DISSIPATION AND RISK ASSESSMENT OF SELECT INSECTICIDES USED FOR PEST MANAGEMENT IN CABBAGE AND CAULIFLOWER

By

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DECLARATION

I, hereby declare that this thesis entitled **"DISSIPATION AND RISK ASSESSMENT OF SELECT INSECTICIDES USED FOR PEST MANAGEMENT IN CABBAGE AND CAULIFLOWER"** is a bonafide record of research work done by me during the course of research and the thesis has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship or other similar title, of any other University or Society.

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LIST OF ABBREVIATIONS

%	Per cent
@	At the rate of
a.i.	Active ingredient
ADI	Acceptable Daily Intake
BQL	Below quantification level
CD	Critical Difference
CRM	Certified Reference Material
DAS	Days after sowing
DAS	Days after spraying
DF	Dilution Factor
EC	Emulsifiable concentrate
ECD	Electron Capture Detector
EU	European Union
et al.	And others
FAO	Food and Agriculture Organization
FSSAI	Food Safety and Standards Authority of India
g	Gram
GAP	Good Agricultural Practices
$g\ L^{-1}$	Gram per litre
GC	Gas Chromatography
GOK	Government of Kerala
ha^{-1}	per hectare
KAU	Kerala Agricultural University
Kg	Kilogram
L	Litre
LOD	Limit of Detection
LOQ	Limit of Quantification
MPI	Maximum Permissible Intake
MRL	Maximum Residue Limit

MRM	Multi Residue Monitoring
NaCl	Sodium Chloride
mL	Millilitre
mg	Milligram
ppm	Parts per million
PRRAL	Pesticide Residue Research and Analytical Laboratory
RSD	Relative standard deviation
SC	Suspension concentrates
SL	Soluble Liquid
SP	Soluble Powder
SD	Standard deviation
sp	Species
TMRC	Theoretical Maximum Residue Concentration
viz.,	Namely
WG	Wettable granules
WTO	World Trade Organisation

INTRODUCTION

1. INTRODUCTION

India is one among the top ten WTO members in exports of agricultural commodities and its key export markets include the USA, the European Union, ASEAN, SAARC countries and West Asia. Of late, Indian exports of food products are facing rejections and ban in key markets due to the lack of compliance with food safety and health standards, chiefly owing to the presence of pesticide residues. In order to meet the health standards and food safety, India needs to implement Good Agriculture Practices (GAP), minimizing the use of harmful chemicals. To protect the consumers from undesirable exposure to pesticide residues in food, maximum residue levels (MRLs) which is the highest possible level of pesticide residue that is legally authorized, is laid down. MRL is set the countries on their own, for traded agricultural commodities. They are food specific and serve as monitoring tools. In India, pesticide residues in foods are regulated under Prevention of Food Adulteration Act, 1954 and now under Food Safety and Standard Act, 2005. It is important to focus on food quality and standards in the domestic market, so that the products are produced and processed adhering to international food safety requirements (Sharma, 2015). There is a rising public concern about the adverse effects of chemical pesticides on human health, environment and bio diversity. Central government and State Governments are now focusing on monitoring of pesticide residues in various food stuffs. Agricultural production by excluding or minimizing chemicals is a major challenge especially in the case of cultivation of vegetable crops.

Cabbage (*Brassica oleracea* L. var. *capitata*) and cauliflower (*Brassica oleracea* L. var. *botrytis*) are the two major cole crops widely grown all over India. Until recently cultivation of these vegetables in Kerala was possible only in the hill tracts of Idukki and Wayanad districts. However, with the development of tropical varieties, these cole crops are being raised in the plains. As these crops are highly pest prone, farmers apply insecticides injudiciously to achieve the targeted yield. Indiscriminate use of insecticides in these vegetable crops results in prevalent deposits of residues. Since cabbage and cauliflower are consumed as raw or as salad, residue related problems are more severe.

Several new generation insecticides have been developed and released for pest management in cabbage and cauliflower. The Central Insecticide Board and Registration Committee (CIBRC) have recommended several newer pesticides with novel modes of action (CIBRC, 2015). These are replacing older insecticides due to the advantages such as lower dosage, selectivity and safety to human and environment. In order to exploit their potential in pest management with minimum adversities on human health and environment, it is essential to study the pesticide behavior, and also about their persistence or dissipation under different agro climatic zones. Such investigation on dissipation and risk assessment of these insecticides in cabbage and cauliflower in different agro climatic zones of Kerala has not been undertaken before.

Pesticide use in agriculture should be in such a way that it is harmless to the soil microbial wealth. Unlike other vegetables, chances of soil contamination by pesticides are much higher in cabbage and cauliflower as they are low lying crops. Soil enzymes derived from micro organisms play an important role in organic matter turn over and degradation of xenobiotics (Bam, 2008). Any toxicant from the external environment added to the soil may alter the micro organisms and thus their enzyme activities. Hitherto no studies were undertaken on the effect of insecticides on soil enzyme activity in cabbage and cauliflower grown in Kerala.

The food crops treated with pesticides invariably contain unpredictable amount of these chemicals. Therefore, it becomes imperative to find out some techniques for decontaminating them. Many of the decontamination methods bring down the pesticide residues below Maximum Residue Limit (Aaruni, 2016). There are several decontamination methods of old generation insecticides that can be practiced easily in households, as per the literature. However, information on decontamination of new generation insecticides are meager.

Considering the above facts, present study was undertaken with following objectives

- To study the pesticide use pattern in cabbage and cauliflower
- To study the dissipation of select insecticides in cabbage and cauliflower
- To assess the potential risk of insecticides on human health.
- To determine their effect on soil microbial activity
- To evaluate the efficacy of “Veggie Wash” to eliminate residues
- To estimate the residues in cooked food

REVIEW OF LITERATURE

2. REVIEW OF LITERATURE

Cabbage and cauliflower are the major cruciferous vegetables in India and their production is limited due to severe incidence of pest and diseases. Farmers apply insecticides indiscriminately to combat the pest result in the contamination of pesticide residues in the harvested produce. Public is more concerned about the pesticide residues in vegetables and sometimes produce lead to harmful health impact on human and microbial population in soil. Literature available on pest management, pesticide use pattern, pesticide residues in vegetables, effect of pesticides on soil enzymes and decontamination methods used in cabbage and cauliflower are reviewed hereunder.

2.1 PESTS IN CABBAGE AND CAULIFLOWER

2.1.1 Major Pests

Diamond back moth, *Plutella xylostella* Linnaeus was reported as most abundant lepidoptera found in cabbage (Reid and Bare, 1952). High infestation was reported from Tamil Nadu (Abraham and Padmanabhan, 1968), Maharashtra (Khaire *et al.*, 1987), Himachal Pradesh (Bhattia and Verma, 1993), Asia (Zhang, 1994), Belgaum district of Karnataka (Singh and Singh, 1999), Dharwad, Karnataka (Reena, 2000), Karanataka (Vastrad, 2000), Bangladesh (Ahmed *et al.*, 2002). *P. xylostella* was reported as the major pest of crucifers all over India (Devi *et al.*, 2004). Severe infestation of *P. xylostella* was recorded in cabbage from Bihar (Ojha *et al.*, 2004), cabbage in Dharwad (Neelkanth, 2006), cabbage in Meerut (Kumar *et al.*, 2007). Incidence of *P. xylostella* was also reported in cabbage by Shaila (2007) and in cauliflower (Deeplata and Rao, 2012). Peak activity of *P. xylostella* was reported during first week of January (Bana *et al.*, 2012*)*. Higher incidence was recorded during November in cabbage and cauliflower (Shah *et al.*, 2013), during March in West Bengal (Patra *et al.*, 2013). *P. xylostella* was reported as key pest infesting cabbage and cauliflower grown in hills of Kerala and cause 38 and 26 per cent damage to cabbage heads and cauliflower curds respectively (Ravi *et al*., 2014). Incidence of *P. xylostella* was also reported in cabbage during second week of February in cabbage (Mishra and Singh, 2015) during September in Pakistan (Ahmed *et al*., 2015) and first week of November in cauliflower (Dewanda and Sabiha, 2016).

Tobacco caterpillar *Spodoptera litura* Fabricius was reported as a major pest and widely distributed throughout tropical and temperate Asia, Australia and Pacific Island (Kranz *et al*., 1977). Prevalence of *S. litura* was observed in cabbage during warmer month of September to December (Lee, 1986) and in Karnataka (Mallapur, 1988). Peak activity was reported in cauliflower during December (Narasimhamurthy *et al*., 1998). Infestation of *S.litura.* was recorded in Theni (Raja *et al.,* 2004). During November to February, *S. litura.* occurrence was severe (Badjena and Mandal, 2005). Occurrence of pest also noted in cabbage (Shaila, 2007) and high infestation was noted during rainy and winter season in cabbage (Patait *et al*., 2008). *S .litura* was recorded as major pest in cabbage and cauliflower in plains of Kerala (Ravi *et al*., 2014) in eastern plain zones (Singh *et al*., 2015) in cauliflower from Punjab (Maqsood *et al*., 2016). It was reported during August to November and January to April in cauliflower (Dewanda and Sabiha, 2016).

2.1.2 Minor Pests

Study conducted by Sachan and Srivastava (1972) recorded the incidence of head borer *Hellula undalis* Fabricius, cabbage looper, *Trichoplusia ni* Hubner in cabbage. Raju and Sivaprakasagam (1989) recorded the incidence of mustard aphid, *Lipaphis erysimi* Kaltenbach, cabbage semilooper, *T. ni* Hubner, and cutworms, *Agrotis ipsylon* Hubner on crucifers. Seasonal abundance of leaf webber *Crocidoloma binotalis* Zeller was reported in Taiwan especially during May to December in cauliflower (Lee, 1986). In Himachal Pradesh, wide distribution of cabbage butterfly *Pieris brassicae* Linnaeus, was reported (Bhatia and Verma, 1993). Abundance and multiplication of *C. binotalis* during December in cauliflower was reported by Narsimhamurthy *et al.* (1998).

Maximum population of *C. binotalis* was recorded in spring cabbage during March Chaudhari *et al.* (2001). In Manipur, *C. binotalis* was reported as sporadic pest during early, mid and late season of cauliflower (Devjani and Singh, 2002). Wide distribution of *P. brassicae* was reported along the plains of Himalayan region (Raquib, 2004). Incidence of cabbage semilooper, *T. ni* was reported during December (Ojha *et al.*, 2004). Incidence and well distribution was recorded in several countries (Anurag *et al.*, 2009; Dadang *et al.*, 2009). *C. binotalis* found to be infesting and causing damage to cabbage during curd formation stage (Venkateswarlu *et al.*, 2011). Sharma *et al.* (2012) recorded the incidence Green peach aphid (*Myzus persicae* Sulzer), Corn earworm (*Helicoverpa zea* Boddie), Cabbage maggot (*Delia radicum*) in cabbage and cauliflower at Jaipur. Sharma and Rao (2012) reported the incidence of green peach aphid, corn ear worm, cabbage maggot etc. from cabbage and cauliflower. Ravi *et al.* (2014) reported the incidence of pierid butterfly, *Appias lyncida* Cramer, flea beetle, *Phyllotreta chotanica* Duvivier, for the first time in plains of Kerala. Cabbage and cauliflower were severely attacked by cabbage aphid, *Brevicoryne brassicae* Linnaeus (Mishra and Singh, 2015). Debbarma *et al.* (2017) reported the incidence of pests belongs to lepidoptera (29.63 %), homoptera (14.81 %), orthoptera (14.81 %), hemiptera (7.81 %), coleoptera (7.41 %), diptera (7.41 %), hymenoptera (3.70 %), thysanoptera (3.70 %), dermaptera (3.70 %), dictyoptera (3.70 %) and acarina (3.70 %) in cabbage and cauliflower from Tamil Nadu.

2.2 PEST MANAGEMENT IN CABBAGE AND CAULIFLOWER

Cabbage and cauliflower are the most important cruciferous vegetables cultivated in about 0.738 m ha, producing 14.694 MT per annum in India (Vanitha *et al.,* 2013). Around 37 insect pests have been reported to infest cabbage in the country. In Kerala, the vegetables are infested by eleven pests including cutworm, diamond back moth, pierid butter fly and flea beetle (Ravi *et al.,* 2014). To achieve the desired yield, farmers apply insecticides frequently and at rates higher than the recommended dose resulting in high level of pesticide residues in cabbage and cauliflower. Studies on the management of pests of cabbage and cauliflower using chemical insecticides is summarised in Table 1.

