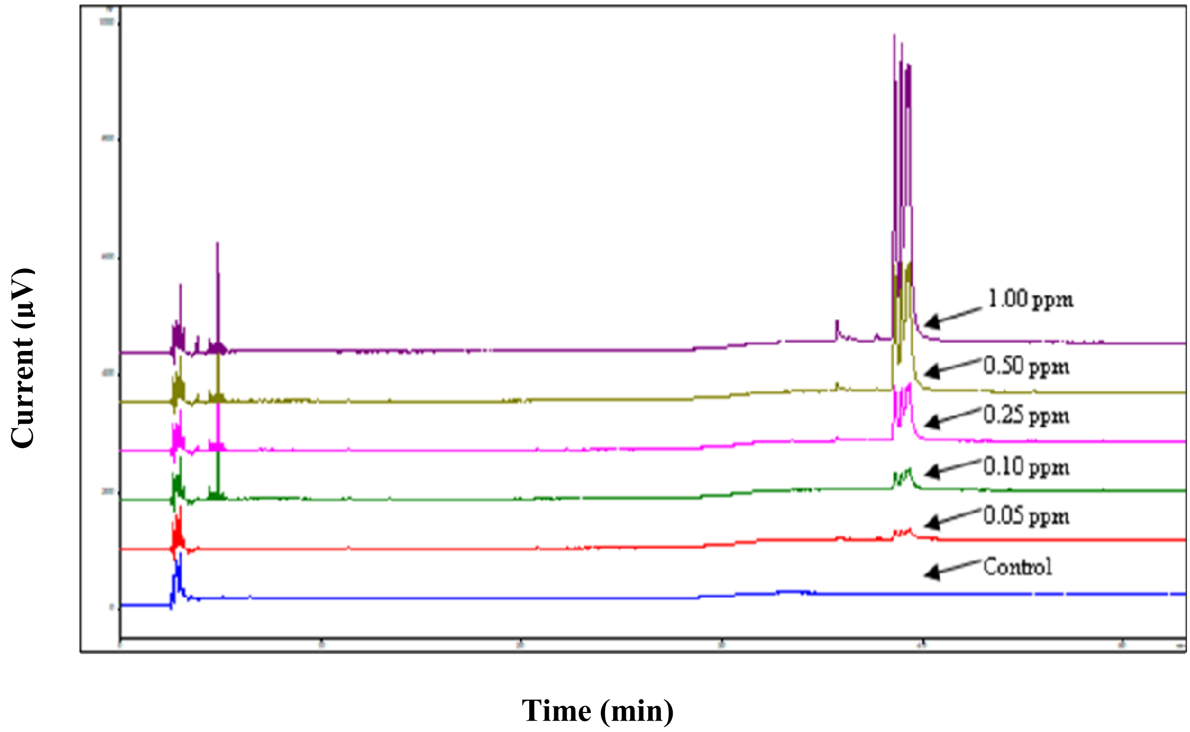



**Fig 4.4 Overlay chromatogram of response of different concentrations of cypermethrin in cauliflower**

#### 4.1.1.1.5 Linearity of profenofos

To establish the linearity of profenofos, correlation coefficient ($R^2$) was worked out by running the standards of various concentrations *viz.,* 0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$ in GC–FPD and plotting the linearity graph. The Fig 4.5 shows the linear response of profenofos in GC–FPD with correlation coefficient of 0.999.

#### 4.1.1.1.6 Recovery of profenofos from fortified cauliflower curds

The data presented in Table 4.3 indicates that the recovery of profenofos from cauliflower curds at different fortification levels *viz*., 0.05, 0.10, 0.25, 0.50 and 1.00 mg kg$^{-1}$ was 96.80, 93.60, 97.04, 92.20 and 94.98 per cent, respectively. The average recovery of profenofos varied from 92.20 – 97.04 per cent.

Similar trend of recoveries have been reported by Banshtu *et al*. (2018) who observed an average recovery of 88.00 – 94 per cent on fortification of cauliflower curds at five various concentrations of profenofos (0.05 – 1.00 mg kg$^{-1}$). Katroju *et al.* (2014) in their study also recovered 88 – 94 per cent of profenofos from tomato fruits when fortified at different levels *viz.,* 0.05 and 0.10 mg kg$^{-1}$. Raveendranath *et al*. (2014) observed 90.6±1.15, 90.6±2.30 and 100±2.0 per cent recovery of profenofos from cucumber samples at 0.05, 0.25 and 0.5 mg kg$^{-1}$ fortification levels, respectively. Profenofos when fortified at 0.05, 0.10, 0.20, 0.50 and 1.00 mg kg$^{-1}$ in tomato fruits gave recovery percentages of 88.00, 86.00, 89.00, 91.00 and 93.00, respectively (Banshtu *et al.,* 2015). Rani *et al*. (2019) reported recovery of profenofos ranged between 89.11- 99.73 per cent from chilli fruits at 0.1 and 0.5 ppm fortification levels which are in close proximity to the present results. Priyadarshini *et al*. (2017) recorded 83.06 – 106.66 per cent of average recovery at three different fortification levels (0.05 – 0.50 mg kg$^{-1}$) for profenofos from fortified curry leaf samples.

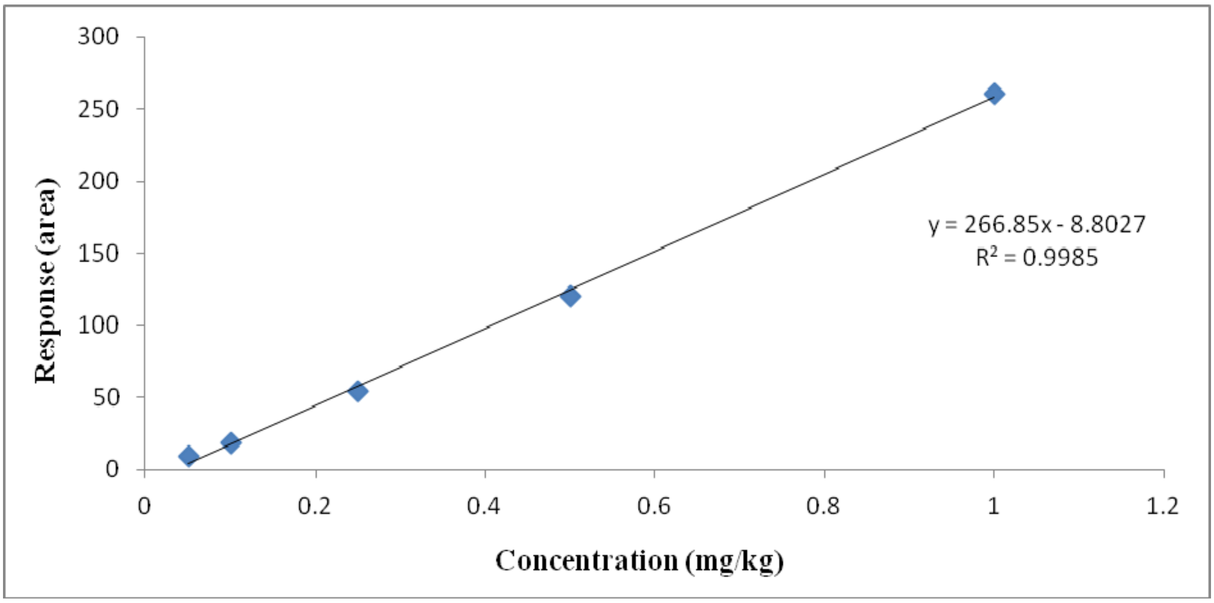



**Fig. 4.5 Linearity of profenofos in cauliflower**

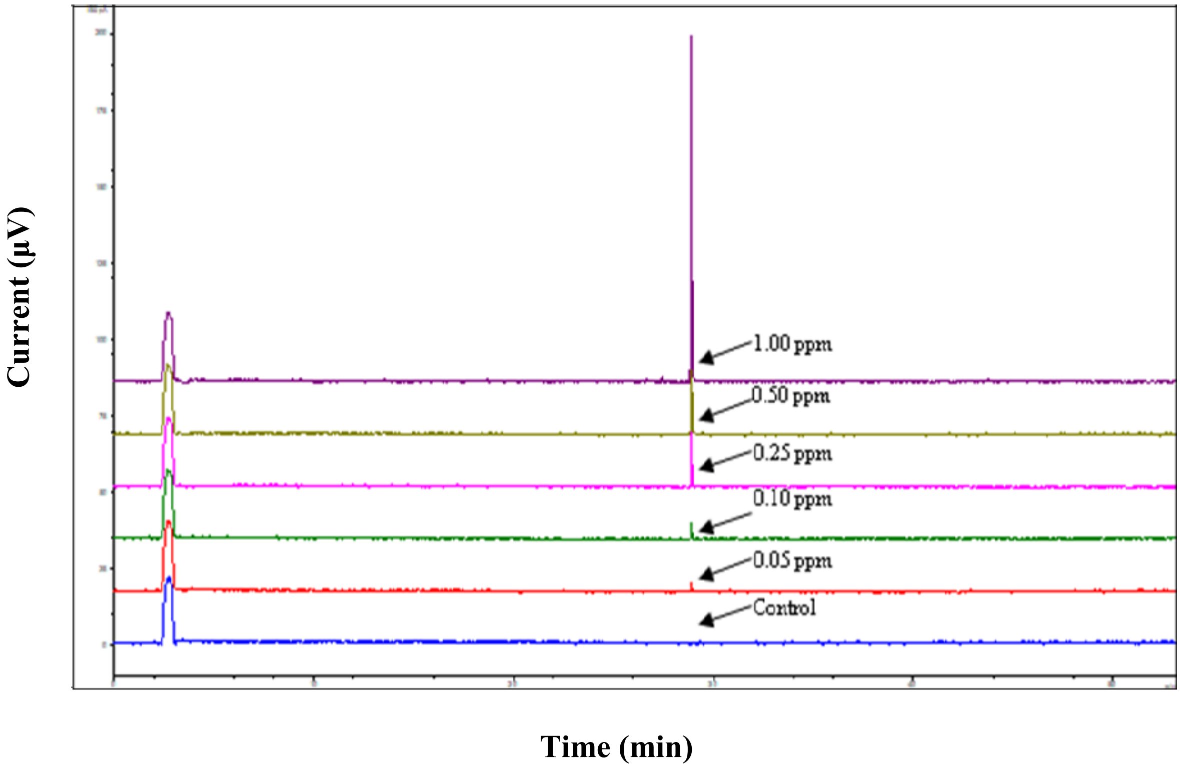



**Fig 4.6 Overlay chromatogram of response of different concentrations of profenofos in cauliflower**

**Table 4.3 Recovery of profenofos from fortified cauliflower curds**

| Fortification levels (mg kg$^{-1}$) | Recovery (mg kg$^{-1}$) | | | | | | Average recovery (%) |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | Mean amount recovered ± SD | |
| 0.05 | 0.047 | 0.049 | 0.051 | 0.042 | 0.053 | 0.048 ±0.0042 | 96.80 |
| 0.10 | 0.101 | 0.085 | 0.093 | 0.082 | 0.107 | 0.094 ±0.0105 | 93.60 |
| 0.25 | 0.223 | 0.245 | 0.251 | 0.278 | 0.216 | 0.243 ±0.0246 | 97.04 |
| 0.50 | 0.475 | 0.501 | 0.456 | 0.418 | 0.455 | 0.461 ±0.0304 | 92.20 |
| 1.00 | 0.942 | 0.976 | 1.023 | 0.962 | 0.846 | 0.950 ±0.0652 | 94.98 |

#### 4.1.1.2 Soil

##### 4.1.1.2.1 Recovery of chlorpyrifos from fortified cauliflower cropped soil

The data presented in Table 4.4 shows that the recovery of chlorpyrifos from fortified cauliflower field soil at various fortification levels *viz*., 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00 mg kg$^{-1}$ was found to be 92.00, 92.80, 91.60, 97.44, 94.80 and 90.74 per cent, respectively. Hence, the average recovery from cauliflower field soil varied from 90.74 – 97.44 per cent.

Singh *et al.* (2019) recovered an average of 92.80 – 99.20 per cent of chlorpyrifos from fortified cucumber cropped soil at different fortification levels of 0.05, 0.1, 0.25, 0.5 and

1.00 mg kg$^{-1}$ which is well in line to the results thus obtained. Jyot *et al*. (2013) reported a per cent recovery of 88.03±3.91, 86.07±1.94 and 88.05±3.07 for chlorpyrifos at 0.01, 0.05 and 0.10 mg kg$^{-1}$ level of fortification from soil under chilli crop. Rani *et al*. (2013) fortified chlorpyrifos at 0.01, 0.10 and 0.25 mg kg$^{-1}$ and have shown the recovery of 86.35±4.0, 88.05±2.9 and 89.60±2.0 per cent in tomato cropped soil, respectively. The average per cent recovery of chlorpyrifos from okra field soil at the fortification levels of 0.1 and 0.25 mg kg$^{-1}$ was 89.00±0.041 and 92.00±2.79 per cent, respectively (Samriti *et al*., 2012). However, the mean per cent recovery of chlorpyrifos in soil under curry leaf at the fortification levels of 0.5, 0.25 and 0.05 mg kg$^{-1}$ was 126.97, 90.85 and 90.63 per cent, respectively (Gogikar *et al*., 2017b).

**Table 4.4 Recovery of chlorpyrifos from fortified cauliflower cropped soil**

| Fortification levels (mg kg$^{-1}$) | Recovery (mg kg$^{-1}$) | | | | | | Average recovery (%) |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | Mean amount recovered ± SD | |
| 0.01 | 0.008 | 0.009 | 0.009 | 0.01 | 0.01 | 0.009 ± 0.0009 | 92.00 |
| 0.05 | 0.048 | 0.051 | 0.050 | 0.041 | 0.042 | 0.051 ± 0.0046 | 92.80 |
| 0.10 | 0.092 | 0.101 | 0.081 | 0.088 | 0.096 | 0.099 ± 0.0076 | 91.60 |
| 0.25 | 0.246 | 0.260 | 0.219 | 0.251 | 0.242 | 0.249 ± 0.0153 | 97.44 |
| 0.50 | 0.462 | 0.489 | 0.427 | 0.490 | 0.502 | 0.513 ± 0.0301 | 94.80 |
| 1.00 | 0.890 | 0.886 | 0.827 | 0.906 | 1.028 | 1.065 ± 0.0738 | 90.74 |

**4.1.1.2.2 Recovery of cypermethrin from fortified cauliflower cropped soil**

The data presented in Table 4.5 indicates that the recovery of cypermethrin from fortified cauliflower field soil at various levels viz. 0.05, 0.10, 0.25, 0.50 and 1.00 mg kg$^{-1}$ was 92.40, 91.40, 93.52, 97.48 and 91.20 per cent, respectively. Therefore, the average recovery of cypermethrin from cauliflower field soil ranging between 91.20 – 97.48 per cent.