2.3 PESTICIDE RESIDUES IN VEGETABLES

Agrochemicals constitute the pivotal input to boost agricultural production especially in modern intensive agriculture using high yielding varieties of crops. However, there is vivid evidence that use of pesticide in plant protection operation has adversely after soil and water quality leading to serious environmental consequences (Beevi *et al.*, 2014). Among the different sources of exposure to pesticides, food appears to be the most significant as pesticide residues were constantly detected in some of the raw agricultural commodities. Data generated by PRRAL, Vellayani centre (PAMSTEV, 2017) revealed that 9.69 per cent of samples of the different food commodities (> 4000 samples tested over six years) were found to be contaminated with pesticide residues. Out of 9.69 per cent, samples, 3.92 per cent samples had pesticide residues above Maximum Residue Limit (MRL) fixed by Food Safety Standards Authority of India (FSSAI). Commodity wise data showed that among spices: cardamom (79.20 %); among vegetables: curry leaf (60.76 %), cowpea (44.44 %), green chilli (43.75 %), bittergourd (33.33 %), capsicum (17.24 %), cauliflower (12.21 %), bhindi (10.33 %), cabbage (5.16 %), brinjal (4.22 %) and tomato (2.34 %); among cereals: wheat (15.71 %) and rice (13.57 %) had detectable levels of pesticide residues (Mathew *et al.*, 2012). Overall analysis of the data indicated variation in the number and magnitude of pesticides detected in these commodities.

Study conducted by Mukerjee (2003) in New Delhi revealed that monitored vegetable samples are contaminated with pesticides residue, and more than 31 per cent of samples were above prescribed tolerance level. Cauliflower samples were contaminated with chlorpyriphos, quinalphos, and cypermethrin and they were above MRL. Similar study conducted by Kumari *et al.* (2004) in Haryana recorded 100 per cent contamination with pesticides *viz.*, organophosphate, and synthetic pyrethroids. Study also revealed that 3 out of 10

Table 1. Pest management in cabbage and cauliflower

Sl. No	Treatment	Concentration	Pest	Reference
1	Profenofos 50 % EC	0.05%	*S. litura*	Prasad and Nandihalli, 1985
2	Profenofos 50 % EC	0.05%	*S. litura*	Murthy *et al.*, 1997
3	Spinosad 48 % SC Novaluron 10 % EC	0.05% 0.01%	*P. xylostella*	Dhanaraj , 2000
4	Spinosad 2.5 % SC	15 g a.i ha^{-1} 25 g a.i ha^{-1}	*P. xylostella*	Peter *et al.*, 2000
5	Thiodicarb 75% WP Indoxacarb 15 % EC Chlorpyrifos 20 % EC Spinosad 48 % SC	0.08 % 0.02 % 0.05 % 0.02 %	*S. litura*	Khalid *et al.*, 2001
6	Indoxacarb 14.5 % SC	0.072 g a.i ha^{-1}	*T. ni*	Liu *et al.*, 2002
7	Profenofos 50 % EC	0.05%	*Crocidolomia pavonana*	Sreekanth *et al.*, 2002
8	Spinosad 45 % SC	0.02%	*S. litura*	Soujanya *et al.*, 2004
9	Spinosad 45 % SC	0.02%	*S. litura*	Mallareddy *et al.*, 2004
10	Emamectin benzoate 5 % SG	10 g a.i ha^{-1} 8.75 g a.i ha^{-1}	*P. xylostella*	Suganyakanna *et al.*, 2005
11	Malathion 50 % EC	700 mL ha^{-1}	*S. litura*	Jat and Bhardwaj, 2005
12	Emamectin benzoate 5 % SG	150 g a.i ha^{-1} 200 g a.i ha^{-1}	*P. xylostella*	Kumar and Devappa, 2006
13	Spinosad 45 % SC Emamectin benzoate 5 % SG Indoxacarb 14. 5 % SC	600 mL ha^{-1} 170 g ha^{-1} 333 mL ha^{-1}	*P. xylostella*	Gill *et al.*, 2008
14	Spinosad 14.5 % SC	0.4 mL L^{-1}	*P. xylostella*	Mandal *et al.*, 2009
15	Indoxacarb 14.5 % SC	75 g a.i ha^{-1}	*P. xylostella*	Kumar *et al.*, 2011
16	Chlorantraniliprole 18.5 % SC	10 g a.i ha^{-1}	*P. xylostella*	Venkatateswarlu *et al.*, 2011

17	Imidacloprid 200 SL	30 g a.i ha^{-1} 20 g a.i ha^{-1} 10 g a. i ha^{-1}	*L. erysimi*	Anjumoni *et al.*, 2011
18	Profenofos 40 % + cypermethrin 4 % Triazophos 35 % + deltamethrin 1 %	1 L ha^{-1}	*L. erysimi*	Gupta *et al.*, 2013
19	Indoxacarb 15.8 % SC Cypermethrin 10 % EC Malathion 0.015 % EC	0.01% 0.03% 0.15%	*S. litura*	Ravi, 2013
20	Spinosad 45 % SC Flubendiamide 48 % SC Emamectin benzoate 5 % SG	0.05 mL L^{-1} 0.0.3 mL L^{-1} 0.2 g L^{-1}	*P. xylostella*	Dotasara *et al.*, 2017
21	Tolfenpyrad 15 % SC Emamectin benzoate 5 % SG Cynatraniliprole10.26 % OD	1000 mL ha^{-1} 150 g a.i ha^{-1} 600 mL ha^{-1}	*S. litura*	Kamde, 2017
22	Chlorantraniliprole 18.5 % SC Spinosad 45 % SC	0.05 % 0.10 %	*S. litura* *P. xylostella*	Annual report, 2018

cauliflower samples and 8 out of 10 cabbage samples were contaminated with chlorpyriphos above MRL and quinalphos residues were above MRL for single cauliflower sample among 5 analyzed. In Agra, summer and winter vegetable samples are contaminated with organochlorine pesticides and detected residues were lindane, endosulfan and DDT (Bhanti and Taneja, 2005). Farm gate vegetables *viz.*, brinjal (18), okra (15), cauliflower (11), cabbage (8), and green chilli (12) are contaminated with organochlorines, organophosphates and synthetic pyrethroids in Bihar (Singh *et al.*, 2006). In a monitoring study conducted on vegetables in Lucknow, revealed the presence of organochlorine, organophosphates and synthetic pyrethroids (Srivastava *et al.*, 2011; Tomaz, 2012).

2.4 DISSIPATION OF INSECTICIDE RESIDUES IN CABBAGE AND CAULIFLOWER

Recently challenges of ensuring global food security have received increasing attention from the scientific community (Barrett 2010; Godfray *et al.*, 2010). Also a great concern for human health demands foods free of pesticide residues. Pesticides are essential in modern agricultural practices, but due to their biocidal activity and potential risk to the consumer, the control of pesticide residues in foods is a growing source of concern for the general population. Looking at the toxicity of various pesticides, it is important to find out the dissipation pattern of insecticides in the harvested produce and to find out the half life and waiting period. The literature related to the persistence and degradation of insecticides on cabbage and cauliflower are presented in Table 2 and 3.

2.5 RISK ASSESSMENT OF INSECTICIDES IN VEGETABLES

The main intention of the introduction of pesticides was to prevent and control insects, pests and diseases in the field crops. Initially the use of pesticides reduced pest attack and paved way for increasing the crop yield as expected. Simultaneously, increased use of chemical pesticides has resulted in contamination of environment and also caused many long-term effects on the

Table 2. Dissipation of insecticides in cabbage

Sl. No.	Insecticide		Dosage (g a.i. ha^{-1})	Initial concentration (mg kg^{-1})	Days taken to reach BDL	Half-life (days)	Reference
1	Imidacloprid	Year 2000	20	BDL	0	0.60	Gajbhiye *et al.*, 2004
			40	0.06	2	2.15	
		Year 2001	20	0.15	5	0.70	
			40	0.24	5	1.70	
2	Spinosad		17.5	2.97	10	-	Sharma *et al.*, 2007
			35	5.85	15	-	
3	Chlorpyrifos		300	1.83	10	2.00	Zhang *et al.*, 2007
	Cyhalothrin		15	0.27	6	1.60	
	Cypermethrin		40	0.37	8	2.30	
	Deltamethrin		10	0.10	2	1.50	
	Dimethoate		200	3.90	10	1.60	
	Fenvalerate		75	1.36	12	2.20	
4	Chlorfenapyr		75	1.02	10	2.98	Ditya and Sarkar, 2010
			100	1.90	10	3.62	
5	Flubendiamide		24	0.33	10	-	Mohapatra *et al.*, 2010
			48	0.49	15	-	
	Des-iodoflubendiamide		24	BDL	0	-	
			48	BDL	0	-	
6	Quinalphos		500	0.41	7	3.02	Chahil *et al.*, 2011
			1000	0.75	10	2.70	
7	Indoxacarb		52.2	0.18	3	2.88	Urvashi *et al.*, 2012
			104.4	0.39	5	1.92	

8	Emamectin benzoate		8.5	0.11	1	0.88	Singh *et al.*, 2013
			17	0.21	5	1.25	
9	Flubendiamide		12.5	0.16	7	3.6	Paramasivam and Banerjee, 2013
			25	0.31	10	3.4	
	Des-iodoflubendiamide		12.5	BDL	0	-	
			25	BDL	0	-	
10	Profenofos		1000	0.99	10	4.91	Reddy *et al.*, 2017
11	Quinalphos	Plains	500	0.24	5	-	Padmanabhan and Paul, 2018
		Hills	500	2.66	7	-	
12	Chlorpyrifos	300		1.52	15	1.91	Beevi *et al.*, 2018
	Profenofos	500		1.02	15	2.01	

Table 3. Dissipation of insecticides in cauliflower

Sl. No	Insecticide		Dosage (g a.i. ha^{-1})	Initial concentration (mg kg^{-1})	Days taken to reach BDL	Half-life (days)	Reference
1	Quinalphos		250	5.79	12	1.61	Gupta and Parihar, 1989
			500	9.52	15	2.12	
2	Fenvalerate		75	1.26	7	1.19	Gupta and Singh, 2001
			150	2.30	10	1.46	
3	Imidacloprid	Year 2000	20	2.20	5	0.70	Gajbhiye *et al.*, 2004
			40	3.90	15	1.16	
		Year 2001	20	0.82	5	1.08	
			40	1.78	10	1.30	
4	Endosulfan		350	3.45	15	1.81	Deivendran *et al.*, 2006
	Dichlorvos		110	0.30	5	2.08	
5	Spinosad		17.5	2.66	10	-	Sharma *et al.*, 2007
			35	3.89	15	-	
6	Spinosad		15	0.51	5	1.20	Mandal *et al.*, 2009
			30	1.36	7	1.58	
7	Indoxacarb		52.2	0.23	3	1.12	Takkar *et al.*, 2011
			104.4	0.45	7	1.31	

8	Profenophos	400	0.39	12	2.9	Gupta *et al.*, 2013
		800	0.69	15	3.3	
	Cypermethrin	40	0.08	1	1.5	
		80	0.211	5	2.1	
	Triazophos	350	0.85	12	2.6	
		700	1.21	15	3.0	
	Deltamethrin	10	0.11	3	2.2	
		20	0.27	8	2.6	
9	Chlorantraniliprole	9.25	0.18	3	1.36	Kar *et al.*, 2013
		18.50	0.29	5	1.25	
10	Quinalphos	500	1.20	15	4.8	Mohapatra and Deepa, 2013
		1000	1.84	15	5.3	
11	Fipronil	56	0.09	3	2.59	Duhan *et al.*, 2015
12	Chlorpyrifos	300	1.70	15	2.75	Padmanabhan , 2015
	Quinalphos	250	1.72	15	2.31	
	Ethion	500	4.18	30	4.13	
	Triazophos	500	4.97	15	2.64	

society. The use of pesticides on food crops leads to unwarranted residues, which may constitute barriers to exporters and domestic consumptions when they exceed maximum residue limit (MRL). Risk assessment studies play a critical role in the evaluation of the potential human health hazards associated with pesticide exposure.

Sanyal *et al.* (2008) studied the risk assessment of acetamiprid on chilli by comparing TMRC (Theoretical Maximum Residue Concentration) and it was found that MPI (Maximum Permissible Intake) was higher than TMRC and consumption of acetamiprid treated chilli is safe for consumption. Consumption of thiacloprid treated egg plant was risky upto 3 days and more safety is required while applying thiacloprid in field level (Saimandir *et al.*, 2009). Dietary risk assessment of quinalphos revealed no appreciable risk arising through cabbage consumption since dietary intake was far below the Acceptable Daily Intake (ADI), hence consumption of quinalphos treated cabbage does not pose any health impact on human (Aktar *et al.,* 2010). The TMRC values for bifenthrin on tomato was found to be less than the MPI values even on the 0th day following the application make it safe for the consumption (Chauhan, 2011). Study on risk assessment in cauliflower after spraying indoxacarb at recommended dose did not caused any significant health impact on human since TMRC values were far below than MPI (Takkar *et al.*, 2011). Bhardwaj *et al.* (2012) reported that consumption of fipronil treated cabbage (at recommended dose) was safe even on the day of spraying. Study conducted by Paramasivam *et al.* (2014) reported that gherkin fruit was safe for the consumption even on the day of spraying.

2.6 EFFECT OF PESTICIDES ON SOIL ENZYMES

Enzymes are specialized proteins that combine with a specific substrate and act to catalyze a biochemical reaction. In soils, enzyme activities are essential for energy transformation and nutrient cycling. Pesticides in soil undergo a variety of degradative, transport, and adsorption or desorption processes depending on the chemical nature of the pesticide (Laabs *et al.*, 2007) and soil properties. Microbial biomass is an important indicator of microbial activities and provides direct assessment of the linkage between microbial activities and the nutrient transformations and other ecological processes (Schultz and Urban, 2008).

Pesticides pollute air, soil, water resources and contaminate the food chain. Studies on soil enzymes help to know the impact of pesticide use on human health and environment. Soil is a natural system containing microbes which are the driving force behind many soil processes, including transformation of organic matter, nutrient release and degradation of xenobiotics (Zabaloy *et al.*, 2008). Many studies have shown that biological parameters have been used to assess soil quality and health as affected by agricultural practices (Truu *et al.*, 2008; Garcia-Ruiz *et al.*, 2009). Soil enzymes can be used as potential indicators of soil quality for sustainable management because they are sensitive to ecological stress and land management practices (Tejada, 2009).

2.6.1 Effect of Pesticides on Urease Activity

Urease is an enzyme that catalyses the hydrolysis of urea into carbon dioxide and ammonia and is a key component in the nitrogen cycle in soils. Decreased urease activity in soil due to the application of pesticides reduces urea hydrolysis, which is generally beneficial as it helps to maintain nitrogen availability to plants (Antonious, 2003). On the contrary, the fungicides carbendazim and validamycin enhanced urease activity, respectively up to 70 per cent and to 13 to 21 per cent (Qian *et al.,* 2007; Yan *et al.,* 2011).

Studies conducted in England, revealed the effect of organophosphate insecticides *viz.,* malathion, fenitrothion and phorate on soil urease activity. Inhibition of enzyme activity was noticed and similar inhibition was exhibited by Inhibition of enzyme activity was noticed with malathion and fenitrothion (Lethbridge and Burns, 1975). Study of pyrethroids (Permethrin) on urease activity indicated that there was no inhibition on the activity of urease enzyme at the doses of 0.5 and 5 μg g^{-1} while, only maneb inhibited the urease activity throughout 14 days (Tu, 1980). Application of pesticides *viz.,* streptomycin, chlorfenvinphos, chlorpyriphos, diazinon, ethion, ethoprop, fensulfothion, fonophos, leptophos, malathion, parathion, phorate, thionazin, triazophos, trichloronat, terbufos, chlordane, dieldrin, lindane, carbofuran, oxamyl and permethrin did not inhibited the activity of urease enzyme in clay soils in Canada (Tu, 1981). In china, Yao *et al.* (2006) studied the effect of acetamiprid on urease activity at different concentrations (0.50, 5.00 and 50 mg kg^{-1}) and concluded that enzyme activity did not varied significantly due to the application of different concentrations of acetamiprid.

Pesticides *viz.,* diazinon (insecticide), linuron (herbicide) and mancozeb+ dimethomorph (fungicides) inhibited urease activity (Cycon *et al.,* 2005). Effects of diazinon and imidacloprid in soil was studied by Ingram *et al.* (2005) and recorded the significant inhibition of urease by diazinon , but imidacloprid does not inhibited enzyme activity. Urease was not inhibited by an organophosphorous insecticide fenamiphos upto 100 mg kg^{-1} soil (Caceres *et al.,* 2009). Application of carbendazim enhanced the activity of urease in China (Yan *et al.*, 2011)

Significant inhibition of urease enzyme was recorded by the application of carbofuran (Basavaraj, 1984). Increased urease activity was observed in experimental plots in West Bengal when treated with metalaxyl (Sukul, 2006). Punitha *et al.* (2012) studied the effect of acetamiprid on urease at different intervals (10, 20, 30, 45 and 60 days) and the highest inhibition of urease activity was recorded on 10th day after incubation in soils of Karnataka. Increasing trend in enzyme activity was also observed from 20th day and utmost activity was recorded on 60th day after incubation. Thiamethoxam @ 2.1 g a.i. kg^{-1} and 8.4 g a.i. kg^{-1} did not inhibit the activity of soil urease (Jyot *et al.*, 2015).

2.6.2 Effect of Pesticides on Phosphatase Activity

Phosphatases represent a broad range of intracellular as well as soil-accumulated activities that catalyse the hydrolysis of both the esters and anhydrides of phosphoric acid. They play a crucial role in the phosphorous acquisition in microorganisms and plants, and thus its cycling within the soil.

Insecticides *viz.*, amitraz and tebupirimiphos inhibited the activity of phosphatase for 1 week, however inhibition did not persisted for more than one week in sandy soils (Tu, 1995). Omar and Abdel-Sater (2001) reported that alkaline phosphatase activity was increased after application of selcron (insecticide) even at higher concentrations and suggested that it was due to the resistance of alkaline phosphatase to pesticides at alkaline pH. Significant inhibition in phosphatase was recorded in treatment with acetamiprid at normal field rate (5 mg kg^{-1}) and higher concentration (50 mg kg^{-1}) (Yao *et al.*, 2006).

Inhibitory activity of alkaline phosphatase was reported when treated with chlorpyriphos and significant inhibition was noticed for chlorpyriphos treated plots compared to teflubenzuron (Jastrzębska, 2011). Defo *et al.* (2011) reported that application of endosulfan had no changes in the activity of phosphatase enzyme activity over a period of 30 days and after 60 days, inhibitory action of phosphatase was recorded at the concentration of 1010 µg g^{-1}.

Kennedy and Arathan (2004) reported significant reduction in the activity of phosphatase enzyme up to 30 days after the application of carbofuran at 1 and 1.5 kg a.i. ha^{-1}. They also reported that application at the recommended dose (0.5 kg a.i ha^{-1}) did not pose any changes in its activity. Initial increase followed by reduced activity of phosphatase was recorded in soils of West Bengal when treated with metalaxyl (Sukul, 2006). Punitha *et al.* (2012) studied the influence of acetamiprid on enzyme activity in selected soils of Karnataka and reported that the highest inhibition of enzyme activity after 10 days of spraying. Soils without insecticide treatment showed the higher enzyme activity in various locations of Karnataka.

Madhuri and Rangaswamy (2002) reported that application of insecticides *viz.*, dichlorvos, phorate and methomyl at 2.5 kg ha^{-1}, chlorpyriphos and methyl parathion at 5.0 kg ha^{-1} resulted in a reduction in enzyme activity with increase in incubation period over a period of 20 days. Kalyani *et al.* (2010) recorded the stimulation of phosphatase activity by endosulfan (5 to 40 %). Thiamethoxam when applied at recommended dose (2.1g a.i kg^{-1}) and 8.4 g a.i kg^{-1} as seed treatment, significantly inhibited the activity of phosphatase enzyme in cotton soil at Punjab (Jyot *et al.*, 2015). Walia *et al.* (2018) studied the effect of malathion on soil enzymes in Punjab. They found out that malathion did not inhibited phosphatase enzyme on 0th day at different concentration. But on the seventh day, activity of phosphatase enzyme was initiated up to two weeks of application.

2.6.3 Effect of Pesticides on Dehydrogenase Activity

Dehydrogenase occurs in all living microbial cells, and it is linked with microbial respiratory processes (Bolton *et al.*, 1985). It is an indicator of overall microbial activity of soils. Stimulation of dehydrogenas enzyme activity was observed by benomyl (18 to 21 %) and chlorothalonil (8 to 15 %) (Chen *et al.*, 2001). Yao *et al.* (2006) studied the effect of acetamiprid on activity of dehydrogenase enzyme in upland and reported that application induced the activity of dehydrogenase for two weeks. Inhibition of chlorpyriphos was reported by Jastrazebska (2011). Study conducted by Defo *et al.* (2011) recorded that endosulfan does not pose any effect on the activity of dehydrogenase enzyme.

Sharma *et al.* (2010) reported that chlorpyriphos significantly inhibited soil dehydrogenase activity to an extent of 5 to 40 per cent. Similarly Kalyani *et al.* (2010) reported that endosulfan significantly stimulated the activity of dehydrogeanse enzyme. Srinivasulu and Rangaswamy (2013) studied the activities of dehydrogenase enzyme after application of monocrotophos and chlorpyriphos individually as well as in comibination with carbendazim and mancozeb. They reported an increase in dehydrogenase activity when treated with monocrotophos singly or in combination with mancozeb.

Kalam *et al.* (2004) reported the inhibition of dehydrogenase activity after application of profenophos. Quinalphos inhibited the dehydrogenase activity (30 %) after 15 days of incubation (Mayanglambam *et al.*, 2005). Caceres *et al.* (2009) reported that fenamiphos does not pose any effect on activity of dehydrogenase enzyme. Sharma *et al.* (2010) reported the inhibition of endosulfan in the activity of dehydrogenase activity. Generally, whatever the dose considered, fungicides, herbicides and insecticides show inhibitory effects or no effects on the dehydrogenase activity, except endosulfan and mancozeb.

2.7. DECONTAMINATION METHODS FOR THE REMOVAL OF PESTICIDE RESIDUES FROM VEGETABLES

Indiscriminate use of pesticides for combating insect pests has led to their residues in food chain and exerted harmful effects on human being (Khanday *et al.,* 2014). Estimation of residues of insecticides in raw and processed food is on the vanguard among preventive measures in public health safety. Food processing at domestic level would offer a suitable means to tackle the current scenario of unsafe food (Kaushik *et al.,* 2009). Pressure cooking for five minutes reduced pesticides to the tune of 30-93 per cent from tomatoes and other vegetables (Nair *et al.*, 2013). Washing followed by cooking removed 81.97, 79.35, 70.47 and 70.09 per cent residues of quinalphos, chlorpyriphos, triazophos and ethion respectively in cauliflower (Padmanabhan, 2015).

Mathew (2014) reported that the decontamination technique of Kerala Agricultural University, “Veggie wash” to eliminate pesticide residues from 22 types of vegetables.The effect of decontamination methods in the removal of pesticides from vegetables are summarised in Table 4 to 6.

Table 4. Effect of washing in removal of pesticide residues from vegetables

Crop	Decontamination methods	Pesticides	Removal of pesticides (%)	References
Bitter gourds	Washing	Endosulfan	59.05	Nath and Agnihotri, 1984
Brinjal	Washing under tap water	Decamethrin	29 - 50	Raha *et al.*, 1993
Tomato and Brinjal	Washing	Alphamethrin	10 - 30	Gill *et al.*, 2001
Okra	Washing	Endosulfan	30	Randhawa *et al*, 2007
Tomato			25	
Spinach			22.2	
Brinjal			10.3	
Potato			24.0	
Cauliflower			27.0	
Brinjal	Washing	Cypermethrin	26	Kumari, 2008
Cabbage	Washing under running tap	Quinalphos	69.02 - 77.68	Aktar *et al.*, 2010
Brinjal	Washing	Cypermethrin	33.42–35.00	Kaur, 2011
		Deltamethrin	25.00–27.90	
Cabbage Cauliflower	Washing with tap water	Chlorantraniliprole	17 - 40	Kar *et al.*, 2012
Green Chilli	Washing	Acetamiprid	40 - 60	Yang *et al.*, 2012
Cauliflower	Plain water washing	Emamectin benzoate	40.69	Panhwar and Sheik, 2013
		Diafenthiuron	39.07	
		Imidacloprid	21.71	
		Bifenthrin	25.0	
		Endosulfan	28.1	
		Profenofos	14.32	

Capsicum Cauliflower	Normal water washing	Chlorpyriphos	25 to 42	Chandra *et al.*, 2014
	Hot water washing	Chlorpyriphos	36 to 74	
	Normal water washing	Monocrotophos	23-39	
	Hot water washing	Monocrotophos	35-72	
Cauliflower	Normal wash	Chlorpyriphos	31.19	Padmanabhan, 2015
		Quinalphos	55.81	
		Triazophos	28.46	
		Ethion	46.70	

Table 5. Effect of cooking in removal of pesticide residues from vegetables

Crop	Decontamination methods	Pesticides	Removal of pesticides (%)	References
Cauliflower	Cooking after washing	Endosulphan	94.49	Dinabandhoo and Sharma, 1994
		Fenvalerate	37.97	
		Monocrotophos	11.64	
		Endosulphan	94.49	
Tomatoes	Cooking	HCB, lindane, p,p- DDT	30.70 - 45.40	Abou-Arab, 1999
		Dimethoate, profenofos and pirimiphos-methyl	71 - 81.6	
Cauliflower, brinjal, tomato, okra	Cooking	Endosulfan	15 - 30	Randhawa *et al.*, 2007
			60 - 67	
			13 – 35	
Cauliflower, brinjal, tomato, okra	Cooking	Chlorpyriphos	12-48	
Okra	Tap water washing along with cooking	Cypermethrin	71.64 - 78.87	Samriti, 2010
Brinjal	Cooking in boiled water	Cypermethrin	41.40 - 36.40	Walia *et al.*, 2010
	Cooking in oil		45.20	
	Cooking in water		41.40	
	Microwave cooking		40.89	
Cabbage	Cooking	Quinalphos	41.30 - 45.20	Aktar *et al.*, 2010
Egg plant	Cooking	Chlorpyriphos	24.30	Ling *et al.*, 2011
Cabbage			18.30	
Tomato			29.60	