Our results obtained are in line with those documented by Chauhan *et al*. (2018) who obtained an average recovery of 95.00±0.07 and 98.50±1.15 per cent on fortification of okra cropped soil samples with cypermethrin at 0.005 and 0.01 µg/g. Similiarly, Mayannavar *et al*. (2017) reported recovery of 78.40, 92.93 and 82.20 per cent, respectively on fortification of okra field soil at three different levels with cypermethrin (0.05, 0.25 and 0.50 mg kg$^{-1}$). Banshtu *et al*. (2015) recorded an average recovery of 86.80 – 90.00 per cent of cypermethrin from fortified tomato field soil at different fortification levels between 0.05 – 1.00 mg kg$^{-1}$. The mean per cent recovery of cypermethrin (93.22±3.89, 95.78±2.94 and 89.04±3.89 per cent) was reported from soil samples taken from chilli crop at 0.01, 0.05 and 0.10 mg kg$^{-1}$ fortification levels, respectively (Jyot *et al*., 2013). Samriti and Kumari (2011) recorded average recovery of cypermethrin ranging between 87.60 – 95.91 per cent from okra cropped soil at 0.10 and 0.25 μg g$^{-1}$ spiking level. The average recovery of cypermethrin in pomegranate cropped soil reported by Mohapatra (2014) was 88.3±5.8, 90.7±4.7 and 94.3±4.0 per cent, respectively at 0.05, 0.25 and 0.50 mg kg$^{-1}$ levels of fortification.

**Table 4.5 Recovery of cypermethrin from fortified cauliflower cropped soil**

| Fortification levels (mg kg$^{-1}$) | Recovery (mg kg$^{-1}$) | | | | | | Average recovery (%) |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | Mean amount recovered ± SD | |
| 0.05 | 0.046 | 0.040 | 0.052 | 0.051 | 0.042 | 0.046 ± 0.0053 | 92.40 |
| 0.10 | 0.082 | 0.086 | 0.094 | 0.096 | 0.099 | 0.091 ± 0.0071 | 91.40 |
| 0.25 | 0.213 | 0.224 | 0.260 | 0.244 | 0.228 | 0.234 ± 0.0184 | 93.52 |
| 0.50 | 0.462 | 0.480 | 0.532 | 0.492 | 0.471 | 0.487 ± 0.0273 | 97.48 |
| 1.00 | 1.022 | 0.986 | 0.842 | 0.802 | 0.908 | 0.912 ± 0.0930 | 91.20 |

#### 4.1.1.2.3 Recovery of profenofos from cauliflower cropped soil

The average recovery of profenofos from cauliflower cropped soil at five different fortification levels *viz*., 0.05, 0.10, 0.25, 0.50 and 1.00 mg kg$^{-1}$ was found between 86.80 – 97.12 per cent, i.e. 94.80, 86.80, 94.16, 97.12 and 90.80 per cent, respectively (Table 4.6).

Our findings are in agreement with the average recovery of 82.00 – 96.33 per cent obtained by Brar *et al*. (2017) for profenofos from brinjal cropped soil at different fortification levels i.e. 0.05, 0.10, 0.25, 0.5 and 1.0 mg kg$^{-1}$. Banshtu *et al*. (2015) reported recovery of profenofos ranged between 86.00 –92.00 per cent from tomato field soil samples at different fortification levels between 0.05 – 1.00 mg kg$^{-1}$ which is in resemblance with the results thus obtained. Similar trend of recoveries have been reported by Reddy *et al.* (2014) who recovered 85.25 and 87.38 per cent profenofos from cabbage cropped soil at fortification levels of 0.01 and 0.10 mg kg$^{-1}$, respectively. However, the recovery percentage of profenofos was 100.08 and 112.96 per cent in sandy loam soil when spiked at two different levels viz., 0.50 and 1.00 μg g$^{-1}$, respectively (Rana *et al.*, 2016).

**Table 4.6 Recovery of profenofos from fortified cauliflower cropped soil**

| Fortification levels (mg kg$^{-1}$) | Recovery (mg kg$^{-1}$) | | | | | | Average recovery (%) |
|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | $R_4$ | $R_5$ | Mean amount recovered ± SD | |
| 0.05 | 0.053 | 0.041 | 0.048 | 0.046 | 0.049 | 0.047 ± 0.0044 | 94.80 |
| 0.10 | 0.082 | 0.083 | 0.088 | 0.099 | 0.082 | 0.087 ± 0.0073 | 86.80 |
| 0.25 | 0.261 | 0.214 | 0.252 | 0.234 | 0.216 | 0.235 ± 0.0210 | 94.16 |
| 0.50 | 0.482 | 0.461 | 0.527 | 0.531 | 0.427 | 0.486 ± 0.0442 | 97.12 |
| 1.00 | 1.029 | 0.854 | 0.843 | 0.886 | 0.928 | 0.908 ± 0.0753 | 90.80 |

## 4.2 INSECTICIDE PERSISTENCE STUDIES

### 4.2.1 Initial deposits and persistence of test insecticide (s) in/on cauliflower curds

There are a considerable number of factors responsible for residual deposits of pesticides like formulation, concentration, type of sprayer used, weather conditions, substrate characteristics, distance between the nozzle and plant surface and carrier properties etc. Besides these factors, the persistence of residues on plant surface is also impacted by plant type (erect or prostrate), shape of plant parts (broad, narrow or linear) and growth of plant parts (slow or fast) (Ebling, 1963) whereas the residual dissipation rate for a given pesticide depends on several factors, including the species cultivated (its crop formation physics, cuticle characteristics, growth rate, pH dependency, etc.), climatic conditions, application parameters (formulation, the number of applications, penetration rate, volume of water, type of nozzle, pressure, and height between the boom and the canopy) (Lin *et al*., 2001) and the mode of action of any specific pesticide which are the factors that most influence variability in the residual pattern of pesticides for a given ecosystem (Fantke *et al*., 2011; Rahman *et al*., 2015). Keeping these factors as constant, the levels of insecticides will become main focus for discussion regarding deposits and dissipation pattern of insecticides.

#### 4.2.1.1 Initial deposits of chlorpyrifos

The average initial deposits of chlorpyrifos were 1.931 mg kg$^{-1}$ and 2.856 mg kg$^{-1}$ on cauliflower curds (Table 4.7 & 4.8) at single dose (@ 300 g a.i./ha) and at two times the single dose (@ 600 g a.i./ha). The initial deposits of chlorpyrifos at standard dose (@300 g a.i./ha) were 1.48 times lower than that obtained from double dose (600 g a.i./ha).

The results of present findings were parallel to those of Islam *et al*. (2009) who observed residues of chlorpyrifos on cauliflower curds to be 1.628 mg kg$^{-1}$ at recommended dose (0.25 L ha$^{-1}$) and 2.243 mg kg$^{-1}$ at double the recommended dose (0.5 L ha$^{-1}$), respectively. Jyot *et al*. (2013) reported the mean initial deposits of chlorpyriphos on green chilli fruits as 0.59 and 2.02 mg kg$^{-1}$ following the third application at rate of 500 and 1000 g a.i./ha. The initial deposits of chlorpyriphos on okra fruit were observed to be 2.225 mg kg$^{-1}$ when sprayed @ 300 g a.i. ha$^{-1}$ which were 1.8 times lower than those obtained from its double dose i.e. 4.021 mg kg$^{-1}$ (Moudgil, 2015). Brar *et al*. (2018) reported a initial deposits of 1.092 mg kg$^{-1}$ at single dose (300 g a.i./ha) and 1.982 mg kg$^{-1}$ at double dose (600 g a.i./ha) of chlorpyrifos in brinjal which is approximately 1.81 times lesser at single dose, indicating a closer proximity with the present results. Sushil *et al*. (2018) reported that the mean initial residues of chlorpyrifos in hot pepper were 1.191 mg kg$^{-1}$ when applied at recommended dose @ 300 g a.i. ha$^{-1}$. Initial deposits of chlorpyrifos obtained by Singh *et al*. (2019) on cucumber fruits were 0.980 mg kg$^{-1}$ at single dose (300 g a.i./ha) and 1.860 mg kg$^{-1}$ at double dose (600 g a.i./ha). This difference in the initial deposits may be attributed to difference in dosages and substrates under study.

#### 4.2.1.2 Persistence of chlorpyrifos in/on cauliflower curds

At standard dose, the initial deposits of 1.931 mg kg$^{-1}$ dissipated to 0.874, 0.378, 0.074 and 0.015 mg kg$^{-1}$ after 1, 3, 5 and 7 days of application, respectively. At double dose, the initial deposits of 2.856 mg kg$^{-1}$ dissipated to 1.340, 0.506, 0.125, 0.054 and 0.015 in 1, 3, 5, 7 and 10 days, respectively. The per cent dissipation values of the initial deposit at standard dose were found to be 54.74, 80.41, 96.15 and 99.21 at 1, 3, 5 and 7 days intervals, respectively and at double dose, the per cent dissipation values were 53.07, 82.29, 95.62, 98.10 and 99.46 at 1, 3, 5, 7 and 10 days intervals, respectively (Table 4.7, 4.8 and Fig. 4.7).

The results obtained are in line with those obtained by Raina and Raina (2008) in their studies showed initial deposits of 0.56-0.86 and 1.29-1.43 mg kg$^{-1}$ of chlorpyrifos on cauliflower curds for two consecutive years at single (@ 500 g a.i./ha) and double dose (@ 1000 g a.i./ha), respectively. Chlorpyrifos dissipated to below determination limit on 9$^{th}$ and 15$^{th}$ day at respective doses. Bhojan *et al*. (2019) recorded that the initial deposits of chlorpyrifos 20 EC (3.47 µg g$^{-1}$) at 200 g a.i./ha in green chillies dissipated to 50.57, 76.84, 90.05 and 97.34 per cent on 1, 3, 5 and 7 days intervals. Similarly, at double dose (400 g a.i./ha) dissipation rate was 49.81, 79.05, 89.70, 95.99 and 98.73 per cent at 1, 3, 5, 7 and 10 days. Chlorpyrifos was found below BDL on the 10$^{th}$ and 15$^{th}$ day at both the concentrations. The results of present findings showed a close propinquity to those obtained by Wani *et al*. (2019) who observed the initial deposits of 1.37 mg kg$^{-1}$ on green pea dissipating to 0.02 mg kg$^{-1}$ on 10$^{th}$ day after last application, thereby representing a loss of 98.54 per cent at recommended dose of chlorpyrifos 20EC (300 g a.i. ha$^{-1}$), which then reached below detectable limit (< 0.01 mg kg$^{-1}$) on 15th day of application. Kumari and Chauhan (2015) recorded a initial deposits of 0.397 mg kg$^{-1}$ of chlorpyrifos in chilli samples which subsequently dissipated to 0.385, 0.278, 0.180, 0.134 and 0.085 mg kg$^{-1}$ at 1, 3, 5, 7 and 10 days intervals at single dose (160 g a.i./ha), respectively and at double the standard dose (320 g a.i./ha), initial deposits of about 1.021 mg kg$^{-1}$ of chlorpyrifos dissipated to 0.997, 0.695, 0.485, 0.360 and 0.258 mg kg$^{-1}$ at 1, 3, 5, 7 and 10 days, respectively and the residues reached below detectable levels (0.01 mg kg$^{-1}$) on 15$^{th}$ and 30$^{th}$ days of application in single dose and double dose, respectively, showing per cent dissipation of 97.48 and 98.14 per cent. Jyot *et al*. (2013) recorded that the average initial deposits of 0.59 mg kg$^{-1}$ when chlorpyrifos was applied at 500 g a.i. ha$^{-1}$ and 2.02 mg kg$^{-1}$ when applied at 1000 g a.i. ha$^{-1}$ dissipated to 0.57, 0.41, 0.27, 0.14 and 0.09 mg Kg$^{-1}$ at single dose and 1.30, 0.72, 0.55, 0.47 and 0.23 mg kg$^{-1}$ at double the standard dose after 1, 3, 5, 7 and 10 days of application, respectively and the residues reached below detectable limit (< 0.01 mg kg$^{-1}$) after the 15th day of application in both the doses.

**Table 4.7 Persistence of chlorpyrifos (@ 300 g a.i./ha) in/on cauliflower curds**

| Interval (Days) | Residues (mg kg$^{-1}$) | | | | Dissipation (%) |
|---|---|---|---|---|---|
| | **$R_1$** | **$R_2$** | **$R_3$** | **Mean residues ± SD** | |
| 0 | 1.872 | 1.973 | 1.948 | 1.931 ±0.053 | – |
| 1 | 0.826 | 0.882 | 0.914 | 0.874 ± 0.045 | 54.74 |
| 3 | 0.398 | 0.327 | 0.410 | 0.378 ± 0.045 | 80.41 |
| 5 | 0.072 | 0.077 | 0.074 | 0.074 ± 0.003 | 96.15 |
| 7 | 0.015 | 0.019 | 0.012 | 0.015 ± 0.004 | 99.21 |
| 10 | BDL | BDL | BDL | BDL | – |
| Control | ND | ND | ND | ND | – |

BDL = Below Determination Limit (<0.01 mg kg$^{-1}$); ND = Not Detected

Singh *et al*. (2019) recorded the residues of chlorpyrifos in cucumber dissipated to 0.656, 0.330, 0.092 and 0.059 mg kg$^{-1}$ at 1, 3, 5 and 7$^{th}$ day after application from an initial residue level of 0.980 mg kg$^{-1}$ showing a dissipation percentage of 93.98 per cent on 7$^{th}$ day at single dose (300 g a.i. ha$^{-1}$) while at double dose (600 g a.i. ha$^{-1}$), initial deposits of 1.860 mg kg$^{-1}$ dissipated to 1.126, 0.623, 0.201, 0.102 and 0.057 mg kg$^{-1}$ at 1, 3, 5, 7 and 10$^{th}$ day after application with dissipation percentage of 96.93 per cent on 10$^{th}$ day and residues reached BDL at 10$^{th}$ and 15$^{th}$ days after application at single and double dose , respectively. Sushil *et al*. (2018) showed that the residues of chlorpyrifos persisted up to 20 days in hot pepper when chlorpyrifos 20 per cent was applied at the rate of 300 g a.i. ha$^{-1}$, which attained BDL on 25$^{th}$ day. The variation in rate of dissipation in different crop may be due to changes in the crop matrix, shape and size, environmental conditions etc.