Brinjal	Washing followed by boiling/cooking	Cypermethrin	36.98 - 41.66	Kaur and Reena,2011
		Deltamethrin	32.55 - 37.20	
Green chilli	Washing and cooking	Fenobucarb, Fosthiazate, Iprobenfos	39-100	Yang *et al.*, 2012
		Acetamiprid	20	
Tomato	Cooking	Profenofos	42.90	Harinathareddy*et al.*, 2014
Cucumber	Washing plus cooking	Profenophos	73.06	Raveendranath, *et al.*, 2014
		Quinolphos	83.05	
Cauliflower	Washing and cooking	Chlorpyriphos	79.35	Padmanabhan, 2015
		Quinalphos	81.97	
		Triazophos	70.09	
		Ethion	70.47	
Brinjal	Cooking	Triazophos	66.34	Brar *et al.*, 2017

Table 6. Evaluation of Veggie Wash in removal of insecticide residues

Crop	Treatment with Veggie Wash	Pesticides	Removal (%)	References
Coriander leaves	Dipping in KAU veggie wash at 10 mL L^{-1} followed by three normal washing and cooking in closed pan	Dimethoate	55.44	Aaruni, 2016
		Quinalphos	83.30	
		Chlorpyriphos	63.62	
		Profenophos	54.44	
		Ethion	73.94	
		Bifenthrin	56.03	
		Lambda-cyhalothrin	43.17	
		Cypermethrin	36.14	
		Fenvalerate	63.68	
Amaranthus	Dipping in veggie wash @ 10 mL L^{-1} for 10 min.	Chlorpyriphos	61.20	
		Cypermethrin	75.40	
		Profenophos	78.50	
		Quinalphos	73.70	
		Fenvalerate	76.40	
		Ethion	77.90	
		Lamdacyhalothrin	76.90	
Amaranthus	Dipping in veggie wash @ 10 ml/L for 10 min.	Dimethoate	85.60	
		Bifenthrin	68.30	
Green chilli	Dipping in veggie wash @ 10 ml/L for 10 min.	Chlorpyriphos	61.00	PAMSTEV, 2017
		Cypermethrin	66.00	
		Malathion	100.00	
		Fenvalerate	64.00	
		Ethion	70.00	
		Bifenthrin	63.00	
		Chlorpyriphos	61.00	

Coriander leaves	Dipping in veggie wash @ 10 ml/L for 10 min.	Chlorpyriphos	50.90	PAMSTEV, 2017
		Cypermethrin	81.10	
		Fenvalerate	63.70	
		Lamdacyhalothrin	50.50	
		Dimethoate	54.80	
		Bifenthrin	76.10	
Curry leaves	Dipping in veggie wash @ 10 ml/L for 10 min.	Chlorpyriphos	52.00	PAMSTEV, 2017
		Cypermethrin	64.00	
		Profenophos	56.00	
		Quinalphos	44.00	
		Dimethoate	74.00	
		Ethion	55.00	
		Malathion	75.20	
		Methyl parathion	69.00	
		Fenvalerate	44.00	
		Lamdacyhalothrin	82.00	
Okra	Dipping in veggie wash @ 10 ml/L for 10 min.	Chlorpyriphos Cypermethrin	55.10 49.00	
		Profenophos	66.20	
		Quinalphos	61.00	
		Fenvalerate	66.00	
		Ethion	60.30	
		Lamdacyhalothrin	60.00	
		Dimethoate	57.20	
		Bifenthrin	58.00	
		Chlorpyriphos Cypermethrin	55.10 49.00	

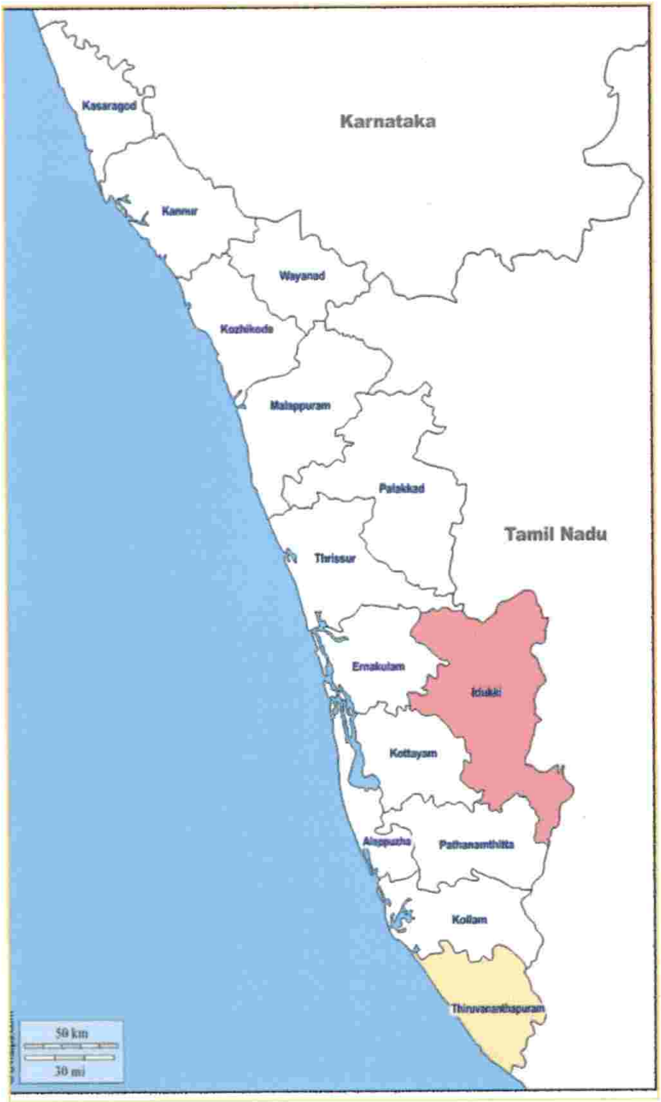
MATERIALS AND METHODS

3. MATERIALS AND METHODS

The present study on "Dissipation and risk assessment of select insecticides used for pest management in cabbage and cauliflower" was carried out during November 2016 to January 2018 at Farmers field, Kalliyoor and Cardamom Research Station, Pampadumpara. It aimed to assess the dissipation of select insecticides recommended by CIBRC for the management of pest in cabbage and cauliflower grown under two different climatic conditions and to assess their potential risks to human health and to determine their effect on soil microbial activity. The study also envisaged to estimate the residues in cooked samples and to evaluate the efficacy of "Veggie Wash" to eliminate residues. Field experiments were conducted in two different agro climatic conditions *viz.*, Thiruvananthapuram (plains) and Idukki (hills) district of Kerala from November 2016 to January 2018. Samples for residue analysis were collected from treated plots and analyzed using Gas Chromatography (GC) and Liquid Chromatography- Tandem spectrometry (LCMS/MS) at Pesticide Residue Research and Analytical Laboratory, Kerala Agricultural University, Vellayani.

3.1 SURVEY ON PESTICIDE USE PATTERN IN CABBAGE AND CAULIFLOWER

Detailed survey on pesticide consumption pattern in cabbage and cauliflower was undertaken to obtain a preliminary back ground on the pesticide used in cabbage and cauliflower using the questionnaire (Appendix I) among farmers in plain (Thiruvananthapuram) and hills (Idukki) districts of Kerala (Plate 1). Twenty five farmers each from Thiruvananthapuram and Idukki districts cultivating a minimum 100 nos. of cabbage or cauliflower were surveyed to collect the information on pests infested and plant protection practices. Survey locations were selected based on the popularity in cultivation of cabbage and cauliflower.



Thiruvananthapuram district (8.4875° N,76.9486 ° E)
Idukki district (9.7980 ° N, 77.1616 ° E).

Plate 1. Survey locations conducted in Kerala

3.2. DISSIPATION OF INSECTICIDES IN CABBAGE AND CAULIFLOWER

3.2.1 Method Validation for Pesticide Residue Analysis in Cabbage and Cauliflower

3.2.1.1 *Chemicals and Reagents*

The reference standards of chlorantraniliprole flubendiamide, indoxacarb, emamectin benzoate, fipronil, quinalphos, cypermethrin, acetamiprid, thiomethoxam and dimethoate with purity percentage of 98.30, 98.60, 93.60, 99.30, 95.40, 99.40, 95.10, 99.90, 99.30 and 99.60 respectively were procured from Sigma Aldrich. Acetonitrile and methanol of LiChrosolv grade, sodium chloride, anhydrous sodium sulphate and anhydrous magnesium sulphate of GR grade were purchased from Merck Specialties Private Limited, Mumbai and the solid reagents were activated before use. Primary secondary amine (PSA) sorbent was purchased from Agilent Technologies, USA. All the glass wares were thoroughly washed as per the standard operating procedure to avoid the interferences from any contaminants during analysis. The suitability of solvents and other chemicals were ensured by running reagent blanks before actual analysis.

3.2.1.2 *Preparation of Standard Solution*

3.2.1.2.1 *Primary Stock Solution*

Standard stock solutions (400 μg mL^{-1}) of chlorantraniliprole, flubendiamide, indoxacarb emamectin benzoate, fipronil, acetamiprid and thiamethoxam were prepared in methanol. The working standard of 10 μg mL^{-1} was prepared by serial dilution, and mixing of individual stock solutions. The standard mixtures required for plotting calibration curve (1.00, 0.50, 0.25, 0.10, 0.05 and 0.025 μg mL^{-1}), were prepared by serially diluting the working standard with methanol and were used for spiking samples and studying the linear dynamic range in the liquid chromatographic analysis. All standard solutions were stored in a refrigerator at -20° C. The recovery studies were conducted at 0.05, 0.25 and 0.50 µg g^{-1} with five replications at each level.

Standard stock solutions of quinalphos, cypermethrin and dimethoate (400 µg mL^{-1}) were prepared in hexane. The working standard of 10 µg mL^{-1} was prepared by serial dilution, and mixing of individual stock solutions. The standard mixtures required for plotting calibration curve (1.00, 0.50, 0.25, 0.10, 0.05 and 0.025 µg mL^{-1}), were prepared by serially diluting the working standard mixture with n-hexane and were used for spiking samples and studying the linear dynamic range in the gas chromatographic analysis. All standard solutions were stored in a refrigerator at -20° C. The recovery studies were conducted at 0.05, 0.25 and 0.50 µg mL^{-1} with five replications at each level.

3.2.1.2.2 *Intermediate Stock Solution*

A pesticide intermediate solution was prepared by transferring 1 mL of each pesticide solution to a 20 mL graduated test tube and diluted with hexane for GC and methanol for LC. An intermediate stock solution was prepared by mixing appropriate quantities of each pesticide stock solution and diluting them accordingly.

3.2.1.2.3 *Working standards*

Working standards of individual pesticides were prepared by diluting intermediate stock solution. To find the retention time of insecticides working standards were used and these were stored in a refrigerator at -20°C until further use.

3.2.1.3 *Fortification and Recovery Experiment*

Methods for analysis of residues of the insecticides mentioned in Table 7 in two different matrices *viz.*, cabbage and cauliflower were validated by Modified Standard Method AOAC 18th edition 2007: 2007.01 at Pesticide Residue Research and Analytical Laboratory, College of Agriculture, Vellayani satisfying the validation parameters *viz.*, accuracy, precision, repeatability, reproducibility etc.

The analytical method was validated for linearity, limit of detection (LOD), limit of quantification (LOQ), recovery and precision. Different concentrations of analytical standards were prepared and calibration curve was constructed. The limit of detection (LOD) determined by considering a signal to noise ratio of 3 and limits of quantification (LOQ) were determined by considering a signal to noise ratio of 10. Recovery studies were conducted by spiking different concentrations (0.05, 0.25 and 0.50 $mgkg^{-1}$) of analytical standards of chlorantraniliprole, flubendiamide, indoxacarb, emamectin benzoate, fipronil, quinalphos, cypermethrin, acetamiprid, thiamethoxam and dimethoate in untreated cabbage heads and cauliflower curds. Five replicates were analyzed at each spiking level. Accuracy of analytical methods was determined based on repeatability and relative standard deviation which is generally considered satisfactory for residue quantification

3.2.2 Field Experiment in Cabbage and Cauliflower

Studies on dissipation of insecticides were conducted in two different agro climatic conditions *viz.*, Thiruvananthapuram district representing the plains (8.4875° N,76.9486 ° E) and Idukki district representing the hills (9.7980 ° N, 77.1616 ° E) of the state. Experiments were conducted in a randomized block design and each treatment was replicated thrice (Plate 2). Cabbage and cauliflower were raised with a spacing of 60×45 cm by following package of practices of Kerala Agricultural University (KAU, 2016) with a plot size of 5 ×5 m^2 during November, 2016 to

a) Thiruvananthapuram

b)Idukki

Plate 2. View of experimental plot

January 2017. Insecticides with label claim in CIBRC (except thiamethoxam) against caterpillar and sucking pests of cabbage and cauliflower were selected for the study (Table 7). The field doses were fixed as per the recommendation of KAU (2015). The spray fluid used in the field experiment was 500 L ha^{-1}

Table 7. Details of insecticides selected for the study

Insecticides	Trade name	Dose (g a.i ha^{-1})	Field dose (g or mL L^{-1})
Chlorantraniliprole 18.5 % SC	Coragen	30	0.30 mL L^{-1}
Flubendiamide 39.35 % SC	Fame	18.24	0.10 mL L^{-1}
Indoxacarb 14.5 % SC	Avaunt	75	1.00 mL L^{-1}
Emamectin benzoate 5% SG	Proclaim	10	0.40 g L^{-1}
Fipronil 5% SC	Regent	50	2.00 mL L^{-1}
Quinalphos 25% EC	Ekalux	375	3.00 mL L^{-1}
Cypermethrin 10 % EC	Cymbush	70	1.50 mL L^{-1}
Acetamiprid 20 % SP	Manik	10	0.10 g L^{-1}
Thiamethoxam 25 % WG	Actara	37.50	0.30 mg L^{-1}
Dimethoate 30 % EC	Rogor	200	1.50 mL L^{-1}
Untreated control	-	-	

3.2.2.1 *Sampling*

Insecticides were sprayed using a knap sack sprayer at fifty per cent cabbage head and cauliflower curd initiation stage. Samples (cabbage and cauliflower) were collected at an interval of 0, 1, 3, 5, 7, 10, 15 and 20 days after spraying or until residues reaches below quantification level. Cabbage and cauliflower samples (2 kg) were harvested and bought to the laboratory in a sealed cover.

3.2.2.2 *Residue Extraction*

A modified QuEChERS method was adopted for residue extraction and clean up (AOAC, 2007). Head and curds samples were chopped and homogenized before blending. Homogenization was done by using a high-volume homogenizer (Blixer 6 vv Robot Coupes) for 2-3 min. Cabbage and cauliflower (25 g each) were transferred into a 250 mL centrifuge tube and added 50 mL of Lichlorosolv grade acetonitrile followed by homogenization with a high speed homogenizer (Heidolph Silent Crusher-M) at 14000 rpm for 3 min. A 10 g activated sodium chloride (NaCl) was added and vortexed for 2 min for the separation of acetonitrile layer. Subsequently samples were centrifuged for 5 min. at 2500 rpm and 12 mL of supernatant was transferred to 50 mL centrifuge tubes containing 6 g of anhydrous sodium sulphate and vortexed for 2 min. Acetonitrile extracts were subjected to clean up by dispersive solid phase extraction. For this 8 mL of supernatant aliquot was transferred to 15 mL centrifuge tubes containing 0.2 g PSA and 1.20 g anhydrous magnesium sulphate. The mixtures were then shaken in vortex for two minutes and again centrifuged for 5 min. at 2500 rpm. The supernatant aliquot (5 mL) was transferred into turbovap tube and concentrated to dryness under a gentle steam of nitrogen using a turbovap set at 40° C and 7.5 psi nitrogen flow. The residue was reconstituted into 2 mL using methanol and filtered through a 0.2 micron filter and transferred into glass auto sampler vial for LC-MS/ MS analysis. For analysis with GC, 4 mL of supernatant aliquot was transferred to turbo tubes and concentrated to dryness using turbovap. The residue reconstituted was 1 mL with n-hexane and transferred into glass auto sampler vial for GC analysis and GC-MS for confirmation.

3.2.2.3 *Estimation of Pesticide Residues*

LCMS/MS

The chromatographic separation was achieved using Waters Acquity UPLC system equipped with a reversed phase Atlantis d C18 (100 ×2.1 mm, 5 µm particle size) column. A gradient system involving the following two eluent components: (A) 10 % methanol in water + 0.1 % formic acid + 5 mM ammonium acetate; (B) 10 % water in methanol + 0.1 % formic acid + 5 mM ammonium acetate was used as mobile phase for the separation of selected insecticides. The gradient elution was done as follows: 0 min isocratic 20 % B, increased to 90 % in 4 min, then raised to 95 % with 5 min and increased to 100 % B in 9 min. decreased to the initial composition of 20 % B in 10 min and held for 12 min for re-equilibration. The flow rate was maintained constant at 0.8 mL min^{-1} and injection volume was 10 µL. The column temperature was maintained at 40 °C. The effluent from the LC system was introduced into triple quadrupole API 3200 MS/MS system equipped with an electrospray ionization interface (ESI), operating in the positive ion mode for chlorantraniliprole, flubendiamide, indoxacarb, emamectin benzoate, acetamiprid and thiamethoxam etc and in negative mode for fipronil. The source parameters for chlorantraniliprole, flubendiamide, indoxacarb, emamectin benzoate, acetamiprid and thiamethoxam were temperature 550 °C, ion gas (GSI) 50 psi, ion gas (GS2) 60 psi, ion spray voltage 5,500 V and curtain gas 13 psi. For fipronil the source temperature was 550 °C, ion source gas (GS1) 50 psi, ion source gas (GS2) 60 psi, ion spray voltage −4,500 V and curtain gas 15 psi. The multiple reaction monitoring (MRM) scan mode was selected and the parameters are listed in Table 8. Retention time of chlorantraniliprole, flubendiamide, indoxacarb, emamectin benzoate, fipronil, acetamiprid and thiamethoxam were 3.10, 3.90, 4.30, 3.50, 3.17, 1.50 and 0.80.

Table 8. Retention time (RT) and Multiple Reaction Monitoring (MRM) transitions of the insecticides in LC-MS/MS

Name of the compound	RT (min.)	MRM transitions		Declustering potential (DP)	Entrance potential (EP)	Collision cell entrance potential (CEP)	Collision Energy (CE)	Collision cell exit potential (CXP)	Quantitative/ Qualitative ion pair
		Quantitative ion pair (Q1)	Qualitative ion pair (Q3)						
Chlorantraniliprole	3.10	484.0	285.9	50.0	6.0	36.0	25.0	2.0	Quantitative
			452.9	50.0	6.0	36.0	25.0	4.0	Qualitative
Flubendiamide	3.90	683.0	274.0	70.0	10.0	44.3	50.0	4.0	Quantitative
			152.0	70.0	10.0	44.3	50.0	4.0	Qualitative
Indoxacarb	4.30	528.0	203.0	70.0	10.0	38.3	50.0	4.0	Quantitative
			150.0	70.0	10.0	38.3	50.0	4.0	Qualitative
Emamectin benzoate	3.50	872.5	126.2	70.0	10.0	51.7	50.0	4.0	Quantitative
			158.2	70.0	10.0	51.7	50.0	4.0	Qualitative
Fipronil	3.17	434.9	330.0	-36.0	-6.0	-23.0	-23.0	-6.0	Quantitative
			250.0	-36.0	-6.0	-23.0	-36.0	-6.0	Qualitative
Acetamiprid	1.50	223.1	126.0	46.0	9.0	19.0	29.0	1.0	Quantitative
			99.0	46.0	9.0	19.0	54.0	1.0	Qualitative
Thiamethoxam	0.80	292.0	211.0	31.0	7.0	19.0	19.0	2.0	Quantitative
			181.0	31.0	7.0	19.0	32.0	2.0	Qualitative

GC-ECD

Estimation of cypermethrin residues was performed using Gas Chromatograph (Shimadzu 2010 AT) equipped with Electron Capture Detector (ECD). Target compound was separated by using DB 5 capillary column (0.25μm film thickness × 0.25 mm × 30 m) with nitrogen as carrier gas. Operating conditions of GC were; column flow (-0.79 mL min^{-1}.), injected volume (2μl), injector temperature (-250° C), detector temperature (300° C) and column oven temperature programmed between 170 to 270° C@ 3.5° C min^{-1}. The retention time of cypermethrin under the above conditions was 61.848 min. The residues confirmed in GC-MS (Shimadzu GC-MS QP 2010 Plus). Helium was used as carrier gas in GC-MS operated with Electron Impact Ionization (70eV). In GC-MS, injector temperature, column and column flow was similar to that of GC. Ion source temperature and interface temperature were 200 ° C and 290 ° C respectively. Simultaneous SIM/Scan mode was selected for the confirmation of cypermethrin were 181, 163 and 127.

GC-FPD

Residue estimation of quinalphos and dimethoate was done with Gas chromatography equipped (Shimadzu 2010 AT) with Flame Photometric Detector (FPD). Target compounds were separated by using DB- 5 capillary (30 × 0.25× 0.25 μm film thickness), column with nitrogen gas as carrier. Zero air and hydrogen were used for generating flame. Operating conditions of GC were column flow (1 mL min^{-1}), injector temperature (250°C), detector temperature (280°C) and column oven temperature programmed between 170 to 270° C @3.5° C. The retention time of quinalphos and dimethoate under the above conditions were 14.091 and 7.293 min. respectively. The residues of quinalphos and dimethoate were confirmed in GC-MS (Shimadzu GC- MS QP 2010 Plus). Helium was used as carrier gas in GC-MS operated with Electron Impact Ionization (70eV). In GC-MS, injector temperature, column, column flow was similar to that of GC. Simultaneous SIM/Scan mode was selected for the confirmation of quinalphos and dimethoate. The ions (m/z) selected for the confirmation of quinalphos were146, 118, 157 and 156 and those for dimethoate were 87, 93, 125 and 63.

3.2.2.4 *Residue Quantification*

Based on the peak area of the chromatogram obtained for various insecticides, the quantity of residue was determined as detailed below.

The residues were estimated using the formula,

Pesticide residue ($\mu g\ g^{-1}$) = Concentration obtained from chromatogram by using Calibration curve × Dilution factor

$$\text{Dilution factor} = \frac{\text{Volume of the solvent added (mL)} \times \text{Final volume of extract (mL)}}{\text{Weight of sample (g)} \times \text{Volume of extract taken for concentration (mL)}}$$

The persistence of insecticides was generally expressed in terms of half-life (D_T 50) *i.e.,* time for disappearance of pesticide to 50 per cent of its initial concentration, which was one of the safety parameters, used in pesticide degradation studies.

The dissipation of insecticide residues in cabbage and cauliflower was analyzed by using a first-order dissipation kinetics equation *i.e.* $Ct = Co\ e^{-kt}$, where Ct is the pesticide concentration ($\mu g\ g^{-1}$) at time t (d), Co is the apparent initial concentration ($\mu g\ g^{-1}$), k is the dissipation rate constant. The half-life ($t_{1/2}$) was determined as $DT_{50} = \ln 2/k$. To determine the half-life of the insecticides as per the procedure outlined by Hoskins (1961), which was done using Microsoft Excel 2007 spreadsheet.

3.3 RISK ASSESSMENT OF INSECTICIDES

Theoretical maximum residues concentration (TMRC) was calculated and compared with maximum permissible intake (MPI) to evaluate the risk to the consumer for the insecticides in cabbage and cauliflower. Safety parameters were evaluated by comparing the TMRC and MPI (Bhattacharya *et al.*, 2017). The TMRC values were calculated by multiplying residues with Indians average consumption of cabbage and cauliflower per person per day as 80 g (FAO, 2009) and compared with MPI. MPI was calculated by multiplying acceptable daily intake (ADI) and average body weight of an Indian. ADI of insecticides under present study were taken from the WHO (2012). and average body weight was considered as 55 kg (Mukherjee and Gopal, 2000).

3.4 EFFECT OF PESTICIDE RESIDUES ON SOIL MICROBIAL ACTIVITY IN CABBAGE AND CAULIFLOWER

The soil enzyme activity tests used as a measure of the metabolic activity of micro organisms in the soil. Tests were conducted to assess the effect of insecticide residues on soil microbes through dehydrogenase (Casida *et al.*, 1964), phosphatase (Tabatabai and Bremner, 1969) and urease (Bremner and Mulvany, 1978) activities of the soils. Samples were collected from the experimental fields of cabbage and cauliflower described in 3.2.2 (plains and hills) before and 3, 5, 10 and 15 days after application of the insecticides and the effect of insecticide residues on the micro flora was assessed.

3.4.1 Sampling

Soil samples were collected from each treatment at a depth of 0 to 15 cm after spraying of insecticides mentioned in experiment 3.2.2 (Table 7) on 1, 3, 5, 7 and 10 days after spraying. Soil samples were collected randomly from each replicates and mixed thoroughly to obtain a composite mixture. Required amount of soil samples

(500 g) were obtained by quartering method. Experiments were conducted to determine the activity of dehydrogenase, phosphatase and urease enzymes after spraying afore mentioned insecticides.

3.4.2 Estimation of Urease Activity

One gram of soil was taken in a 50 mL conical flask. Urea solution (20 mL of 500 ppm) added to each tube and shaken well for mixing urea solution with soil and incubated at 37° C in a BOD incubator. Then added 100 mg calcium sulphate and filtered through Whatman no.1 filter paper. Filtrate from each tube was collected in a separate 50 mL volumetric flask. Later 10 mL of colouring agent was added in to it. Colouring agent was prepared by using p-dimethyl aminobenzaldehyde, ethyl alcohol and concentrated HCL in 1:50:5 ratio. Urease enzyme activity was measured by reading the intensity of colour developed at 420 nm against blank in a spectrophotometer. Blank received only distilled water and colouring agent. The quantity of urea hydrolyzed was calculated by referring to a standard curve and expressed as microgram of urea hydrolyzed per gram of soil per hour at 37° C. Different concentrations of urea solutions were prepared and calibration curve was prepared using optical density values.