**Table 4.8 Persistence of chlorpyrifos (@ 600 g a.i./ha) in/on cauliflower curds**

| Interval (Days) | Residues (mg kg$^{-1}$) | | | | Dissipation (%) |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Mean residues ± SD | |
| 0 | 2.849 | 2.823 | 2.896 | 2.856 ± 0.037 | – |
| 1 | 1.352 | 1.374 | 1.295 | 1.340 ±0.041 | 53.07 |
| 3 | 0.501 | 0.492 | 0.524 | 0.506 ± 0.017 | 82.29 |
| 5 | 0.121 | 0.130 | 0.124 | 0.125 ± 0.005 | 95.62 |
| 7 | 0.058 | 0.052 | 0.053 | 0.054 ± 0.003 | 98.10 |
| 10 | 0.017 | 0.013 | 0.016 | 0.015 ± 0.002 | 99.46 |
| 15 | BDL | BDL | BDL | BDL | – |
| Control | ND | ND | ND | ND | – |

BDL = Below Determination Limit (<0.01 mg kg$^{-1}$); ND = Not Detected

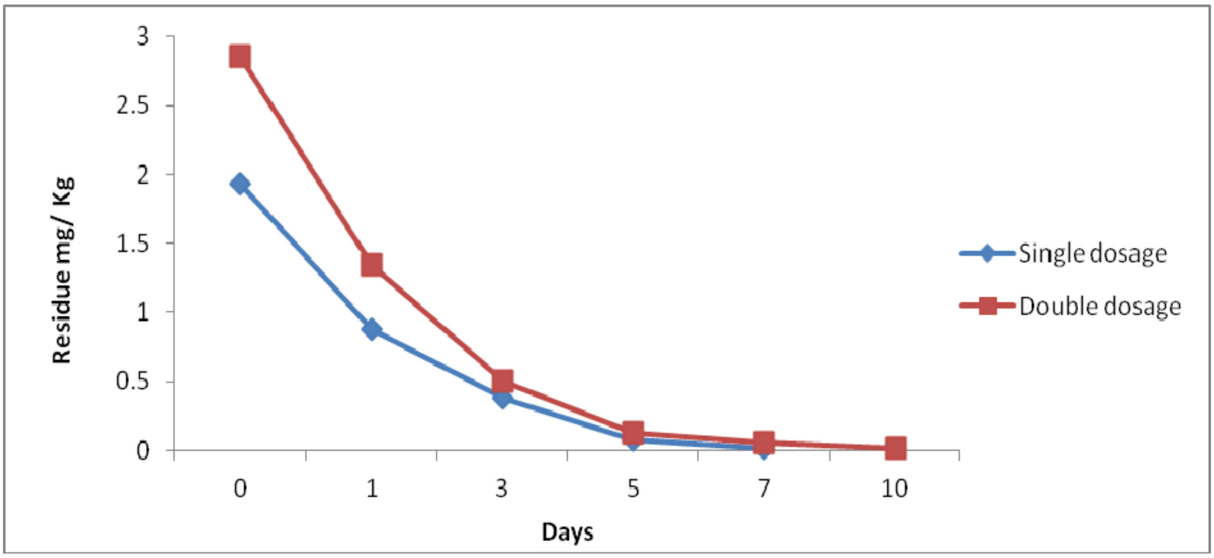



**Fig. 4.7 Dissipation pattern of chlorpyrifos (@ 300 and 600 g a.i./ha) in/on cauliflower curds**

#### 4.2.1.3 Initial deposits of cypermethrin

The data presented in Table 4.9 & 4.10 revealed that the average initial deposits (two hours after application) of cypermethrin were 0.533 mg $kg^{-1}$ @ 50 g a.i./ha and 0.807 mg $kg^{-1}$ @ 100 g a.i./ha on cauliflower curds. The initial deposits of cypermethrin at standard dose (50 g a.i./ha) were 1.51 times lower than that obtained from double dose (100 g a.i./ha).

The results of present findings are in a closer proximity to those obtained by Mayannavar *et al*. (2017) where persistence studies yielded 0.32 mg $kg^{-1}$ and 0.75 mg $kg^{-1}$ of initial residues of cypermethrin on okra fruits at standard (50 g a.i./ha) and double dose (100 g a.i./ha), respectively. Similarly, Banshtu and Patyal (2016) observed initial deposits of cypermethrin on cauliflower curds were 0.629 - 0.681 mg $kg^{-1}$ at recommended rate (50 g a.i. $ha^{-1}$) and 1.139-1.167 mg $kg^{-1}$ at double the recommended rate (100 g a.i. $ha^{-1}$). Banshtu *et al*. (2015) observed the mean initial deposits of cypermethrin on tomato fruits as 0.259 - 0.298 and 0.300 - 0.500 mg $kg^{-1}$ following the application @ 40 and 80 g a.i. $ha^{-1}$, respectively. Chandra *et al*. (2014) presented the data that showed the initial residue deposits of cypermethrin at 100, 200 and 300 g a.i. $ha^{-1}$ were 0.378, 0.685 and 0.862 mg $kg^{-1}$, respectively on okra crop at the experimental field Vasco-Da-Gama, Goa. Nahar *et al*. (2012) on analysis of cypermethrin (Ripcord 10EC) reported initial deposits of 0.29 and 0.55 ppm at recommended dose (@ 1 ml/L) and double the recommended dose (@ 2 ml/L), respectively on tomato fruits showing similarity with the results obtained in present study.

#### 4.2.1.4 Persistence of cypermethrin in/on cauliflower curds

The initial deposits of cypermethrin dissipated to 0.357, 0.127 and 0.080 mg $kg^{-1}$ after $1^{st}$, $3^{rd}$ and $5^{th}$ day of application, respectively at standard dose (50 g a.i./ha). At double dose, the initial deposits of cypermethrin were 0.807 mg $kg^{-1}$ which dissipated to 0.531, 0.192, 0.089 and 0.071 mg $kg^{-1}$ after 1, 3, 5 and 7 days, respectively (Table 4.9, 4.10 and Fig 4.8). Persistence data showed that the cypermethrin residues on cauliflower curds were reduced from 0.533 – 0.080 mg $kg^{-1}$ in 0 to 5 days, thus recorded 33.06 to 84.94 per cent dissipation at standard dose and at double dose, residues were reduced from 0.807 – 0.071 mg $kg^{-1}$ in 0 to 7 days and recorded 34.24 to 91.20 per cent dissipation on cauliflower curds (Fig. 4.8).

The results of present findings were in line with those obtained by Mayannavar *et al.* (2017) who recorded that initial residues of cypermethrin on okra fruits when applied at doses of 50 g a.i. $ha^{-1}$ and 100 g a.i. $ha^{-1}$, respectively dissipated to 0.24, 0.17 and 0.07 mg $kg^{-1}$ after

1, 3 and 5 days, respectively at single dose; while at double dose, the initial residues dissipated to 0.61, 0.29, 0.14 and 0.07 mg $kg^{-1}$ after 1, 3, 5 and 7 days of application and the residues reached below detectable limit (< 0.05 mg $kg^{-1}$) on 7th and 10th day at respective doses. Likewise, Banshtu and Patyal (2016) reported that the initial deposits of cypermethrin on cauliflower curds reached to BDL on 7th day when applied @ 50 g a.i./ha and 10th day when applied @ 100 g a.i./ha. Chauhan *et al*. (2018) recorded that initial deposits of 0.119 mg $Kg^{-1}$ when cypermethrin was applied at 50 g a.i./ha dissipated to 0.090, 0.067, 0.030, 0.020 and 0.010 mg $kg^{-1}$ after 1, 3, 5, 7 and 10 days of application and reached below detectable limit (< 0.01 mg $kg^{-1}$) after 10th day of application, thus showing dissipation percentage of 91.59 per cent. The corresponding values for 100 g a.i./ha of cypermethrin were 0.272, 0.212, 0.147, 0.071, 0.038, 0.024 and 0.014 mg $kg^{-1}$ after 0, 1, 3, 5, 7, 10 and 15 days of application, respectively and the residues dissipated below detectable limit (< 0.01 mg $kg^{-1}$ ) after 15th day of application with dissipation percentage of 94.85 per cent. Patel *et al*. (2016) observed that initial deposits of cypermethrin (@ 0.009 per cent) were 0.56 and 0.62 µg $g^{-1}$ during summer and rabi season, respectively in brinjal fruits which dissipated to 94.64 and 91.93 per cent at 7th and 10th day in respective seasons. Similarly, Rahman *et al.* (2015) observed that cypermethrin persisted in eggplant fruits till 5 days when applied at the rate of 1 ml $L^{-1}$ and the residues were 2.575, 1.961, 0.762 and 0.031 ppm at 0, 1, 3 and 5 days, respectively whereas it persisted till 10 days when applied at double the recommended dose (@ 2 ml $L^{-1}$) and residues varied between 3.157 – 0.196 ppm.

**Table 4.9 Persistence of cypermethrin (@ 50 g a.i./ha) in/on cauliflower curds**

| Interval (Days) | Residues (mg $kg^{-1}$) | | | | Dissipation (%) |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Mean residues ± SD | |
| 0 | 0.541 | 0.521 | 0.538 | 0.533 ±0.011 | – |
| 1 | 0.392 | 0.361 | 0.318 | 0.357 ± 0.037 | 33.06 |
| 3 | 0.131 | 0.129 | 0.120 | 0.127 ± 0.006 | 76.25 |
| 5 | 0.079 | 0.082 | 0.080 | 0.080 ± 0.002 | 84.94 |
| 7 | BDL | BDL | BDL | – | – |
| Control | ND | ND | ND | ND | – |

BDL = Below Determination Limit (< 0.050 mg $kg^{-1}$); ND = Not Detected

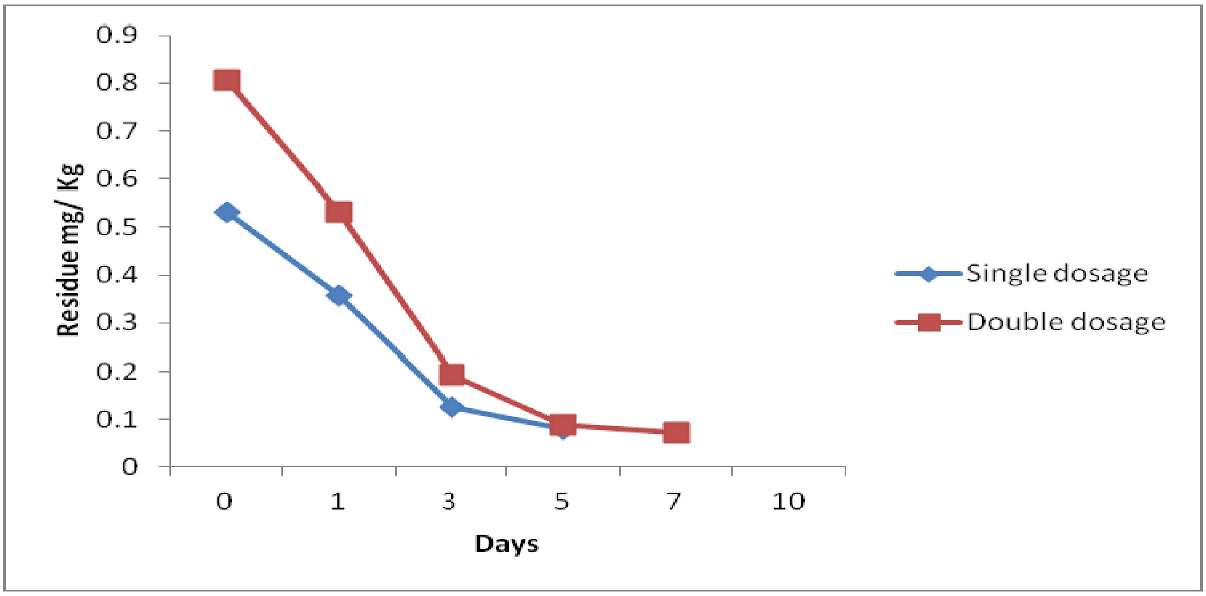



**Fig. 4.8 Dissipation pattern of cypermethrin (@ 50 and 100 g a.i./ha) in/on cauliflower curds**

**Table 4.10 Persistence of cypermethrin (@100g a.i./ha) in/on cauliflower curds**

| Interval (Days) | Residues (mg $kg^{-1}$) | | | | Dissipation (%) |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Mean residues ± SD | |
| 0 | 0.782 | 0.822 | 0.817 | 0.807 ± 0.022 | – |
| 1 | 0.523 | 0.541 | 0.528 | 0.531 ± 0.009 | 34.24 |
| 3 | 0.188 | 0.191 | 0.196 | 0.192 ± 0.004 | 76.25 |
| 5 | 0.083 | 0.090 | 0.094 | 0.089± 0.006 | 88.97 |
| 7 | 0.072 | 0.073 | 0.068 | 0.071 ± 0.003 | 91.20 |
| 10 | BDL | BDL | BDL | – | – |
| Control | ND | ND | ND | ND | – |

BDL = Below Determination Limit (< 0.050 mg $kg^{-1}$); ND = Not Detected

**4.2.1.5 Initial deposits of profenofos**

Data presented in Table 4.11 & 4.12 revealed that the average initial deposits (two hours after application) of profenofos were 2.682 mg $kg^{-1}$ at single dose @ 500 g a.i./ha and 5.228 mg $kg^{-1}$ at two times the single dose @ 1000 g a.i./ha on cauliflower curds. The initial deposits of profenofos at standard dose (500 g a.i./ha) were 1.95 times lower than that obtained from double dose (1000 g a.i./ha).

The results of present findings were in a closer proximity to those obtained by Anugu *et al*. (2017) where persistence studies yielded 2.60 mg $kg^{-1}$ of initial deposits of profenofos 50EC on chilli samples when applied at the rate 400 g a.i.$ha^{-1}$. Akbar *et al*. (2020) on analysis of profenofos @ 988 g a.i./ha reported initial deposits of 2.557 mg $kg^{-1}$ on cauliflower curds showing similarity with the results obtained in present study. Likewise, Brar *et al.* (2017) recovered initial residues of 1.966 mg $kg^{-1}$ and 2.460 mg $kg^{-1}$ of profenofos (Profex 50 EC) from brinjal fruits collected after two foliar sprays at single dose (500 g a.i./ha) and double dose (1000 g a.i./ha), respectively and reported 1.25 fold increase in deposits due to higher dose over lower dose.

**4.2.1.6 Persistence of profenofos in/on cauliflower curds**

The initial deposits of profenofos dissipated to 1.466, 0.619, 0.155 and 0.059 mg $kg^{-1}$ after $1^{st}$, $3^{rd}$, $5^{th}$ and $7^{th}$ day of application, respectively at standard dose (500 g a.i./ha). At double dose (1000 g a.i./ha), the initial deposits of profenofos were 5.228 mg $kg^{-1}$ which dissipated to 2.476, 1.255, 0.371, 0.213 and 0.064 mg $kg^{-1}$ after 1, 3, 5, 7 and 10 days, respectively (Table 4.11, 4.12 and Fig 4.9). Persistence data showed that the profenofos residues on cauliflower curds were reduced from 2.682 – 0.059 mg $kg^{-1}$ in 0 to 7 days, thus recorded 45.32 to 97.79 per cent dissipation at standard dose and at double dose, residues were reduced from 5.228 – 0.064 mg $kg^{-1}$ in 0 to 10 days and recorded 52.64 to 98.78 per cent dissipation on cauliflower curds (Fig. 4.9).

Our results are in line with those obtained by Chandel *et al.* (2018) who reported that the mean initial residues (1.418 mg $kg^{-1}$) of profenofos when applied at 500 g a.i. $ha^{-1}$ dissipated to 0.819, 0.269, 0.136 and 0.064 mg $kg^{-1}$ after 1, 3, 5 and 7 days of application on okra crop and reached below detectable limit (0.05 mg $kg^{-1}$) at $10^{th}$ day of application. For double dose of profenofos (1000 g a.i. $ha^{-1}$), the initial residues (2.801 mg $kg^{-1}$) dissipated to 1.119, 0.535, 0.244, 0.110 and 0.074 mg $kg^{-1}$ after 1, 3, 5, 7 and 10 days of application and reached BDL on $15^{th}$ day of application. However, Banshtu and Patyal (2017b) reported that the initial deposits of profenofos on cauliflower curds reached to BDL on $10^{th}$ day when applied @ 400 g a.i./ha and $15^{th}$ day when applied @ 800 g a.i./ha. Anugu *et al*. (2017) recorded that initial deposits (2 hours after last spray) of 2.60 mg $kg^{-1}$ when profenofos 50EC was applied at 400 g a.i./ha dissipated to 1.07, 0.74, 0.44 and 0.13 mg $kg^{-1}$ at 1, 3, 5 and 7 days after last spray, respectively and reduced to below determination level (BDL) by $10^{th}$ day in chilli crop.