3.4.3 Estimation of Phosphatase Activity

One gram of soil was taken in 50 mL tubes and added 0.2 mL toluene, 4 mL of modified universal buffer and 1 mL p- nitrophenyl phosphatase. Tubes were swirled and incubated at 37 °C for 1 hr. After 1 hr, each tube was added with 1 mL of 0.5 M $CaCl_2$ and 4 mL of 0.5 M NaOH. Tubes were swirled thoroughly and suspension was filtered through whatman no.1 filter paper and collected filtrate were made up to 50 mL. Measured the yellow colour using spectrophotometer at 420 nm. Blanks were prepared by the addition of 1 mL p- nitrophenol solution after the addition of 0.5 M $CaCl_2$ and 0.5 M NaOH. Hydrolyzed p-nitrophenol phosphate was computed referring to a standard graph and expressed as microgram per gram of soil per hour at 37 °C.

3.4.4 Estimation of Dehydrogenase Activity

Six gram of air dried soil was taken and added 0.2 g $CaCO_3$. The tubes were added with 1 mL of 3 per cent aqueous solution of 2, 3, 5-triphenyl tetrazolium chloride (TTC) and 2.5 mL distilled water, mixed thoroughly with a glass rod and incubated at 37° C for 24 hrs in a biological oxygen demand (BOD). The activity was expressed as microgram of TPF formed per gram of soil per hour at 37 °C. The TPF formed was extracted from each tube separately in 50 mL volumetric flasks by transferring the soil in to a funnel having Whatman no. 1 filter paper. The soil was washed with enough quantity of methanol till filtrate run free of colour. The filtrate was diluted with methanol for a final volume of 50 mL, and the intensity of pink colour was determined in a spectrophotometer at 485 nm against methanol as a blank. The TPF formed from TTC reduction was determined by referring to a standard graph and expressed as microgram of TPF formed per gram of soil per hour at 37 °C.

3.5 ESTIMATION OF PESTICIDE RESIDUES IN COOKED SAMPLES OF CABBAGE AND CAULIFLOWER

The insecticides which showed more persistence in each location were selected for residue analysis in cooked samples. Cabbage and cauliflower were raised in plains and hills with a spacing of 60×45 cm by following package of practices of Kerala Agricultural University (KAU, 2016) with a plot size of 5 ×5 m^2. The selected insecticides were sprayed at recommended doses at maturity and the heads and curds were collected 2 hrs. after spraying. These were chopped and cooked for 5, 10 and 15 min. at 100 °C and analyzed for residue at PRRAL, as explained in experiment 3.2.

Design : Factorial CRD- (3^2)

Treatments : 3

Replications : 5

3.6 EVALUATION OF "VEGGIE WASH"

Formula of "Veggie Wash" for cleaning vegetables from pesticides has been standardized in the PRRAL, Kerala Agricultural University, Vellayani under the State Plan scheme entitled "Production and marketing of "Safe to Eat" (Pesticide free) vegetables, fruits and food products for sale through government outlets".

Cabbage and cauliflower raised in Thiruvananthapuram district (plain) has been sprayed with chemicals mentioned in experiment 3.2.2 (Table 7) at maturity. Samples were taken on 1, 3, 5, 7 and 10 days after spraying. Cabbage and cauliflower samples were subjected to the following decontamination methods.

T1 - Soaking 500 g cabbage and cauliflower in one litre of 1 % of "Veggie Wash" for 10 minutes followed by washing in water

T2 - Soaking 500 g cabbage and cauliflower in one litre of water for 10 minutes

T3 - No washing

The treated samples were analyzed for pesticide residues as mentioned in the experiment 3.2

Design : Factorial CRD- (3×5×2)

Treatments : 10

Replications : 3

STATISTICAL ANALYSIS

The data on various parameters were analysed statistically by using Analysis of Variance technique (ANOVA) (Panse and Sukhatme, 1985) and significance was tested by 'F' test (Snedecor and Cochran, 1967). In the cases where the effects were found to be significant, CD values were calculated at five per cent and one per cent probability levels. Means were compared by Duncan's Multiple Range Test (DMRT) (Duncan, 1955).

RESULTS

4. RESULTS

4.1 PESTICIDE USE PATTERN IN CABBAGE AND CAULIFLOWER

Pests of cabbage and cauliflower recorded during the survey are presented in Table 9. Tobacco leaf eating caterpillar, *Spodoptera litura* Fabricius and painted bug, *Bagrada hilaris* Burmeister were observed in both plains and hills. Pierid butterfly, *Appias lyncida* Cramer was recorded only from plains and cabbage aphid, *Liaphis erysime* (Kaltenbach) and flea beetle, *Phyllotreta chotanica* Duvivier were recorded from hills (Plate 3).

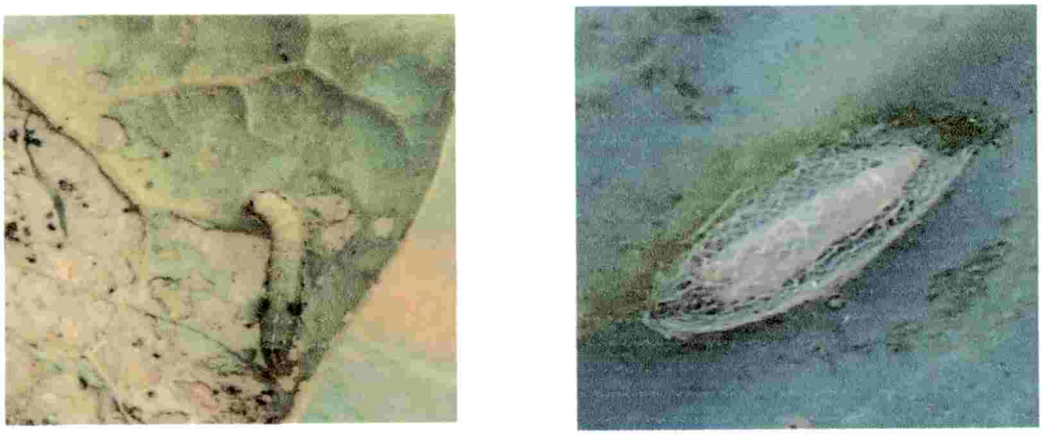
Information on pesticide use pattern among farmers cultivating cabbage and cauliflower in Idukki and Thiruvananthapuram districts are presented in Table 10. In Thiruvananthapuram district, the percentage of farmers applying botanicals for pest management was 40 to 48 per cent, while 8 to 12 per cent farmers applied insecticides and botanicals + chemicals together. Farmers in Thiruvananthapuram district (34 %) did not adopt any plant protection practices at all. In Idukki district it was recorded that the dependency on chemical insecticides was at an extent of 84 per cent in both crops, whereas only 16 per cent farmers depended on botanicals for pest management.

As for the usage of pesticides, farmers in Thiruvananthapuram district relied on flubendiamide, chlorantraniliprole and quinalphos to an extent of 33.33, 16.66 and 50.00 per cent respectively. In Idukki district, the percentage of farmers applying fenvalerate, dimethoate, quinalphos, cypermethrin and mancozeb was recorded 90.47 to 95.23, 71.42 to 76.19, 76.19 to 95.23, 47.61 to 57.14 and 57.14 to 71.42 respectively.

The results of the survey also indicated that, all the farmers in Thiruvananthapuram district used knapsack sprayer for spraying insecticides, while in Idukki 80 to 88 per cent used knapsack sprayer and 12 to 20 per cent, on power sprayer.

Table 9. Pests of cabbage and cauliflower recorded during survey conducted in Thiruvananthapuram and Idukki district

Sl. No	Common Name	Scientific name	Family
a. Plains (Thiruvananthapuram)			
1	Tobacco leaf eating caterpillar	*Spodoptera litura* Fabricius	Noctuidae
2	Pierid butterfly	*Appias lyncida* Cramer	Pieridae
3	Painted bug	*Bagrada hilaris* Burmeister	Pentatomidae
b. Hills (Idukki)			
1	Tobacco leaf eating caterpillar	*Spodoptera litura* Fabricius	Noctuidae
2	Diamond back moth	*Plutella xylostella* Linnaeus	Plutellidae
3	Cabbage aphid	*Lipaphis erysimi* Kaltenbatch	Aphididae
4	Painted bug	*Bagrada hilaris* Burmeister	Pentatomidae
5	Flea beetle	*Phyllotreta chotanica* Duvivier	Chrysomelidae



a) Spodoptera litura

b) Plutella xylostella

c) Appias lyncida

d) Bagrada hilaris

e) Phyllotreta chotanica

f) Liaphis erysime

Plate 3. Insect Pests recorded during survey

Table 10. Pesticide use pattern among cabbage and cauliflower farmers in Thiruvananthapuram and Idukki district

Particulars		Farmers responded (%)			
		Plains		Hills	
		Cabbage	Cauliflower	Cabbage	Cauliflower
Plant protection practices adopted	Botanicals	40	48	16	16
	Biocontrol agents	-	-	-	-
	Chemical insecticides	12	8	84	84
	Botanicals and chemicals	12	8	-	-
	Botanicals and biocontrol agents	-	-	-	-
	No plant protection adopted	36	36		
Pesticides used	Flubendiamide	33.33	33.33	-	-
	Chlorantraniliprole	16.66		-	-
	Fenvalerate	-		90.47	95.23
	Dimethoate	-		71.42	76.19
	Quinalphos	50.00	33.33	76.19	95.23
	Cypermethrin	-	-	47.61	57.14
	Mancozeb	-	-	71.42	57.14
Insecticide appliances used	Knapsack sprayer	100	100	88	80
	Power sprayer	-	-	12	20
Volume of spray fluid/hectare	<500L	12.50	72	12.50	60
	500L	-	-	-	-
	>500L	87.50	28	87.50	40

Adoption of Safety measures	Adopted	12.50	6.25	0	0
	Not adopted	87.50	93.75	100	100
Measurement of chemicals	Bottle cap	12.50	18.75	12	20
	Approximately	87.5	81.25	88	80
Time of application	Morning	100	100	92	88
	Afternoon	0	0	0	0
Source of information about recommended insecticides	Krishi Bhavan	16	12	8	12
	Pesticide dealers/shop	80	76	92	88
	Kerala Agricultural University	4	12	-	-
	Others	-	-	-	-
Frequency of application of pesticides	Weekly	25	18.75	100	100
	Fortnightly	62.50	18.75	-	-
	Need based spray	12.50	62.50	-	-
Awareness of pesticide residues in food	Aware	88	84	84	92
	Unaware	12	16	16	8

* Per cent farmers responded was calculated based on the total number of farmers applied chemical insecticides in each location.

For both crops, 100 per cent of the farmers in Thiruvananthapuram district used knapsack sprayer to spray the insecticide whereas in Idukki district, it was 88 per cent. The remaining 12 per cent in Idukki district used power sprayer.

It was also revealed that the farmers in Thiruvananthapuram and Idukki were unaware about the desired spray volume to be used for a hectare of land. In Thiruvananthapuram, 12.50 per cent farmers used less than 500 L per hectare as spray fluid and 87.50 per cent farmers used more than 500 L per hectare. In Idukki, 60 to 72 per cent of farmers used less than 500 L per hectare as spray fluid and 28 to 40 per cent used more than 500 L.

Survey exposed the fact that farmers in both the locations were oblivious about the toxicity of insecticides. In Thiruvananthapuram district, 87.50 to 93.75 per cent farmers did not use any protective measures while applying insecticides. Only 6.25 - 12.50 per cent farmers in Thiruvananthapuram district adopted safety measures. None of the farmers in Idukki district adopted any safety measure.

It was noted that farmers preferred morning hours to apply insecticides. It was recorded that 100 per cent of the farmers in Thiruvananthapuram district applied insecticides in morning while it was 88 to 92 per cent in Idukki district.

The bottle cap method used to measure chemicals was resorted by 12.50 to 18.75 per cent of farmers of Thiruvananthapuram district while the remaining 81.25 to 87.50 per cent used an approximation to measure the chemicals. In Idukki district, 12 to 20 per cent used the bottle cap method and the remaining 80 to 88 per cent used an approximate measure.

The survey also revealed that, pesticide dealers were the main source of information about recommended insecticides. In Thiruvananthapuram district, 76 to 80 per cent of the farmers responded that pesticide dealers to be their source of information regarding the selection of insecticides. It was concluded that 12 to 16 and 4 to 12 per cent resorted to Krishibhavan and KAU. In Idukki, 8 to 12 per cent farmers gathered information from Krishibhavan and 88 to 92 per cent from pesticide dealers.

Considering the spray interval, it was recorded that 18.75 to 25 per cent of the farmers in in Thiruvananthapuram district applied pesticides weekly, 18.75 to 62.50 fortnightly and 12.50 to 62.50 resorted to need based application. Majority of farmers (88 to 92 %) were aware of the pesticide residues in food whereas only 8 to 12 per cent were not aware about pesticide residues.