**Table 4.11 Persistence of profenofos (@ 500 g a.i./ha) in/on cauliflower curds**

| Interval (Days) | Residues (mg kg$^{-1}$) | | | | Dissipation (%) |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Mean residues ± SD | |
| 0 | 2.633 | 2.691 | 2.721 | 2.682 ±0.045 | – |
| 1 | 1.492 | 1.425 | 1.482 | 1.466 ± 0.036 | 45.32 |
| 3 | 0.591 | 0.644 | 0.623 | 0.619 ± 0.027 | 76.90 |
| 5 | 0.151 | 0.156 | 0.159 | 0.155 ± 0.004 | 94.21 |
| 7 | 0.058 | 0.061 | 0.059 | 0.059 ± 0.002 | 97.79 |
| 10 | BDL | BDL | BDL | – | – |
| Control | ND | ND | ND | ND | – |

BDL = Below Determination Limit (< 0.050 mg kg$^{-1}$); ND = Not Detected

Reddy *et al.* (2017b) when tested profenofos 50 EC @ 1000 g a.i./ha for dissipation pattern on cabbage found that, mean initial residues of profenofos were 0.99 mg kg$^{-1}$ which further dissipated to 0.85, 0.82, 0.16 and 0.07 mg kg$^{-1}$ by 1, 3, 5 and 7 days after last spray, respectively and below determination level (BDL) by 10th day. Brar *et al.* (2017) recorded that the initial residues on brinjal (1.966 mg kg$^{-1}$ and 2.460 mg kg$^{-1}$ when applied at doses of 500 g a.i. ha$^{-1}$ and 1000 g a.i. ha$^{-1}$, respectively) dissipated slowly to 0.950, 0.416, 0.190 and 0.070 mg kg$^{-1}$ after 1, 3, 5 and 7 days, respectively at single dose; while at double dose, the initial residue dissipated to 1.063, 0.696, 0.363, 0.087 and 0.070 mg kg$^{-1}$ after 1, 3, 5, 7 and 10 days of application and the residues reached below detectable limit on 10$^{th}$ and 15$^{th}$ days at respective doses. Deore *et al.* (2018) recorded that initial residues of profenofos 50 EC on brinjal (0.56 mg kg$^{-1}$ when applied at 500 g a.i. ha$^{-1}$) dissipated slowly to 0.39, 0.26, 0.13 and 0.09 mg kg$^{-1}$ with dissipation percentage of 30.54, 52.69, 76.05 and 84.43 per cent after 1, 3, 5 and 7 days of application, respectively and the residues reached below detectable limit on 10$^{th}$ day.

**Table 4.12 Persistence of profenofos (@1000g a.i./ha) in/on cauliflower curds**

| Interval (Days) | Residues (mg kg$^{-1}$) | | | | Dissipation (%) |
|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Mean residues ± SD | |
| 0 | 5.199 | 5.254 | 5.232 | 5.228 ± 0.028 | – |
| 1 | 2.487 | 2.442 | 2.499 | 2.476 ± 0.030 | 52.64 |
| 3 | 1.253 | 1.228 | 1.285 | 1.255 ± 0.029 | 75.99 |
| 5 | 0.346 | 0.391 | 0.376 | 0.371± 0.023 | 92.90 |
| 7 | 0.215 | 0.205 | 2.196 | 0.213 ± 0.007 | 95.93 |
| 10 | 0.061 | 0.067 | 0.064 | 0.064 ± 0.003 | 98.78 |
| 15 | BDL | BDL | BDL | – | – |
| Control | ND | ND | ND | ND | – |

BDL = Below Determination Limit (< 0.050 mg kg$^{-1}$); ND = Not Detected

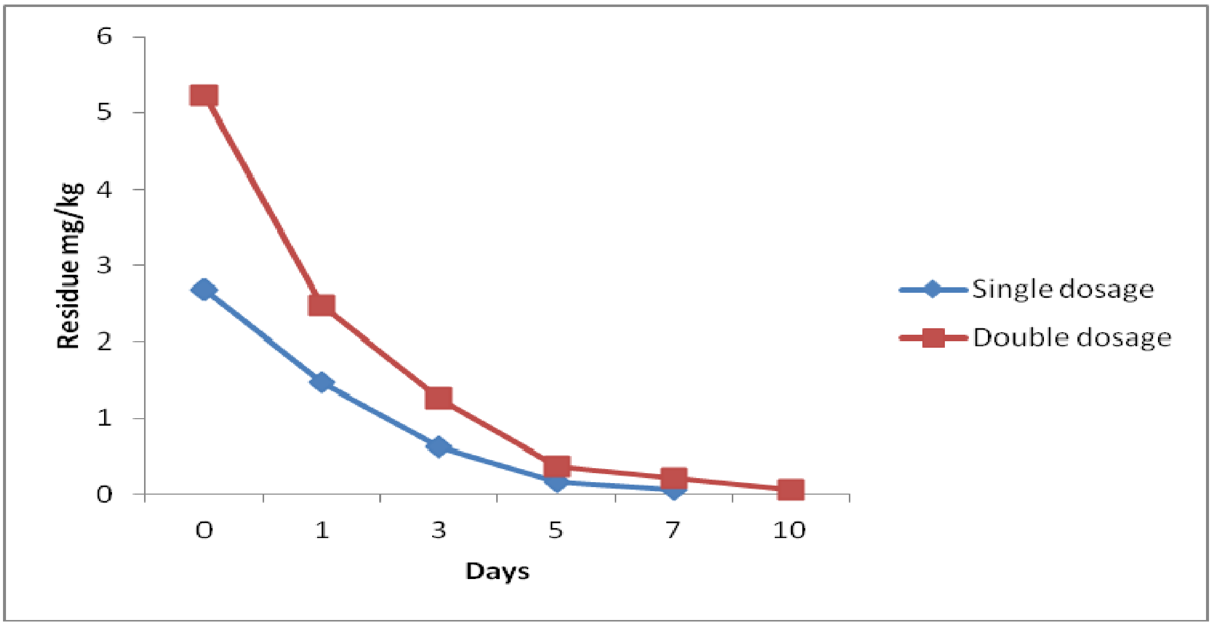



**Fig. 4.9 Dissipation pattern of profenofos (@ 500 and 1000 g a.i./ha) in/on cauliflower curds**

### 4.2.2 Residues of test insecticides in soil

#### 4.2.2.1 Residues of chlorpyrifos from cauliflower field soil

The residues of chlorpyrifos were found to be below determination limit (0.05 mg $kg^{-1}$) from soil samples collected at 20 days after last application of both the doses in cauliflower field soil (Table 4.13).

**Table 4.13 Residues of chlorpyrifos (@ 300 and 600 g a.i./ha) in cauliflower field soil**

| Interval (Days) | Chlorpyrifos residues (mg $kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | @ 300 g a.i./ha | | | | @ 600 g a.i./ha | | | |
| | $R_1$ | $R_2$ | $R_3$ | Mean residues ±SD | $R_1$ | $R_2$ | $R_3$ | Mean residues ± SD |
| 20 DAS | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| Control | ND | ND | ND | - | ND | ND | ND | - |

BDL = Below Determination Limit; ND = Not Detected

Our results are in line with Ahlawat *et al.* (2017) who analyzed the tomato and green pea cropped soil samples at the time of harvest and observed no detectable residues of chlorpyrifos when both the crops were sprayed @ 300 g a.i. $ha^{-1}$. Sushil *et al.* (2018) observed that the residues of chlorpyrifos dissipated completely in soil after harvesting when applied @ 300 g a.i./ha on hot pepper crop. Similarly, Gogikar *et al.* (2017b) reported that residues of chlorpyrifos in curry leaf cropped soil reduced to BDL at the time of harvest (45 days after last spray) when sprayed at 300 g a.i. $ha^{-1}$.

#### 4.2.2.2 Residues of cypermethrin from cauliflower field soil

The data presented in Table 4.14 shows that in cauliflower field soil the residues of cypermethrin were found to be below determination level (0.05 mg $kg^{-1}$) after harvest of cauliflower crop from the treatments having application of cypermethrin at standard (50 g a.i./ha) and double dose (100 g a.i./ha).

The results of present investigation were in agreement with Mayannavar *et al*. (2017) who obtained the results showing that the soil sample collected at harvest, i.e. on the $30^{th}$ day after second application of cypermethrin @ 50 g a.i. $ha^{-1}$ and 100 g a.i. $ha^{-1}$ in okra field soil were below detectable levels (BDL) of 0.05 mg $kg^{-1}$. Similiarly, Cherukuri *et al*. (2015) in an experiment conducted at Rajendranagar, Hyderabad also reported that residues of cypermethrin were found below determination level after $15^{th}$ days of second application of cypermethrin (@50 g a.i./ha) from tomato cropped soils.

**Table 4.14 Residues of cypermethrin (@ 50 and 100 g a.i./ha) in cauliflower field soil**

| Interval (Days) | Cypermethrin residues (mg $kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | @ 50 g a.i./ha | | | | @ 100 g a.i./ha | | | |
| | $R_1$ | $R_2$ | $R_3$ | Mean residues ±SD | $R_1$ | $R_2$ | $R_3$ | Mean residues ±SD |
| 20 DAS | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| Control | ND | ND | ND | - | ND | ND | ND | - |

BDL = Below Determination Limit; ND = Not Detected

#### 4.2.2.3 Residues of profenofos from cauliflower field soil

The data presented in Table 4.15 shows that in cauliflower field soil the residues of profenofos were found to be below determination level (0.05 mg $kg^{-1}$) after harvest of cauliflower crop from the treatments having application of profenofos at standard (500 g a.i./ha) and double dose (1000 g a.i./ha).

The results of present investigation were in agreement with Singh *et al*. (2016) who obtained the results showing that the residues were below detectable levels of 0.05 mg $kg^{-1}$ at $10^{th}$ and $15^{th}$ days after second application of profenofos @ 500 g a.i. $ha^{-1}$ and 1000 g a.i. $ha^{-1}$, respectively in capsicum field soil. Similiarly, Brar *et al*. (2017) in an experiment conducted at Nauni, Solan also observed that residues of profenofos were found below determination level after $10^{th}$ and $15^{th}$ days of second application of profenofos @ 500 and 1000 g a.i./ha, respectively in brinjal cropped soil.

**Table 4.15 Residues of profenofos (@ 500 and 1000 g a.i./ha) in cauliflower field soil**

| Interval (Days) | Profenofos residues (mg $kg^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | @ 500 g a.i./ha | | | | @ 1000 g a.i./ha | | | |
| | $R_1$ | $R_2$ | $R_3$ | Mean residues ±SD | $R_1$ | $R_2$ | $R_3$ | Mean residues ±SD |
| 20 DAS | BDL | BDL | BDL | BDL | BDL | BDL | BDL | BDL |
| Control | ND | ND | ND | - | ND | ND | ND | - |

BDL = Below Determination Limit; ND = Not Detected

## 4.3 STATISTICAL CONSTANTS OF TEST INSECTICIDES

The statistical constants obtained due to the analysis of persistence data of chlorpyrifos, cypermethrin and profenofos tested on cauliflower are being given in Table 4.16.

### 4.3.1 Residue half life value ($RL_{50}$)

#### 4.3.1.1 Chlorpyrifos

The data presented in Table 4.16 indicated that chlorpyrifos deposits dissipated to half at standard dose (@ 300 g a.i./ha) in 1.03 days as compared to 1.32 days at double dose (@ 600 g a.i./ha) from cauliflower curds indicating difference in dissipation behavior of insecticide at both doses. Dissipation at both the doses followed first order kinetics reaction.

Our findings are in line with Raina and Raina (2008) who evaluated a half life value of 1.40-1.50 days at standard (500 g a.i./ha) and 1.50-1.60 days at double dose (1000 g a.i./ha) of chlorpyrifos, respectively for two consecutive years on cauliflower curds. However, Sushil *et al.* (2018) observed a half life of 4.93 days at recommended dose (@ 300 g a.i./ha) of chlorpyrifos on hot pepper. Singh *et al.* (2019) calculated the half-life of chlorpyrifos when applied @ 300 and 600 g a.i. $ha^{-1}$ as 1.64 and 1.91 days on cucumber, respectively. Vinothkumar *et al.* (2019) reported the half-life of chlorpyrifos 20 EC @ 200 g a.i. $ha^{-1}$ and 400 g a.i. $ha^{-1}$ to be 1.41 and 1.65 days in green chillies, respectively. Wani *et al.* (2019) revealed that the half-life of degradation of chlorpyrifos 20 EC when applied @ 300 g a.i. $ha^{-1}$ to be 1.77 days in green pea. The half-life of chlorpyrifos @ 160 and 320 g a.i. $ha^{-1}$ was observed to be 6.02 and 5.67 days in chilli crop at CCSHAU, Hisar (Kumari and Chauhan, 2015). Gogikar *et al.* (2017b) reported half life of chlorpyriphos 20 EC as 1.43 days when applied @ 300 g a.i.$ha^{-1}$ in curry leaf. The variation in the half–life values may be attributed to the factors such as volatility of the compounds, initial deposits, growth and physiology of plants, weather conditions, oxidation, reduction and hydrolytic biodegradation as documented by Juraske *et al.* ( 2008).

**Table 4.16. Statistical constants of test insecticides in/on cauliflower curds**

| Insecticide | Dosage (g a.i. /ha) | Statistical Constants | | | |
|---|---|---|---|---|---|
| | | Regression equation (y = a + bx) | Correlation cofficient ($R^2$) | $RL_{50}$ (Days) | Waiting period (Days) |
| Chlorpyrifos | 300 | y = –0.3117 – 0.2935x | – 0.9941 | 1.03 | 0.97 |
| | 600 | y = –0.3719 – 0.2280x | – 0.9951 | 1.32 | 2.00 |
| Cypermethrin | 50 | y = –0.2951– 0.1702x | – 0.9865 | 1.77 | 6.04 |
| | 100 | y = –0.1488 – 0.1588 x | – 0.9785 | 1.90 | 7.61 |
| Profenofos | 500 | y = –0.4324 – 0.2382 x | – 0.9976 | 1.26 | 7.26 |
| | 1000 | y = –0.6332 – 0.1879 x | – 0.9943 | 1.60 | 10.75 |

**4.3.1.2 Cypermethrin**

The cypermethrin deposits dissipated to half at standard dose (@ 50 g a.i./ha) in 1.77 days as compared to 1.90 days at double dose (@ 100 g a.i./ha) from cauliflower curds, following first order kinetics dissipation of the insecticide at both standard dose and double the standard dose (Table 4.16).

The results of present investigation almost correspond to the findings of Banshtu and Patyal (2016) who calculated the half life of 1.38 – 1.69 days at recommended (@ 50 g a.i./ha) and double the recommended dose (@ 100 g a.i./ha) of cypermethrin (Challenger 25 EC) on cauliflower curds, respectively. Whereas, Banshtu and Patyal (2017b) observed a half life of 1.06 – 1.42 days on application of cypermethrin @ 40 and 80 g a.i./ha, respectively on cauliflower. Similar results were obtained by Mayannavar *et al*. (2017) who observed loss of cypermethrin residues to half after application of Cymbush 25 EC on okra in 2.38 and 2.00 days at single (50 g a.i./ha) and double dose (100 g a.i./ha), respectively. Cherukuri *et al.* (2015) when evaluated cypermethrin 10 EC on tomato fruits reported a half life of 2.41 days at 50 g a.i./ha. Jaswal (2015) reported that the residues of cypermethrin at the rate of 50 g a.i. $ha^{-1}$ reduced to half in 2.2-2.3 days in chilli fruits. Patel *et al.* (2016) observed that half-life values of cypermethrin on brinjal fruits in summer and rabi season were 2 and 2.89 days, respectively at a dosage of 200 g a.i. $ha^{-1}$. The half–life of cypermethrin deposits on okra (variety Varsha Uphar) were 2.74 and 3.31 days following the application of cypermethrin 25 EC at the rate of 50 and 100 g a.i. $ha^{–1}$, respectively at CCSHAU, Hisar (Chauhan *et al*., 2018). Anuradha and Bhuvaneshwari (2020) reported that the dissipation of cypermethrin followed the first order kinetics with a half–life of 4.27 and 4.62 days in curry leaf variety Sengambu when applied at the rate of 50 and 100 g a.i. $ha^{-1}$, respectively.

#### 4.3.1.3 Profenofos

The profenofos deposits dissipated to half at standard dose (@ 500 g a.i./ha) in 1.26 days as compared to 1.60 days at double dose (@ 1000 g a.i./ha) from cauliflower curds, following first order kinetics dissipation of the insecticide at both standard dose and double the standard dose (Table 4.16).

The results of present studies almost corresponds to the findings of Banshtu and Patyal (2017b) who calculated the half life of 1.78 – 2.21 days at recommended (@ 400 g a.i./ha) and double the recommended dose (@ 800 g a.i./ha) of profenofos on cauliflower curds, respectively. Whereas, Akbar *et al*. (2020) observed a half life of 2.99 days on application of profenofos @ 988 g a.i./ha on cauliflower curds. According to the study conducted by Cherukuri *et al*. (2015) the half life value of profenofos 50 EC was found to be 1.57 days when applied at the rate of 500 g a.i. $ha^{-1}$ in tomato. However, the half–life of profenofos deposits on cabbage head was 4.91 days following the application of profenofos at the rate of 1000 g a.i. $ha^{-1}$ (Reddy *et al*., 2017b). Deore *et al*. (2018) reported half life of profenofos as 2.64 days when applied @ 500 g a.i. $ha^{-1}$ on brinjal fruits. Naik *et al*. (2020) recorded the half-life ($t_{1/2}$) for degradation of profenofos 50 EC in pigeonpea as 5.18 and 5.93 days at the standard dose (500 g a.i. $ha^{-1}$) and double the standard dose (1000 g a.i. $ha^{-1}$), respectively.

### 4.3.2 Waiting Period

The time between last application of insecticide on the crop and harvest is referred as waiting period. Dissipation rates have application in consumer safety. For example, these values are used in calculation for predicting residue concentration in harvested produce and for detecting the time interval needed between crop spraying and harvesting or potential processing/ consumption in order to minimize residue concentrations (Lewis and Tzilivakis, 2017). The waiting periods are calculated on the basis of MRLs and persistence data of the insecticide on a particular commodity. In present study, waiting period for chlorpyrifos has been calculated at MRL of 1 mg $kg^{-1}$ for cauliflower (FSSAI, 2018) and for cypermethrin and profenofos at 0.05 mg $kg^{-1}$ (LOQ) as FSSAI (Food Safety and Standards Authority of India) has not fixed MRLs for these insecticides on cauliflower.

#### 4.3.2.1 Chlorpyrifos

On the basis of present study (Table 4.16), waiting period for chlorpyrifos was calculated as 0.97 and 2.00 days at standard (@ 300 g a.i./ha) and double the standard dose (@ 600 g a.i./ha), respectively.

Results were in close line with those of Jyot *et al*. (2013) who suggested waiting period of 1 day for chlorpyrifos on chilli when applied at the rate 1 and 2 L $ha^{-1}$. Raina and Raina (2008) reported safe waiting period of 5.0-6.3 and 7.1-7.3 days for chlorpyrifos on cauliflower at the application rate of 500 g a.i $ha^{-1}$ and 1000 g a.i. $ha^{-1}$, respectively for two consecutive years. Brar *et al*. (2018) suggested the waiting period of chlorpyrifos on brinjal to be 3.81 and 7.13 days at recommended dose (300 g a.i. $ha^{-1}$) and double the recommended dose (600 g a.i. $ha^{-1}$), respectively based on FSSAI MRL of 0.2 mg $kg^{-1}$. Singh *et al*. (2019) reported 7.05 and 9.98 days of waiting period for harvesting of cucumber fruits at single (@ 300 g a.i./ha) and double dose (@ 600 g a.i./ha), respectively.

#### 4.3.2.2 Cypermethrin

The safe waiting period of cypermethrin on cauliflower was suggested as 6.04 and 7.61 days after spray application at standard (@ 50 g a.i./ha) and double dose (@ 100 g a.i./ha), respectively (Table 4.16). The results of present findings showed a close similarity to those obtained by Jaswal (2015) who recommended a waiting period of 6.2 and 7.7 days at the application rate of 50 and 100 g a.i. $ha^{-1}$ in chilli fruits, respectively for safe consumption and waiting period were calculated at 0.05 mg $kg^{-1}$ limit of quantification. Mayannavar *et al*. (2017) suggested a waiting period of 5 days for cypermethrin (Cymbush 25 EC) on okra when worked out at LOQ of 0.05 mg $kg^{-1}$.

#### 4.3.2.3 Profenofos

The safe waiting period of profenofos on cauliflower was suggested as 7.26 and 10.75 days after spray application at standard (@ 500 g a.i./ha) and double dose (@ 1000 g a.i./ha), respectively (Table 4.16).

The results of present findings showed a close similarity to those obtained by Jaswal (2015) who suggested a waiting period as 7.2 and 10.3 days on the basis of 0.05 mg $kg^{-1}$ limit of determination for profenofos in chilli at recommended dose (500 g a.i. $ha^{-1}$) and double the recommended dose (1000 g a.i. $ha^{-1}$), respectively. These studies are corroborative to the findings of Brar *et al*. (2017), who worked out waiting period of 6.3 and 7.9 days for profenofos on brinjal fruits at single and double doses (500 and 1000 g a.i. $ha^{-1}$), respectively. Reddy *et al*. (2017b) reported that waiting period for safe harvest of cabbage heads worked out to be 15 days for profenofos 50 EC @ 1000 g a.i. $ha^{-1}$ and computed waiting period as per EU MRL (0.01 mg $kg^{-1}$). Deore *et al.* (2018) recommended a waiting period of 10 days for profenofos on brinjal when applied at the rate of 500 g a.i./ha and computed waiting period at MRL of 0.05 mg $kg^{-1}$.

## 4.4 DECONTAMINATION STUDIES

Foods after harvest are subjected to various handling and processing operations both at home or industry level, involving a simple washing to more multi-step and complex processing aimed to extend shelf-life, add variety, increase palatability and nutrient availability and to generate income (Bajwa and Sandhu, 2014). The first step in household or commercial food processing is the preparation of food using various mechanical processes, such as removing damaged or soiled items or parts of crops, washing, peeling, trimming or hulling. This often leads to significant declines in the amount of pesticide residues in the remaining edible portions especially in case of contact poisons. In fruits and vegetables, most of the pesticide residues are retained on peel surface (Awasthi, 1993). This is the reason that majority of the residues are removed by common household practices like washing, peeling or treatments with chemical solutions like vinegar, turmeric, sodium bicarbonate, common salt or alcohol etc. Nowadays, many products are available in the market such as nimwash (ITC), veggie clean (Marico) and arka herbiwash (IIHR), etc. that also ensure effective reduction of pesticide residues as well. The effects of food processing on pesticide residue levels may be influenced by the physical location of the pesticide residue as well as the physico-chemical properties of the pesticide such as solubility, volatility, hydrolytic rate constants, water–octanol partition coefficient and thermal degradation (Keikotlhaile *et al.,* 2010).

### 4.4.1 Effect of decontamination processes on insecticide residues in cauliflower curds

Different decontamination treatments *viz.,* tap water washing, lukewarm water washing, saline water washing, washing with sodium bicarbonate solution, washing with acetic acid solution, washing with potassium permanganate solution, washing with veggie clean solution, washing with nimwash solution, washing with arka herbiwash solution were employed to study the effect on chlorpyrifos, cypermethrin and profenofos residues reduction in cauliflower curds at the single and double dose of each insecticide when the test insecticides were sprayed as a mixture. Data are presented in tables 4.17-4.19 and per cent relief illustrated is in figures 4.10-4.14.

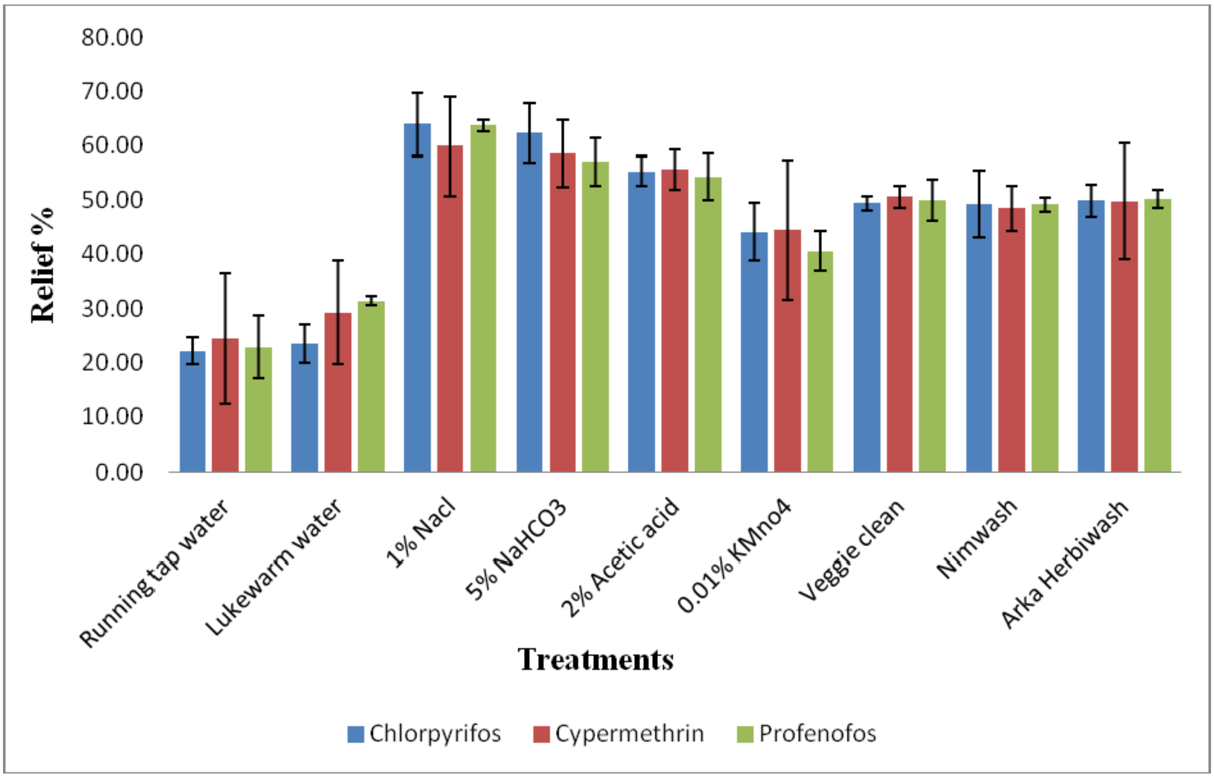



**Fig 4.10 Effect of decontamination processes on residues of test insecticides when applied at single doses**

At single doses, various decontamination processes showed reduction in residues of chlorpyrifos, cypermethrin and profenofos such as running tap water washing (22.27, 24.46 and 22.99 per cent), lukewarm water washing (23.63, 29.34 and 31.58 per cent), saline water washing (63.91, 59.90 and 63.65 per cent), sodium bicarbonate solution dipping (62.40, 58.62 and 57.06 percent), acetic acid solution dipping (55.31, 55.58 and 54.25 per cent), $KMnO_4$ solution dipping (44.12, 44.53 and 40.59 per cent), veggie clean solution dipping (49.46, 50.67 and 49.95 per cent), nimwash solution dipping (49.23, 48.47 and 49.17) and arka herbiwash solution dipping (49.91, 49.74 and 50.31), respectively as shown in Fig 4.10.

Whereas, at double doses, different decontamination treatments showed per cent relief in residues of chlorpyrifos, cypermethrin and profenofos viz., running tap water washing (22.50, 23.70 and 22.86 per cent), lukewarm water washing (24.26, 27.63 and 25.53 per cent), saline water washing (64.95, 63.26 and 63.70 per cent), sodium bicarbonate solution dipping (64.01, 63.11 and 60.05 percent), acetic acid solution dipping (58.71, 56.58 and 61.32 per cent), $KMnO_4$ solution dipping (47.16, 48.22 and 48.16 per cent), veggie clean solution dipping (48.30, 53.42 and 50.50 per cent), nimwash solution dipping (48.93, 54.63 and 49.65) and arka herbiwash solution dipping (48.41, 52.38 and 49.44), respectively as shown in Fig 4.11.

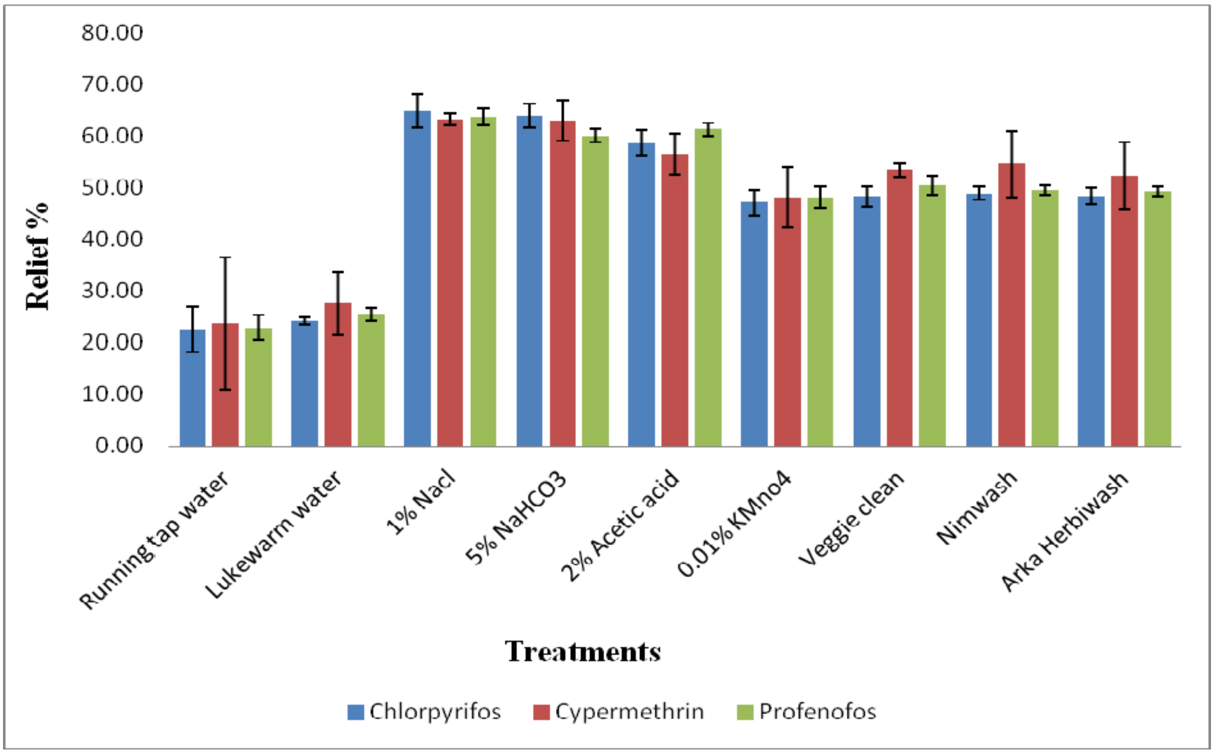



**Fig 4.11 Effect of decontamination processes on residues of test insecticides when applied at double doses**

### 4.4.1.1 Effect of decontamination processes on residues of chlorpyrifos (300 and 600 g a.i. $ha^{-1}$) in cauliflower curds

The data pertaining to the effect of cauliflower curds processing on residues reduction due to application of chlorpyrifos @ 300 and 600 g a.i. $ha^{-1}$ as pre-mix spray are presented in Table 4.17 and Fig 4.12. The per cent relief from chlorpyrifos residues thus obtained in the present study varied between 22.27-63.91 and 22.50-64.95 per cent in cauliflower curds sampled after 48 hrs of spray at single and double dose, respectively.