4.2 DISSIPATION OF INSECTICIDES IN CABBAGE AND CAULIFLOWER

4.2.1 Method Validation for Pesticide Residue Analysis

Efficiency of analytical methods was estimated through recovery experiment. Instrumental parameters such as Limit of Detection (LOD), Limit of Quantification (LOQ) and linearity were validated under laboratory conditions. Results of recovery experiment on cabbage and cauliflower under different spiking levels are represented in Table 11 and 12. The method validation studies indicated good linearity and recovery at three spiking levels *viz.,* 0.25, 0.05, and 0.50 mg kg^{-1}. The linearity of the calibration curve was established in the range of 0.01 to 1 μg ml^{-1}.The limit of quantification of the method was found to be 0.05 μg g^{-1} and limit of detection, 0.015 μg g^{-1}. Purity percentage of compounds such as chlorantraniliprole, flubendiamide, indoxacarb, emamectin benzoate, fipronil, quinalphos, cypermethrin, acetamiprid, thiamethoxam and dimethoate were 98.30, 98.60, 93.60, 99.30, 95.40, 99.40, 95.10, 99.90, 99.30 and 99.60 respectively. The entire compounds analyzed achieved good repeatability and recovery. Satisfactory recoveries were achieved for all compounds within an acceptable range of 70 to 120 per cent with relative standard deviation less than 20 per cent in cabbage and cauliflower.

4.2.2 Field Experiment in Cabbage and Cauliflower

The dissipation of insecticides in cabbage and cauliflower under plains and hills of Kerala are represented in Tables 13 to 22.

Table 11. Percentage recovery of insecticides in cabbage

Insecticides	Fortification levels (mg kg^{-1})					
	0.05 mg kg^{-1}		0.25 mg kg^{-1}		0.50 mg kg^{-1}	
	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)
Chlorantraniliprole	85.40	5.04	85.47	4.18	83.42	4.02
Flubendiamide	92.68	5.01	89.13	6.67	87.84	5.24
Indoxacarb	86.63	5.52	87.35	5.59	92.68	5.01
Emamectin benzoate	108.20	6.28	95.49	7.05	107.67	2.22
Fipronil	87.10	5.32	84.72	3.23	89.77	7.73
Quinalphos	87.84	4.38	89.46	5.63	84.18	6.24
Cypermethrin	90.69	6.36	92.48	6.74	94.75	4.66
Acetamiprid	92.70	8.56	85.13	10.57	83.77	4.79
Thiamethoxam	87.86	2.88	86.84	3.51	89.19	2.69
Dimethoate	95.84	5.82	92.10	5.56	93.18	5.43

RSD – Relative Standard Deviation

Table 12. Percentage recovery of insecticides in cauliflower

Insecticides	Fortification levels (mg kg^{-1})					
	0.05mg kg^{-1}		0.25mg kg^{-1}		0.50 mg kg^{-1}	
	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)	Mean recovery (%)	RSD (%)
Chlorantraniliprole	114.70	2.38	113.70	4.85	110.72	4.02
Flubendiamide	103.88	5.74	103.20	8.75	106.58	4.36
Indoxacarb	94.45	4.25	96.20	3.58	89.45	4.94
Emamectin benzoate	93.25	9.07	100.89	5.85	93.55	4.80
Fipronil	104.16	5.33	102.26	6.02	98.63	3.55
Quinalphos	84.36	5.36	88.38	6.82	87.15	5.54
Cypermethrin	96.35	4.78	93.86	4.56	96.58	2.86
Acetamiprid	93.73	3.78	93.73	4.15	87.90	2.73
Thiamethoxam	87.40	6.22	89.80	5.21	86.63	2.64
Dimethoate	97.84	2.93	89.69	3.48	92.78	5.67

RSD – Relative Standard Deviation

4.2.2.1 *Chlorantraniliprole*

The results of the persistence and dissipation of chlorantraniliprole residue in cabbage and cauliflower under plains and hills are represented in Table 13.

An initial deposit of chlorantraniliprole residue was 0.44 mg kg^{-1} which was dissipated to 0.22 mg kg^{-1} on first day after spraying with 50 per cent dissipation in cabbage under plains. Residues were declined to 0.09 and 0.08 mg kg^{-1} with 79.54 and 81.81 per cent dissipation on third and fifth days after spraying respectively. The residue reached below quantification level (<0.05 mg kg^{-1}) after 7 days of spraying. However, under hills initial deposit of chlorantraniliprole in cabbage heads, two hrs after spraying was 0.53 mg kg^{-1}. Residues were reduced to 0.38 and 0.23 mg kg^{-1} with dissipation percentage of 28.30 and 56.60 per cent respectively under hills after one and three days of spraying. On the fifth day after spraying residues of chlorantraniliprole was reduced to 0.11 mg kg^{-1} with 79.24 per cent dissipation. Persistence of chlorantraniliprole on cabbage was there up to five days after spraying. Half lives of chlorantraniliprole in cabbage under plains and hills were 2.01 and 2.22 days respectively.

Initial deposit of chlorantraniliprole residue in cauliflower grown under plains was 1.51 mg kg^{-1}, two hrs after spraying. One day after spraying residues degraded to 1.08 mg kg^{-1} with 28.47 per cent dissipation. On the fifth and seventh days residues were 1.07 and 1.02 mg kg^{-1} with 32.45 and 34.43 per cent dissipation respectively. About 52.98 per cent residues dissipated on the tenth day and corresponding residue was 0.71 mg $kg^{-1.}$ Residues persisted up to 15th day (0.16 mg kg^{-1}) with 89.40 per cent dissipation. Mean initial deposit was 1.39 mg kg^{-1} in hills after two hrs of spraying at recommended dose. After one day, residue was 1.17 mg kg^{-1} with 15.82 per cent dissipation. On the third day residue was 0.72 mg kg^{-1} with 48.20 per cent dissipation. More than 93.52 per cent residues dissipated on seventh day (0.09 mg kg^{-1}). Half lives of chlorantraniliprole in cauliflower under plains and hills were 5.50 and 1.28 days, respectively.

Table 13. Dissipation of chlorantraniliprole in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Chlorantraniliprole 18.5 % SC							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	0.44±0.035		0.53±0.008		1.51±0.012		1.39±0.044	
1	0.22±0.031	50.00	0.38±0.008	28.30	1.08±0.005	28.47	1.17±0.060	15.82
3	0.09±0.004	79.54	0.23±0.001	56.60	1.07±0.020	29.13	0.72±0.005	48.20
5	0.08±0.008	81.81	0.11±0.002	79.24	1.02±0.015	32.45	0.09±0.002	93.52
7	BQL		BQL		0.99±0.014	34.43	BQL	
10	BQL		BQL		0.71±0.051	52.98	BQL	
15	BQL		BQL		0.16±0.004	89.40	BQL	
20	BQL		BQL		BQL		BQL	
Half-life (Days)	2.01		2.22		5.50		1.28	

BQL – Below Quantification Level, SD - Standard Deviation

4.2.2.2 *Flubendiamide*

The results of flubendiamide residue in cabbage and cauliflower under plains and hills at a recommended dose of 18.24 g a.i ha^{-1} are depicted in Table 14.

Initial deposit of flubendiamide residue on cabbage under plains was 0.37 mg kg^{-1}. One day after spraying, residue dissipated to 0.32 mg kg^{-1} with 13.51 per cent. The detected flubendiamide residues were 0.27, 0.25, 0.21, 0.16 and 0.13 mg kg^{-1} on 3, 5, 7, 10 and 15 days after treatment with dissipation per cent of 27.02, 32.43, 43.24, 56.75 and 64.86 respectively. On the 20th day, residue of flubendiamide under plains reached below quantification level (<0.05 mg kg^{-1}). Half-life of flubendiamide in cabbage under plains was 9.93 days. In hills, an initial deposit of 0.35 mg kg^{-1} was quantified after two hrs of spraying in cabbage. One day after spraying, residue was dissipated to 0.28 mg kg^{-1}. On the third day, residue was recorded as 0.21 mg kg^{-1} with 40 per cent dissipation. An average residue of 0.10 and 0.09 mg kg^{-1}were quantified on the fifth and seventh days respectively with dissipation per cent of 71.42 and 74.28. On the tenth day residues reached below quantification level with half-life of 3.30 days.

The average initial deposit of flubendiamide residue in cauliflower under plains was 1.46 mg kg^{-1} and degradation was gradual, reached below quantification level on the 20th day. After application of insecticide, on the first day, residues reached to 1.35 mg kg^{-1} showing 7.53 per cent dissipation. Later, the residues declined to 1.13, 1.08, 1.01 and 0.66 mg kg^{-1} on 3, 5, 7 and 10th day with dissipation per cent of 22.60, 26.02, 30.82 and 54.79, respectively. On the 15th days, residue was 0.57 mg kg^{-1} with 60.95 per cent dissipation. Half-life of flubendiamide in cauliflower under plains was 10.66 days, while in hills mean initial deposit of flubendiamide on cauliflower was 1.54 mg kg^{-1}. Residues declined to 1.13 mg kg^{-1} on first day with a dissipation of 26.62 per cent. Residues were 0.98, 0.72, 0.65, 0.42 and 0.26 mg kg^{-1} respectively on 3, 5, 7, 10 and 15th

Table 14. Dissipation of flubendiamide in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Flubendiamide 39.5 % SC							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	0.37±0.010		0.35±0.008		1.46±0.025		1.54±0.193	
1	0.32±0.023	13.51	0.28±0.030	20.00	1.35±0.047	7.53	1.13±0.061	26.62
3	0.27±0.009	27.02	0.21±0.030	40.00	1.13±0.040	22.60	0.98±0.817	36.36
5	0.25±0.004	32.43	0.10±0.010	71.42	1.08±0.150	26.02	0.72±0.310	53.24
7	0.21±0.012	43.24	0.09±0.010	74.28	1.01±0.040	30.82	0.65±0.105	57.79
10	0.16 ±0.001	56.75	BQL		0.66±0.020	54.79	0.42±0.127	72.72
15	0.13 ±0.017	64.86	BQL		0.57±0.060	60.95	0.26 ±0.020	83.11
20	BQL		BQL		BQL		BQL	
Half-life (Days)	9.93		3.30		10.66		6.08	

BQL – Below Quantification Level, SD - Standard Deviation

days after spraying, with a dissipation of 36.36, 53.24, 57.79, 72.72 and 83.11 per cent respectively. Half-life of flubendiamide in cauliflower under hills was 6.08 days.

4.2.2.3 *Indoxacarb*

The persistence and dissipation of indoxacarb residue in cabbage and cauliflower under plains and hills are depicted in Table 15.

In cabbage under plains, initial average residue of indoxacarb was 0.67 mg kg^{-1} after two hrs of spraying at recommended dose. Residues on first, third and fifth day after spraying were 0.49, 0.37 and 0.20 mg kg^{-1} with per cent dissipation of 26.86, 44.77 and 70.14 respectively. Residues persisted up to five days. Half life of indoxacarb was 2.98 days. Whereas,mean initial deposit of indoxacarb in hills was 0.71 mg kg^{-1} after two hrs of spraying. On the first day residue was 0.63 mg kg^{-1} with dissipation per cent of 11.26. Subsequently, residues declined to 0.46 and 0.36 mg kg^{-1} with dissipation per cent of 35.21 and 49.29 on third and fifth day. Residues of indoxacarb reached below quantification level on seventh day with a half life of 3.82 days.

Average initial deposits of indoxacarb in cauliflower curds under plains after spraying at recommended dose was 0.98 mg kg^{-1}, which later dissipated to 0.73, 0.49 and 0.41 mg kg^{-1} with a dissipation loss of 25.51, 50.00 and 58.16 per cent on one, three and five days respectively. Half life calculated was 3.96 days. However, in hills, initial average deposits of indoxacarb recorded was 1.02 mg kg^{-1}, subsequently residues were reduced to 0.83, 0.62, 0.46 and 0.26 mg kg^{-1} respectively on 1, 3, 5 and 7 days respectively. Correspondingly, the dissipation per cent was 18.62, 39.21, 54.90 and 74.50 on one, three, five and seven days respectively and residues reached below quantification level on the 10th day. Calculated half-life was 3.70 days.

Table 15. Dissipation of indoxacarb in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Indoxacarb 14.5 % SC							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	0.67 ±0.100	-	0.71 ±0.030	-	0.98±0.001	-	1.02±0.010	-
1	0.49 ±0.001	26.86	0.63 ±0.001	11.26	0.73±0.002	25.51	0.83±0.032	18.62
3	0.37 ±0.008	44.77	0.46 ± 0.040	35.21	0.49±0.010	50.00	0.62±0.010	39.21
5	0.20 ±0.102	70.14	0.36 ± 0.020	49.29	0.41±0.021	58.16	0.46±0.002	54.90
7	BQL		BQL		BQL		0.26±0.001	74.50
10	BQL		BQL		BQL		BQL	
Half-life (Days)	2.98		4.92		3.96		3.70	

BQL – Below Quantification Level, SD - Standard Deviation

4.2.3.4 *Emamectin benzoate*

Dissipation of emamectin benzoate in cabbage and cauliflower under plains and hills are depicted in Table 16.