Results revealed that in unprocessed cauliflower curds, chlorpyrifos residues were 0.572 and 0.883 mg $kg^{-1}$ at single and double dose, respectively. After tap water washing for 1 minute, these residues were declined to 0.445 and 0.683 mg $kg^{-1}$ showing 22.27 and 22.50 per cent dislodging at the respective dosages. Randhawa *et al.* (2007) reported that chlorpyrifos residues reduced by 33.00 per cent in spinach, 30.00 per cent in potato, 25.00 per cent in cauliflower and 10.00 per cent in tomato by washing with tap water. Similarly, Banshtu and Patyal (2018) found tap water washing as least effective, showing up to 37.41, 33.80 and 29.26 per cent loss of chlorpyrifos residues from cauliflower curds sampled on 0, 3 and 7 days after application, respectively which is in closer proximity with present findings. The results are in conformity with Samriti *et al.* (2011) who reported that tap water washing of okra reduced residues of chlorpyrifos in the range of 18.75–31.34 per cent. Brar *et al.* (2018) revealed that washing of the brinjal fruits with tap water was effective in removing chlorpyrifos residues to the tune of 36.17 per cent. Singh *et al.* (2019) revealed that when the chlorpyrifos (300 g a.i. $ha^{-1}$) treated cucumber fruits collected at 1, 3 and 5 days were washed with running tap water for 2 minutes, the residues reduced to 0.458, 0.225 and 0.064 mg $kg^{-1}$, respectively and the per cent relief obtained to the tune of 30.23, 31.79 and 30.07, respectively. Washing of grapes with tap water reduced the residues of chlorpyrifos to 28.00 per cent (Harinathareddy *et al.*, 2015).

**Table 4.17 Effect of decontamination treatments on chlorpyrifos residues in/on cauliflower curds at the application rate of 300 and 600 g a.i. / ha**

| Treatments | Residues @ 300 g a.i. / ha (mg $kg^{-1}$) | | | | Mean Relief (%) ± SD | Residues @ 600 g a.i. / ha (mg $kg^{-1}$) | | | | Mean Relief (%) ± SD |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Mean ± SD | | $R_1$ | $R_2$ | $R_3$ | Mean ± SD | |
| Untreated Control | 0.576 | 0.542 | 0.598 | 0.572± 0.028 | - | 0.856 | 0.910 | 0.882 | 0.883± 0.027 | - |
| Running Tap water | 0.440 | 0.413 | 0.482 | 0.445± 0.035 | 22.27 ± 2.49 | 0.688 | 0.659 | 0.703 | 0.683± 0.022 | 22.50 ± 4.41 |
| Luke warm water | 0.462 | 0.410 | 0.438 | 0.437± 0.026 | 23.63 ± 3.54 | 0.641 | 0.692 | 0.673 | 0.669± 0.026 | 24.26 ± 0.76 |
| 1% NaCl | 0.205 | 0.228 | 0.183 | 0.205± 0.023 | 63.91 ± 5.75 | 0.307 | 0.286 | 0.334 | 0.309± 0.024 | 64.95 ± 3.30 |
| 5 % $NaHCO_3$ | 0.180 | 0.219 | 0.246 | 0.215± 0.033 | 62.40 ± 5.51 | 0.296 | 0.316 | 0.341 | 0.318± 0.023 | 64.01 ± 2.32 |
| 2 % Acetic acid | 0.241 | 0.257 | 0.268 | 0.255± 0.014 | 55.31 ± 2.79 | 0.371 | 0.352 | 0.369 | 0.364± 0.010 | 58.71 ± 2.38 |
| 0.01% $KMnO_4$ | 0.308 | 0.336 | 0.312 | 0.319± 0.015 | 44.12 ± 5.33 | 0.467 | 0.491 | 0.441 | 0.466± 0.025 | 47.16 ± 2.48 |
| Veggie clean | 0.291 | 0.267 | 0.310 | 0.289± 0.022 | 49.46 ± 1.29 | 0.452 | 0.480 | 0.437 | 0.456± 0.022 | 48.30 ± 1.86 |
| Nimwash | 0.273 | 0.314 | 0.281 | 0.289± 0.022 | 49.23 ± 6.20 | 0.447 | 0.466 | 0.439 | 0.451± 0.014 | 48.93 ± 1.23 |
| Arka herbiwash | 0.269 | 0.284 | 0.306 | 0.286± 0.019 | 49.91 ± 3.00 | 0.426 | 0.479 | 0.462 | 0.456± 0.027 | 48.41 ± 1.59 |

Lukewarm water (45-50$^0$C) washing for 10 minutes reduced chlorpyrifos residues further to 0.437 and 0.669 mg kg$^{-1}$ and the per cent relief obtained to the tune of 23.63 and 24.26 at single and double dose, respectively. Our results are in a close similarity to Banshtu and Patyal (2018) who reported that washing of cauliflower curds with lukewarm water (50$^0$C) for 5 minutes sampled at 0, 3 and 7 days after application provided 41.21, 39.29 and 36.58 per cent relief from chlorpyrifos residues, respectively. Begum *et al.* (2016) observed that dipping of brinjal fruits in lukewarm water reduced the chlorpyrifos (1.43 mg kg$^{-1}$) residues to 44.00 per cent. Brar *et al*. (2018) revealed that washing of the brinjal fruits with lukewarm water was effective in removing chlorpyrifos residues to the extent of 48.63 per cent. Singh *et al*. (2019) observed that when chlorpyrifos treated cucumber fruits dipped in lukewarm water, residues reduced in the range of 0.399 to 0.054 mg kg$^{-1}$ showed 39.18 to 40.94 per cent relief.

On washing of cauliflower curds with salt (1 per cent NaCl) water for 10 minutes, residues decreased to 0.205 and 0.309 mg kg$^{-1}$ at single (@ 300 g a.i./ha) and double dose (@ 600 g a.i./ha), respectively and the per cent relief obtained to the tune of 63.91 and 64.95, respectively. Our results are analogous to those of Liang *et al*. (2012) who reported that dipping of cucumber in salt solution (2 percent) for 10 and 20 minutes facilitated the removal of chlorpyrifos residues to an extent of 60.5 and 66.70 per cent, respectively. Chandra *et al.* (2015) revealed that treatment with 2 per cent NaCl in water reduced the chlorpyrifos residues to 59.8- 61.2 per cent in brinjal. Begum *et al.* (2016) observed that dipping of brinjal fruits in 2 per cent common salt water reduced the chlorpyrifos (1.41 mg kg$^{-1}$) residues to 45 per cent. Banshtu and Patyal (2018) reported 43.03 per cent relief from chlorpyrifos residues in cauliflower curds when processed with 2 per cent sodium chloride solution for 5 minutes. Dipping of cauliflower curds samples in 2 per cent sodium chloride solution for 5 minutes reduced chlorpyrifos residues upto to 41.46 per cent (Banshtu *et al*., 2018).

Dipping of cauliflower curds in 5 per cent sodium bicarbonate ($NaHCO_3$) aqueous solution for 10 minutes degraded chlorpyrifos residues to 0.215 and 0.318 mg kg$^{-1}$ contributing to 62.40 and 64.01 per cent relief at single and double dose, respectively. The present findings are in close propinquity with Chandra *et al.* (2015) who reported that treatment with 1 per cent sodium bicarbonate reduced the chlorpyrifos residues to the extent of 62.4 - 65.6 per cent in brinjal. Liang *et al.* (2012) reported that treatment with 2 per cent sodium bicarbonate for 5 and 10 minutes reduces the chlorpyrifos residues to the tune of 75.3

and 77.8 per cent in cucumber, respectively. However, Priyadarshini *et al.* (2017) observed that washing of curry leaf samples with sodium bicarbonate solution reduced the chlorpyrifos residues upto 35.28 per cent only.

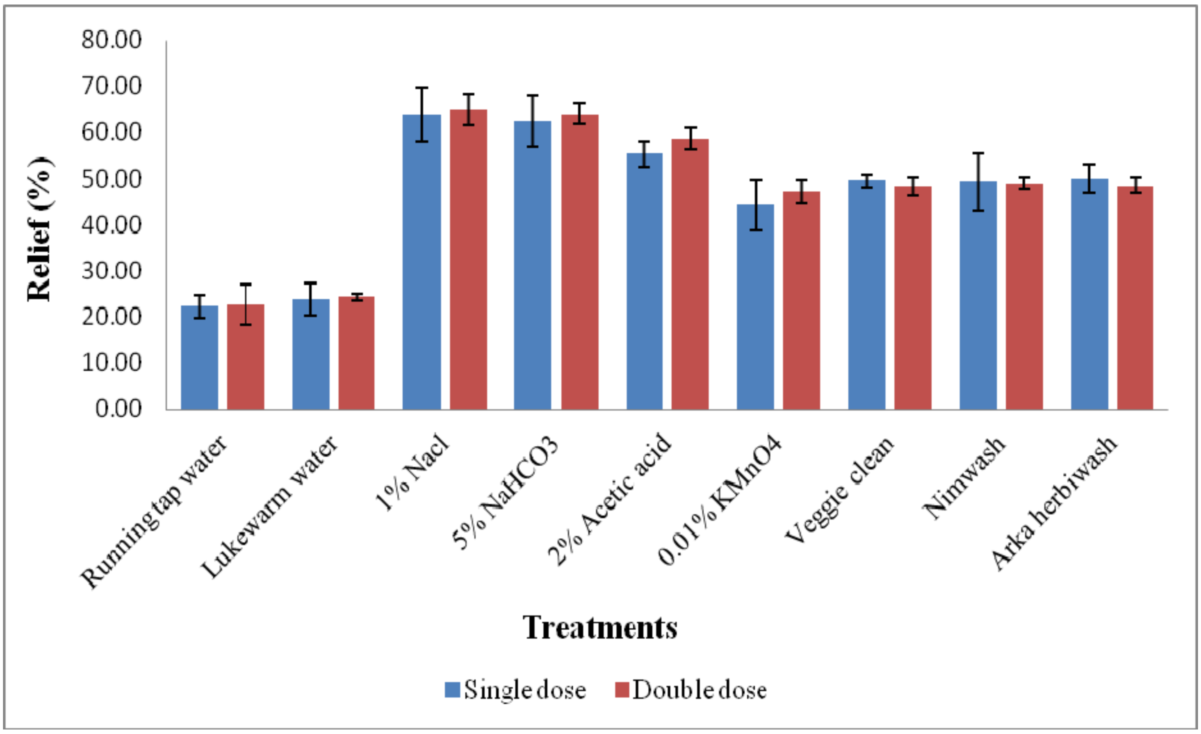



**Fig. 4.12 Effect of decontamination treatments on removal of chlorpyrifos residues from cauliflower curds at the application rate of 300 and 600 g a.i. ha$^{-1}$**

Acetic acid (2 per cent) aqueous solution dipping for 10 minutes reduced residues to 0.255 and 0.364 mg kg$^{-1}$ providing 55.31 and 58.71 per cent relief at both the doses, respectively. Liang *et al.* (2012) performed decontamination of cucumber with acetic acid (2 per cent) for 5 and 10 minutes and obtained up to 54.3 and 63.0 per cent loss of chlorpyrifos residues, respectively. Chandra *et al.* (2015) reported that treatment with 0.5 per cent acetic acid reduces the chlorpyrifos residues to 65.6 – 68.5 per cent in brinjal. Priyadarshini *et al.* (2017) performed decontamination of curry leaf with acetic acid and observed up to 22.26 per cent relief from chlorpyrifos residues.

In washing with 0.01 percent $KMnO_4$ aqueous solution for 10 minutes, chlorpyrifos residues decreased to 0.319 and 0.466 mg kg$^{-1}$ giving 44.12 and 47.16 per cent relief at recommended and double the recommended dose, respectively. According to Osman *et al.* (2014) the extent of residues removal through washing with 1 percent $KMnO_4$ solution ranged between 63.56 to 75.16 per cent for chlorpyrifos treated date fruits.

Washing with veggie clean aqueous solution for 10 minutes degraded chlorpyrifos residues to 0.289 and 0.456 mg $kg^{-1}$ contributing to 49.46 and 48.30 per cent relief at single and double dose, respectively. However, in washing with nimwash aqueous solution for 10 minutes, residues decreased to 0.289 and 0.451 mg $kg^{-1}$ giving 49.23 and 48.93 per cent relief at respective doses, whereas, washing of treated cauliflower curds in 2-4 litre of arka herbiwash aqueous solution for 10 minutes reduced residues of chlorpyrifos upto 0.286 and 0.456 mg $kg^{-1}$ and the per cent relief obtained to the tune of 49.91 and 48.41 at single and double dose, respectively.

#### 4.4.1.2 Effect of decontamination processes on residues of cypermethrin (50 and 100 g a.i. $ha^{-1}$) in cauliflower curds

The data pertaining to the effect of cauliflower curds processing on residues reduction due to application of cypermethrin @ 50 and 100 g a.i. $ha^{-1}$ as pre-mix spray are presented in Table 4.18 and Fig 4.13. The per cent relief from cypermethrin residues thus obtained in the present study varied between 24.46-59.90 and 23.70-63.26 per cent in cauliflower curds sampled after 2 days (48 hrs) of spray at recommended and double the recommended dose, respectively.

In the present investigation the results revealed that in untreated cauliflower curds, cypermethrin residues were 0.245 and 0.357 mg $kg^{-1}$ at single and double dose, respectively. After tap water washing for 1 minute, these residues were decreased to 0.183 and 0.271 mg $kg^{-1}$ showing 24.46 and 23.70 per cent loss at the respective dosages. Mohamed *et al.* (2012) studied effect of washing on cypermethrin treated tomato fruits and found that their residues reduced to 19.40 per cent which is well in agreement with our findings. Tomer and Sangha (2013) revealed that plain water washing results in 33.42-35.00 per cent removal of cypermethrin residues from brinjal. Priyadarshini *et al.* (2017) reported that washing with tap water removed on an average 58.36 per cent of cypermethrin residues from curry leaf samples.

Lukewarm water (45-50$^{0}$C) washing for 10 minutes reduced cypermethrin residues further to 0.172 and 0.258 mg $kg^{-1}$ and the per cent relief obtained to the extent of 29.34 and 27.63 at single and double dose, respectively. Our results are in a close proximity to Jaswal (2015) who reported 37.11-42.06 per cent reduction of cypermethrin residues by lukewarm water washing of chilli fruits. Washing of cucumber fruits with luke warm water provided 36.20 – 100.00 per cent relief from cypermethrin residues was recorded by Thakur (2017).

**Table 4.18 Effect of decontamination treatments on cypermethrin residues in/on cauliflower curds at the application rate of 50 and 100 g a.i. / ha**

| Treatments | Residues @ 50 g a.i. / ha (mg $kg^{-1}$) | | | | Mean Relief (%) ± SD | Residues @ 100 g a.i. / ha (mg $kg^{-1}$) | | | | Mean Relief (%) ± SD |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Mean ± SD | | $R_1$ | $R_2$ | $R_3$ | Mean ± SD | |
| Untreated Control | 0.231 | 0.279 | 0.226 | 0.245± 0.029 | - | 0.351 | 0.379 | 0.342 | 0.357± 0.019 | - |
| Running Tap water | 0.191 | 0.172 | 0.186 | 0.183± 0.010 | 24.46± 12.04 | 0.278 | 0.236 | 0.299 | 0.271± 0.032 | 23.70 ± 12.83 |
| Luke warm water | 0.187 | 0.173 | 0.156 | 0.172± 0.016 | 29.34 ± 9.58 | 0.244 | 0.258 | 0.272 | 0.258± 0.014 | 27.63 ± 6.24 |
| 1% NaCl | 0.108 | 0.083 | 0.099 | 0.097± 0.013 | 59.90 ± 9.09 | 0.124 | 0.142 | 0.128 | 0.131± 0.009 | 63.26 ± 1.22 |
| 5 % $NaHCO_3$ | 0.101 | 0.096 | 0.104 | 0.100± 0.004 | 58.62 ± 6.15 | 0.116 | 0.139 | 0.140 | 0.132± 0.014 | 63.11 ± 3.95 |
| 2 % Acetic acid | 0.102 | 0.114 | 0.109 | 0.108± 0.006 | 55.58 ± 3.69 | 0.153 | 0.149 | 0.162 | 0.155± 0.007 | 56.58 ± 4.03 |
| 0.01% $KMnO_4$ | 0.134 | 0.116 | 0.151 | 0.134± 0.018 | 44.53 ±12.81 | 0.196 | 0.171 | 0.186 | 0.184± 0.013 | 48.22 ± 5.82 |
| Veggie clean | 0.109 | 0.143 | 0.112 | 0.121± 0.019 | 50.67 ± 2.04 | 0.168 | 0.172 | 0.159 | 0.166± 0.007 | 53.42 ± 1.24 |
| Nimwash | 0.127 | 0.131 | 0.119 | 0.126± 0.006 | 48.47 ± 4.13 | 0.143 | 0.162 | 0.180 | 0.162± 0.019 | 54.63 ± 6.37 |
| Arka herbiwash | 0.136 | 0.107 | 0.121 | 0.121± 0.015 | 49.74± 10.65 | 0.180 | 0.152 | 0.176 | 0.169± 0.015 | 52.38 ± 6.51 |

On washing of cauliflower curds with saline water (1 per cent NaCl) for 10 minutes, cypermethrin residues declined to 0.097 and 0.131 mg $kg^{-1}$ at single (@ 50 g a.i./ha) and double dose (@ 100 g a.i./ha), respectively and the per cent relief obtained to the tune of 59.90 and 63.26, respectively. The present results are in close agreement with those of Chandra *et al.* (2015) who reported that treatment with 2 per cent NaCl in water reduces the cypermethrin residues to 61.9- 62.8 per cent in brinjal. Priyadarshini *et al.* (2017) reported that by washing with salt solution, residues of cypermethrin on curry leaf samples were reduced to the extent of 37.93 per cent. Banshtu and Patyal (2018) reported 46.21 per cent relief from cypermethrin residues in cauliflower curds when processed with 2 per cent sodium chloride solution for 5 minutes.

Dipping of cauliflower curds in 5 per cent sodium bicarbonate ($NaHCO_3$) aqueous solution for 10 minutes degraded cypermethrin residues to 0.100 and 0.132 mg $kg^{-1}$ contributing to 59.10 and 63.15 per cent relief at single and double dose, respectively. Our results are in agreement with Chandra *et al.* (2015) who reported that treatment with 1 per cent sodium bicarbonate reduced the cypermethrin residues to the extent of 60.4 - 62.9

per cent in brinjal. Tomer *et al*. (2014) studied that washing with 5 per cent $NaHCO_3$ solution resulted in 89.53 per cent removal of cypermethrin residues from okra fruits. However, Priyadarshini *et al.* (2017) observed that washing of curry leaf samples with sodium bicarbonate solution dislodged the cypermethrin residues upto 19.21 per cent only. Removal of pesticides from the raw agricultural commodities depends upon the solubility of the chemical which in general increases with the increase in the level of commodity temperature depending upon pesticide binding with the matrices which ultimate leads to affect the partitioning coefficient (Kaushik *et al*., 2019).

Dipping of cauliflower curds in 4 litres of aqueous solution of acetic acid (2 per cent) for 10 minutes declined cypermethrin residues to 0.108 and 0.155 mg $kg^{-1}$ providing 55.58 and 56.58 per cent relief at both the doses, respectively. The results showed close proximity with Nair *et al.* (2015) who reported that treating curry leaves with 2 per cent vinegar solution reduced cypermethrin residues by 50.25±1.63 per cent. Chandra *et al.* (2015) reported that treatment with 0.5 per cent acetic acid reduced the cypermethrin residues upto 67.9 – 68.5 per cent in brinjal. Priyadarshini *et al.* (2017) performed decontamination of curry leaf with acetic acid and obtained up to 44.53 per cent loss of cypermethrin residues. Hussnain *et al.* (2021) showed that the highest reduction in cypermethrin residues were recorded to be 0.017±0.014 mg $kg^{-1}$ (83 per cent) by 10 per cent acetic acid in spinach.

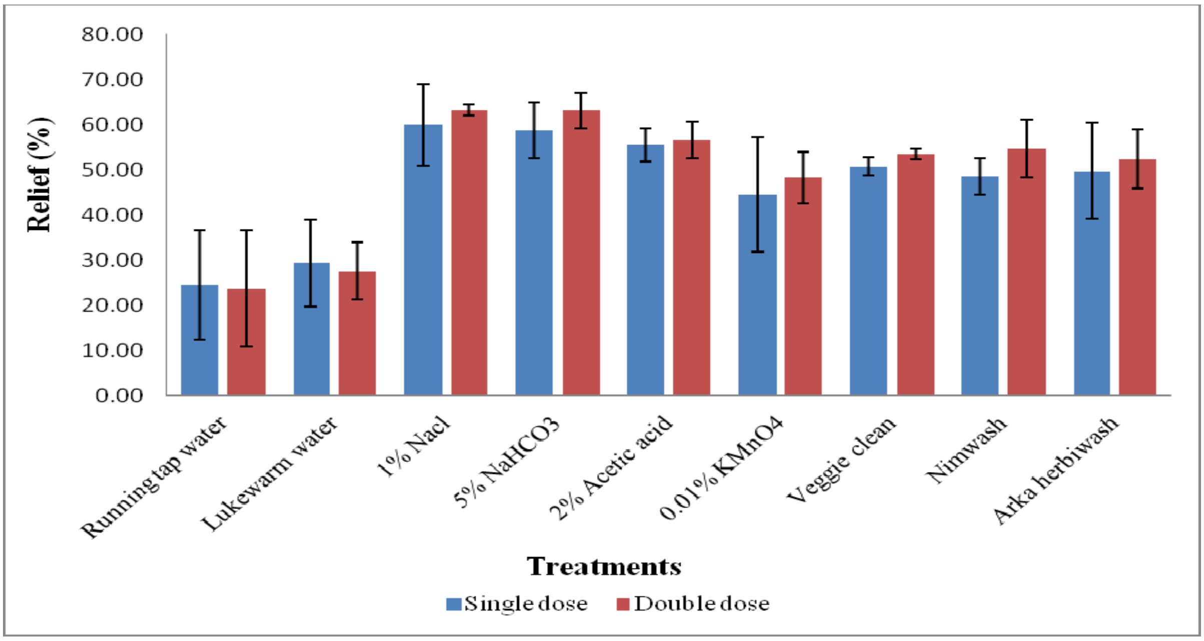



**Fig. 4.13 Effect of decontamination treatments on removal of cypermethrin residues from cauliflower curds at the application rate of 50 and 100 g a.i. $ha^{-1}$**

In washing with 0.01 percent $KMnO_4$ aqueous solution for 10 minutes, cypermethrin residues decreased to 0.134 and 0.184 mg $kg^{-1}$ giving 44.53 and 48.22 per cent relief at recommended and double the recommended dose, respectively. Our results are in close proximity with that of Tomer *et al*. (2014) who found that washing with 2 per cent $KMnO_4$ solution dislodged upto 56.88 per cent of cypermethrin initial deposits from contaminated okra.

Washing with veggie clean aqueous solution for 10 minutes degraded cypermethrin residues upto 0.121 and 0.166 mg $kg^{-1}$ contributing to 50.67 and 53.42 per cent relief at single and double dose, respectively. However, in washing with nimwash aqueous solution for 10 minutes, residues declined to 0.126 and 0.162 mg $kg^{-1}$ giving 48.47 and 54.63 per cent relief at respective doses, whereas washing of treated cauliflower curds in 2-4 litre of arka herbiwash aqueous solution for 10 minutes reduced residues upto 0.121 and 0.169 mg $kg^{-1}$ and the per cent relief obtained to the tune of 49.74 and 52.38 at single and double dose, respectively.

#### 4.4.1.3 Effect of decontamination processes on residues of profenofos (500 and 1000 g a.i. $ha^{-1}$) in cauliflower curds

The data pertaining to the effect of decontamination processes on the reduction of residues due to application of profenofos @ 500 and 1000 g a.i. $ha^{-1}$ as pre-mix spray on cauliflower curds are presented in Table 4.19 and Fig 4.14. The per cent loss of profenofos residues thus obtained in the present study ranged between 22.99-63.65 and 22.86-63.70 per cent in cauliflower curds sampled after 48 hrs of spray at recommended and double the recommended dose, respectively.

The results revealed that in unprocessed cauliflower curds, profenofos residues were 0.639 and 1.255 mg $kg^{-1}$ at single and double dose, respectively. After tap water washing for 1 minute, these residues were reduced to 0.491 and 0.968 mg $kg^{-1}$ showing 22.99 and 22.86 per cent dislodging at the respective dosages. Results are in accordance with Banshtu *et al*. (2018) who reported that washing of cauliflower curds with running tap water reduced the residues of profenofos to the extent of 26.06 and 36.17 per cent in 0 and 3 days old cauliflower samples. Tomer and Sangha (2013) studied that plain water washing results in 14.32 per cent removal of profenofos residues from cauliflower. Washing of cauliflower curds with tap water provided 54.35 per cent relief from profenofos residues (Dhiman and Hiremath 2014). Mohamed *et al.* (2012) studied effect of washing on profenofos treated tomato fruits and found that their residues reduced to 23.30 per cent which is well in agreement with our findings. Sheikh *et al.* (2013) found higher level of reduction (53.66 per cent) of profenofos residues from bittergourd fruits compared to our results. Priyadarshini *et al.* (2017) reported that washing with tap water removed on an average 57.64 per cent of profenofos residues from curry leaf samples.

**Table 4.19 Effect of decontamination treatments on profenofos residues in/on cauliflower curds at the application rate of 500 and 1000 g a.i. / ha**

| Treatments | Residues @ 500 g a.i. / ha (mg kg$^{-1}$) | | | | Mean Relief (%) ± SD | Residues @ 1000 g a.i. / ha (mg kg$^{-1}$) | | | | Mean Relief (%) ± SD |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R_1$ | $R_2$ | $R_3$ | Mean ± SD | | $R_1$ | $R_2$ | $R_3$ | Mean ± SD | |
| Untreated Control | 0.629 | 0.617 | 0.672 | 0.639± 0.029 | - | 1.262 | 1.243 | 1.259 | 1.255± 0.010 | - |
| Running Tap water | 0.512 | 0.489 | 0.473 | 0.491± 0.020 | 22.99 ± 5.84 | 0.966 | 0.992 | 0.945 | 0.968± 0.024 | 22.86 ± 2.43 |
| Luke warm water | 0.436 | 0.422 | 0.454 | 0.437± 0.016 | 31.58 ± 0.88 | 0.921 | 0.937 | 0.945 | 0.934± 0.012 | 25.53 ± 1.30 |
| 1% NaCl | 0.236 | 0.221 | 0.240 | 0.232± 0.010 | 63.65 ± 1.01 | 0.454 | 0.473 | 0.439 | 0.455± 0.017 | 63.70 ± 1.62 |
| 5 % $NaHCO_3$ | 0.253 | 0.296 | 0.273 | 0.274± 0.022 | 57.06 ± 4.36 | 0.499 | 0.484 | 0.521 | 0.501± 0.019 | 60.05 ± 1.27 |
| 2 % Acetic acid | 0.293 | 0.305 | 0.277 | 0.292± 0.014 | 54.26 ± 4.17 | 0.495 | 0.463 | 0.498 | 0.485± 0.019 | 61.32 ± 1.25 |
| 0.01% $KMnO_4$ | 0.351 | 0.389 | 0.399 | 0.380± 0.025 | 40.59 ± 3.62 | 0.626 | 0.652 | 0.673 | 0.650± 0.024 | 48.16 ± 2.00 |
| Veggie clean | 0.335 | 0.315 | 0.308 | 0.319± 0.014 | 49.95 ± 3.81 | 0.624 | 0.638 | 0.601 | 0.621± 0.019 | 50.50 ± 1.80 |
| Nimwash | 0.328 | 0.306 | 0.341 | 0.325± 0.018 | 49.17 ± 1.28 | 0.628 | 0.639 | 0.628 | 0.632± 0.006 | 49.65 ± 0.92 |
| Arka herbiwash | 0.311 | 0.297 | 0.346 | 0.318± 0.025 | 50.31 ± 1.69 | 0.631 | 0.642 | 0.630 | 0.634± 0.007 | 49.44 ± 0.94 |

Lukewarm water (45-50$^0$C) washing for 10 minutes reduced profenofos residues further to 0.437 and 0.934 mg kg$^{-1}$ and the per cent relief obtained to the tune of 31.58 and 25.53 at single and double dose, respectively. The present findings are analogous to the findings of Banshtu *et al*. (2018) who reported a relief of 28.34 and 39.24 percent from profenofos residues in 0 and 3$^{rd}$ day cauliflower samples, respectively when decontaminated with lukewarm water (50$^0$C) for 5 minutes. Jaswal (2015) reported 26.92-54.38 per cent reduction of profenofos residues by lukewarm water washing of chilli fruits. Negi (2015) also found that washing of okra fruits with lukewarm water could remove the residues of profenofos to the tune of 31.25-56.20 per cent.

On washing of cauliflower curds with salt water (1 per cent NaCl) for 10 minutes, residues declined to 0.232 and 0.455 mg $kg^{-1}$ at single (@ 500 g a.i./ha) and double dose (@ 1000 g a.i./ha), respectively and the per cent relief obtained to the tune of 63.65 and 63.70, respectively. Priyadarshini *et al.* (2017) reported that by washing with salt solution, residues of profenofos on curry leaf samples were reduced to the extent of 42.98 per cent. Thakur (2017) studied that dipping of cucumber fruits in 2 per cent sodium chloride solution for 5 minutes at room temperature provided relief of 45.98–100.00 per cent from profenofos residues.

Dipping of cauliflower curds in 5 per cent sodium bicarbonate ($NaHCO_3$) aqueous solution for 10 minutes reduced profenofos residues upto 0.274 and 0.501 mg $kg^{-1}$ contributing to 57.06 and 60.05 per cent loss at single and double dose, respectively. These results are in conformity with Harinathareddy *et al.* (2015) who recorded that washing of grapes collected after 2 hrs of spray with 0.1 per cent sodium bicarbonate solution dislodged the residues of profenofos to the extent of 62.00 per cent. Priyadarshini *et al.* (2017) observed that washing of curry leaf samples with sodium bicarbonate solution reduced the profenofos residues upto 17.63 per cent only.

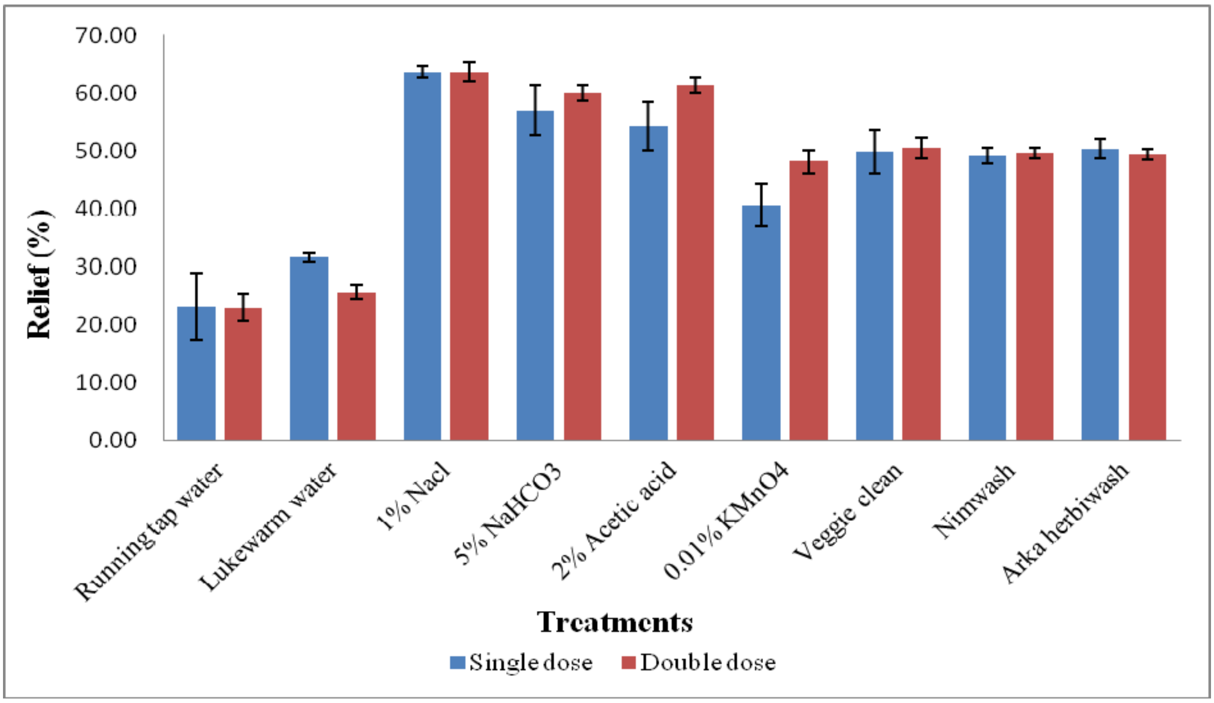



**Fig 4.14 Effect of decontamination treatments on removal of profenofos residues from cauliflower curds at the application rate of 500 and 1000 g a.i. $ha^{-1}$**

Dipping of cauliflower curds in 2 per cent acetic acid aqueous solution for 10 minutes degraded profenofos residues to 0.292 and 0.485 mg $kg^{-1}$ providing 54.26 and 61.32 per cent relief at both the dosages, respectively. The results showed a close proximity with Nair *et al.* (2015) who reported that treating curry leaves with 2 per cent vinegar solution reduced profenofos residues by 52.77±1.44 per cent. Jaswal (2015) suggested that approximately 56.25 per cent residues of profenofos were dislodged by washing chilli fruits with vinegar water. Kelageri *et al*. (2015) reported that washing of tomato fruits with 4 per cent acetic acid solution provided 71.22 per cent relief from profenofos residues. Our findings are in line with that of Harinathareddy *et al*. (2015) who observed that washing of grapes with 2 per cent acetic acid solution removed 60 per cent of profenofos residues. Priyadarshini *et al.* (2017) performed decontamination of curry leaf with acetic acid and obtained up to 50.08 per cent loss of profenofos residues.

In washing with 0.01 percent $KMnO_4$ aqueous solution for 10 minutes, profenofos residues declined to 0.380 and 0.650 mg $kg^{-1}$ giving 40.59 and 48.16 per cent relief at recommended and double the recommended dose, respectively. Shiboob (2012) found that washing with 0.01 per cent $KMnO_4$ solution could be reduced up to 88.11 per cent of profenofos residues in tomato.

Washing with veggie clean aqueous solution for 10 minutes degraded residues upto 0.319 and 0.621 mg $kg^{-1}$ contributing to 49.95 and 50.50 per cent relief at single and double dose, respectively. However, washing with nimwash aqueous solution for 10 minutes decreased residues to 0.325 and 0.632 mg $kg^{-1}$ giving 49.17 and 49.65 per cent relief at respective doses, whereas washing of treated cauliflower curds in 4 litre of arka herbiwash aqueous solution for 10 minutes reduced residues upto 0.318 and 0.634 mg $kg^{-1}$ and the per cent relief obtained to the extent of 50.31 and 49.44 at single and double dose, respectively. These treatments were found equally effective in dislodging profenofos residues at both the doses.

# *Chapter-5*

# SUMMARY AND CONCLUSION

The present investigation **"Residue dynamics of chlorpyrifos, cypermethrin and profenofos on cauliflower"** was carried out in the Department of Entomology, Dr. Y.S. Parmar University of Horticulture and Forestry, Nauni, Solan (H.P.). The work was carried out to generate residue data for utilizing in fixing MRL at national levels, so that the safety of consumers to be ascertained.The obtained experimental results are summarized as:

- QuEChERS technique was used for extraction and cleanup of cauliflower curds and soil samples. Method was validated by spiking matrix at different levels *viz.,* 0.01, 0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$. Recoveries of chlorpyrifos from cauliflower curd samples fortified at six levels were in the range of 92.00 to 97.92 per cent whereas, recovery of chlorpyrifos from cauliflower field soil were in the range of 90.74 to 97.44 per cent. Recoveries of cypermethrin and profenofos from cauliflower curd samples fortified at five levels (0.05, 0.10, 0.25, 0.50 and 1.00 mg $kg^{-1}$) were in the range of 93.20 to 100.40 and 92.20 to 97.04 per cent, respectively and in soil the recovery of cypermethrin and profenofos was found in between 91.20 to 97.48 and 86.80 to 97.12 per cent, respectively at five levels.
- Initial deposits of chlorpyrifos (SA- Safaban 20 EC) when sprayed at recommended dose @ 300 g a.i. $ha^{-1}$ were 1.931 mg $kg^{-1}$ which dissipated to 99.21 per cent at $7^{th}$ day of spray with half life 1.03 days. At double the recommended dose of chlorpyrifos (600 g a.i. $ha^{-1}$), initial deposits were 2.856 mg $kg^{-1}$ which dissipated to 99.46 per cent at $10^{th}$ day of spray with half life 1.32 days.
- Cypermethrin (Challenger 25 EC) persisted for 5 days in cauliflower curds with initial deposits of 0.533 mg $kg^{-1}$ which reduced to their half in 1.77 days when sprayed at 50 g a.i./ha. It persisted for 7 days yielding 0.807 mg $kg^{-1}$ residues with half-life of 1.90 days when applied at 100 g a.i./ha. Initial deposits of cypermethrin dissipated to 84.94 per cent (standard dose) at $5^{th}$ day and 91.20 per cent (double the standard dose) at $7^{th}$ day of last spray application.
- In profenofos (Curacron 50 EC), the initial residues were recorded as 2.682 mg $kg^{-1}$ when sprayed @ 500 g a.i. $ha^{-1}$ and 5.228 mg $kg^{-1}$ when sprayed @ 1000 g a.i. $ha^{-1}$. Initial deposits of single dose dissipated to 97.79 per cent at $7^{th}$ day with half-life of

1.26 days and in double dose residues dissipated to 98.78 per cent at 10$^{th}$ day with half-life of 1.60 days.

- The residues of chlorpyrifos, cypermethrin and profenofos in cauliflower field soil were found below the limit of determination at 20 days after last spray at both the doses.
- Safe waiting periods for chlorpyrifos on cauliflower curds were suggested to be 1 and 2 days at single and double dose, whereas, 6 and 8 days were calculated for cypermethrin for single and double dose, respectively. For profenofos, safe waiting periods were suggested as 7 and 11 days at single and double dose, respectively on cauliflower curds. The waiting periods were worked out at FSSAI MRL of 1 mg $kg^{-1}$ for chlorpyrifos and at the limit of determination of 0.05 mg $kg^{-1}$ for both cypermethrin and profenofos.
- Various decontamination processes proved effective in dislodging the residues remained on cauliflower. Washing of cauliflower curds with running tap water reduced residues of chlorpyrifos, cypermethrin and profenofos by 22.27, 24.46 and 22.99 per cent at single dose and 22.50, 23.70 and 22.86 per cent at double dose, respectively. In lukewarm water washing, residues of chlorpyrifos, cypermethrin and profenofos were reduced to 23.63, 29.34 and 31.58 per cent at recommended dose while at double the recommended dose residues reduced upto 24.26, 27.63 and 25.53 per cent, respectively while in saline water dipping, residues were reduced to 63.91, 59.90 and 63.65 per cent at single dose and 64.95, 63.26 and 63.70 at double dose in respective test insecticides. In sodium bicarbonate solution dipping, residues of chlorpyrifos, cypermethrin and profenofos reduced to 62.40, 58.62 and 57.06 per cent at single doses, respectively whereas 64.01, 63.11 and 60.05 per cent at double doses, respectively. Washing of treated curds with acetic acid solution resulted up to 55.31 – 58.71, 55.58 – 56.58, and 54.26 – 61.32 per cent relief from chlorpyrifos, cypermethrin and profenofos residues, respectively at both the doses. Dipping in potassium permanganate solution dislodged residues of chlorpyrifos, cypermethrin and profenofos upto 44.12, 44.53 and 40.59 per cent at single doses and 47.16, 48.22 and 48.16 per cent at double doses, respectively. Washing with veggie clean solution provided 49.46, 50.67 and 49.95 per cent relief at single doses and 48.30, 53.42 and 50.50 per cent relief at double doses from respective insecticide residues. Washing with nimwash solution removed residues of chlorpyrifos, cypermethrin and profenofos to the tune of 49.23, 48.47 and 49.17 per cent at recommended doses

whereas 48.93, 54.63 and 49.65 per cent at double the recommended doses, respectively. Washing with arka herbiwash solution provided 49.91, 49.74 and 50.31 per cent relief at single doses and 48.41, 52.38 and 49.44 per cent relief at double doses from residues of chlorpyrifos, cypermethrin and profenofos, respectively.

**CONCLUSION**

- Chlorpyrifos and profenofos were observed as most persistent insecticides which persisted for 7 and 10 days followed by cypermethrin which persisted for 5 and 7 days, at single and double dose, respectively.
- In cauliflower cropped soil, the residues of tested insecticides were found below the limit of determination at 20 days after last spray at both the doses.
- The time period between the last spray and harvest (waiting period) of cauliflower curds was suggested as 2, 8 and 11 days for chlorpyrifos, cypermethrin and profenofos, respectively.
- Among the various decontamination processes, saline water dipping was found most effective (removal upto 64.95 per cent) followed by sodium bicarbonate solution dipping (64.01 per cent) which was followed by acetic acid solution dipping (61.32 per cent) and then further followed by washing with nimwash (54.63 per cent), veggie clean (53.42 per cent), arka herbiwash solution (52.38 per cent), potassium permanganate solution dipping (48.22 per cent), lukewarm water washing (31.58 per cent) and tap water washing (24.46 per cent).
- Among the popularly marketed products *viz*., nimwash, veggie clean and arka herbiwash were found equally effective which provided relief from tested insecticides in the range of 48 to 55 per cent.

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## ABSTRACT

The present investigations on **"**Residue dynamics of chlorpyrifos, cypermethrin and profenofos on cauliflower**"** was carried out during 2020-2021 in the department of Entomology, Dr. Y S Parmar University of Horticulture and Forestry, Nauni, Solan. The objectives of the study were to evaluate the persistence of chlorpyrifos, cypermethrin and profenofos in/on cauliflower curds and soil and effect of various decontamination treatments on residues of these insecticides. The persistence study on cauliflower curds recorded initial deposits due to single dose of chlorpyrifos (300 g a.i. $ha^{-1}$), cypermethrin (50 g a.i. $ha^{-1}$) and profenofos (500 g a.i. $ha^{-1}$) as 1.931, 0.533 and 2.682 mg $kg^{-1}$, respectively. However, at double dose the initial deposits were 2.856, 0.807, 5.228 mg $kg^{-1}$ for respective insecticides. Chlorpyrifos and profenofos residues persisted in cauliflower curds upto 7 and 10 days at single and double dose, respectively. Whereas, cypermethrin residues persisted for 5 days at recommended dose and 7 days at double the recommended dose. The residues of chlorpyrifos, cypermethrin and profenofos in cauliflower curds reduced to half in less than 2 days. Residues of test insecticides were below determination level i.e., 0.01 mg/kg (chlorpyrifos) and 0.05 mg/kg (cypermethrin and profenofos) in cauliflower field soil at $20^{th}$ day after last application of both the doses. The waiting periods were worked out by adopting FSSAI MRL i.e., 1 mg/kg for chlorpyrifos and at LOQ i.e., 0.05 mg/kg for cypermethrin and profenofos. From the consumer safety point of view, the safe waiting period of 2, 8 and 11 days was suggested for chlorpyrifos, cypermethrin and profenofos, respectively on cauliflower curds. Among the various decontamination processes, saline water dipping was found most effective which provided upto 64.95 per cent relief followed by sodium bicarbonate solution dipping (64.01 per cent), acetic acid solution dipping (61.32 per cent), washing with nimwash solution (54.63 per cent), veggie clean solution (53.42 per cent), arka herbiwash solution (52.38 per cent), potassium permanganate solution dipping (48.22 per cent), lukewarm water washing (31.58 per cent) and tap water washing (24.46 per cent) from tested insecticide residues in cauliflower.

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