In cabbage, residue of emamectin benzoate was below quantification level even after 2 hr. of spraying in both plains and hills. In cauliflower under plains, the initial deposit of emamectin benzoate was 0.20 mg kg^{-1} when applied at 10 g ha^{-1} under plains. On the first day, loss of 96.50 per cent was observed and the residue reached below quantification level on the third day after spraying. Half life calculated was 0.18 days. Whereas, in hills initial deposit was 0.26 mg kg^{-1} and on the first day, loss of 65.38 per cent was observed. Residues reached below quantification level on third day after spraying. Half life calculated was 0.44 days.

4.2.3.5 *Fipronil*

Dissipation of fipronil in cabbage and cauliflower under plains and hills are depicted in Table 17.

Average initial deposit of fipronil on cabbage under plains at recommended dose was 0.08 mg kg^{-1} which reduced to 0.07 mg kg^{-1} on the first day with 12.50 per cent dissipation. In hills, residue of fipronil was 0.91 mg kg^{-1} after two hrs of spraying and subsequently it declined to 0.48, 0.17 and 0.13 mg kg^{-1} with per cent dissipation of 47.25, 81.31 and 85.71 on one , three and five days after spraying. The residues of fipronil reached below quantification level on three and seven days after spraying in plains and hills respectively. Half life of fipronil was 0.22 and 1.96 days in plains and hills.

In cauliflower, the initial deposits of fipronil was 1.21 mg kg^{-1} on 0th day (2 hr after application) at 20 g a.i ha^{-1} which dissipated to 1.19 and 0.94 mg kg^{-1} on first and third day, recording a dissipation loss of 1.65 and 20.66 per cent, respectively. Later the residues were dissipated to 48.76 and 83.47 per cent with average residues of 0.62 and 0.20 mg kg^{-1}on fifth and seventh days after application. However in hills, after two hrs of spraying a mean deposit of 1.36 mg

Table 16. Dissipation of emamectin benzoate in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Emamectin benzoate 5 % SG							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	BQL		BQL		0.20±0.008		0.26±0.025	
1	BQL		BQL		0.06±0.005	96.50	0.09±0.041	65.38
3	BQL		BQL		BQL		BQL	
Half-life (Days)	-		-		0.51		0.58	

BQL - Below Quantification Level, SD - Standard Deviation

Table 17. Dissipation of fipronil in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Fipronil 5 % SC							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	0.08 ± 0.10	-	0.91 ± 0.12	-	1.21±0.001	-	1.36±0.001	-
1	0.07 ±0.01	12.50	0.48 ± 0.06	47.25	1.19±0.02	1.65	0.96±0.001	29.41
3	BQL		0.17 ± 0.003	81.31	0.94±0.03	20.66	0.76±0.10	44.11
5	BQL		0.13 ± 0.001	85.71	0.62±0.008	48.76	0.48±0.004	64.70
7	BQL		BQL		0.20±0.001	83.47	0.25±0.021	81.61
10	BQL		BQL		BQL		BQL	
Half-life (Days)	4.67		1.73		2.82		3.03	

BQL – Below Quantification Level, SD - Standard Deviation

kg^{-1} and one day after spraying the residue dissipated to 0.96 mg kg^{-1} with a reduction of 29.41 per cent. On the third day residues declined to 0.76 mg kg^{-1} with 44.11 per cent dissipation. About 64.70 per cent of residues were dissipated on fifth day after spraying. On the seventh day, residue was 0.25 mg kg^{-1} which reached below quantification level on 10th day after spraying. Half life calculated was 2.82 and 3.03 days in plains and hills respectively.

4.2.3.6 *Quinalphos*

Dissipation of quinalphos in cabbage and cauliflower under plains and hills are depicted in Table 18.

In cabbage under plains, initial deposit of 2.66 mg kg^{-1} was quantified two hrs after spraying and residues dissipated to 1.20 and 0.14 mg kg^{-1} on one and three days after spraying .The corresponding dissipation was 83.33 and 94.73 per cent respectively. On the fifth and seventh day, residues were 0.11 and 0.09 mg kg^{-1} with per cent dissipation of 95.86 and 96.61 that reached below quantification level on 10 th day. Calculated half life was 1.38 days. Whereas, in hills the initial deposit of quinalphos was 0.24 mg kg^{-1} and residues dissipated to 0.21, 0.16, 0.09 and 0.06 mg kg^{-1} after one, three, five and seven days after spraying with per cent dissipation of 12.50, 33.33, 62.50 and 75.00, respectively. The residues reached below quantification limit on the 10th day after spraying with a half life of 3.37days.

Residue of quinalphos deposits in cauliflower under plains at recommended dose after two hrs of spraying was 3.70 mg kg^{-1} and one day after spraying residue dissipated to 2.07 mg kg^{-1} with a reduction of 44.05 per cent. On third day residues declined to 1.69 mg kg^{-1} with 54.32 per cent reduction. About 58.37 and 87.56 per cent residues were dissipated on fifth and seventh day after spraying. On 10th day residue was 0.16 mg kg^{-1} and reached below quantification level on 15th day after spraying with a half life of 2.34 days. While in hills, initial deposit of quinalphos in cauliflower curds was 3.80 mg kg^{-1} after two hrs of

Table 18. Dissipation of quinalphos in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Quinalphos 25 % EC							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	2.66 ± 0.020	-	0.24 ± 0.021	-	3.70 ± 0.539	-	3.80 ± 0.070	-
1	1.20 ± 0.010	83.33	0.21 ± 0.009	12.50	2.07 ± 0.953	44.05	2.50 ± 0.190	34.21
3	0.14 ± 0.010	94.73	0.16 ±0.005	33.33	1.69 ± 0.286	54.32	1.64 ± 0.030	56.82
5	0.11 ± 0.030	95.86	0.09 ± 0.002	62.50	1.54 ± 0.171	58.37	1.54 ± 0.040	59.47
7	0.09 ± 0.100	96.61	0.06 ± 0.002	75.00	0.46 ± 0.009	87.56	1.13 ± 0.220	70.26
10	BQL		BQL		0.16 ± 0.020	95.67	0.66 ± 0.080	82.63
15	BQL		BQL		BQL		0.33 ± 0.030	91.31
20	BQL		BQL		BQL		BQL	
Half-life (Days)	1.38		3.37		2.34		4.52	

BQL – Below Quantification Level, SD – Standard Deviation

spraying. Residues were 2.50, 1.64, 1.54, 1.13, 0.66 and 0.33 on first, third, fifth, seventh, tenth and fifteenth days respectively. Residues reached below quantification level on 20th day after spraying with a half life of 4.52 days.

4.2.3.7 *Cypermethrin*

Dissipation of cypermethrin in cabbage and cauliflower under plains and hills are depicted in Table 19.

The initial deposit of cypermethrin after two hr of spraying was 0.26 mg kg^{-1} on cabbage under plains. On the next day, residues dissipated to 0.15 mg kg^{-1} indicating 42.30 per cent dissipation. On the third and fifth day residues were 0.11 and 0.09 mg kg^{-1} with a per cent dissipation of 57.69 and 69.23. Residue reached below quantification level on seventh days after spraying with half life of 3.52 days. While in hills, mean initial deposit of 0.34 mg kg^{-1} was recorded after two hrs of spraying. One day after spraying residues reached to 0.30 mg kg^{-1} with 11.76 per cent dissipation. Residues on three, five and seven days were 0.23, 0.18 and 0.07 mg kg^{-1} with per cent dissipation of 32.35, 47.05 and 79.41. Residues were reached below quantification limit on 10th days after spraying with a half life of 3.30 days.

In cauliflower curds, the initial deposits of cypermethrin was 0.23 mg kg^{-1} on 0th day (2 hr after application) at 60 g a.i ha^{-1} which dissipated to 0.20 and 0.15 mg kg^{-1} on first and third day recorded a loss of 13.04 and 34.78 per cent respectively. Later residues declined to 39.13 and 56.52 per cent on with average residues of 0.14 and 0.10 mg kg^{-1} with half life of 6.14 days. However, in hills mean initial deposit was 0.94 mg kg^{-1} after two hr of spraying. One day after spraying residue dissipated to 0.41 mg kg^{-1} with a reduction of 56.38 per cent. On third day residues declined to 0.37 mg kg^{-1} with 60.63 per cent reduction. On the fifth and seventh day residues were 0.35 and 0.25 mg kg^{-1} with a per cent dissipation of 62.76 and 73.40. On the10 th day residue was declined to 0.11 mg kg^{-1} with a per cent dissipation of 88.29. Half life of cypermethrin was 3.99 days.

Table 19. Dissipation of cypermethrin in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Cypermethrin 10% EC							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	0.26±0.004	-	0.34±0.017	-	0.23±0.004	-	0.94±0.004	-
1	0.15 ±0.03	42.30	0.30±0.010	11.76	0.20±0.029	13.04	0.41±0.020	56.38
3	0.11 ±0.006	57.69	0.23±0.070	32.35	0.15±0.002	34.78	0.37±0.001	60.63
5	0.09±0.001	69.23	0.18±0.003	47.05	0.14±0.015	39.13	0.35±0.020	62.76
7	BQL		0.07±0.001	79.41	0.10±0.014	56.52	0.25±0.015	73.40
10	BQL		BQL		BQL		0.11±0.008	88.29
15	BQL		BQL		BQL		BQL	
Half-life (Days)	3.52		3.30		6.14		3.99	

BQL – Below Quantification Level, SD – Standard Deviation

4.2.3.8 *Acetamiprid*

Dissipation of acetamiprid in cabbage and cauliflower under plains and hills are depicted in Table 20.

Residue of acetamiprid in cabbage under plains at recommended dose after two hrs of spraying was 0.31 mg kg^{-1}. On the first day after spraying residues reached to 0.14 mg kg^{-1} with per cent dissipation of 54.83 and on third day it was 0.12 mg kg^{-1} with 61.29 per cent. The average residues were 0.09 and 0.06 on the fifth and seventh days after spraying with 70.96 and 80.64 per cent dissipation. Half life calculated was 3.46 days. However, initial deposit of acetamiprid in cabbage was 0.08 mg kg^{-1} under hills after two hr of spraying and one day after spraying it was 0.06 mg kg^{-1}. Half -life of acetamiprid was 2.16 days. Residues of acetamiprid reached below quantification limit after 10th and 3 rd days after spraying in plains and hills respectively.

In cauliflower, an initial average residue of acetamiprid was 0.45 mg kg^{-1} after two hrs of spraying at recommended dose under plains. Residues on first, third and fifth day after spraying were 0.34, 0.27, 0.22 and 0.14 mg kg^{-1} with per cent dissipation of 24.44, 40.00, 51.11 and 68.88 respectively. Residues were reached below quantification limit after 10 days with half life of 4.50 days. In hills, mean initial deposit was 0.64 mg kg^{-1} after two hrs of spraying under hills. On first day residue was 0.42 mg kg^{-1} with dissipation per cent of 34.37. Subsequently residues were declined to 0.24 and 0.16 mg kg^{-1} with dissipation per cent of 62.50 and 75.00. Residues of acetamiprid became below quantification limit on days seventh days after spraying with a half life of 2.50 days.

4.2.3.9 *Thiamethoxam*

Dissipation of thiamethoxam in cabbage and cauliflower under plains and hills are depicted in Table 21.

Initial mean concentration of thiamethoxam in cabbage two hour after application was 0.18 mg kg^{-1}under plains. The residue of thiamethoxam estimated on the first day was 0.09 mg kg^{-1} with a dissipation loss of 50 per cent. The

Table 20. Dissipation of acetamiprid in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Acetamiprid 20% SP							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	0.31±0.031	-	0.08±0.004	-	0.45±0.005	-	0.64±0.015	-
1	0.14±0.010	54.83	0.06±0.001	33.75	0.34±0.010	24.44	0.42±0.002	34.37
3	0.12±0.007	61.29	BQL		0.27±0.002	40.00	0.24±0.001	62.50
5	0.09±0.003	70.96	BQL		0.22±0.002	51.11	0.16±0.006	75.00
7	0.06±0.001	80.64	BQL		0.14±0.009	68.88	BQL	
10	BQL		BQL		BQL	-	BQL	
15	BQL		BQL		BQL	-	BQL	
Half-life (Days)	3.46		2.16		4.50		2.50	

BQL – Below Quantification Level, SD - Standard Deviation

Table 21. Dissipation of thiamethoxam in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Thiamethoxam 25 % WG							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	0.18±0.006	-	0.12±0.005	-	0.46±0.006	-	0.83±0.037	-
1	0.09±0.001	50.00	0.07±0.003	41.66	0.31±0.002	32.60	0.13±0.009	84.33
3	0.08±0.001	55.55	0.06 ±0.002	50.00	0.22±0.005	52.17	0.08±0.001	90.36
5	0.06±0.02	66.66	BQL		0.17±0.002	63.04	0.06±0.005	92.77
7	BQL		BQL		0.16±0.007	65.21	BQL	
10	BQL		BQL		0.10±0.002	78.26	BQL	
15	BQL		BQL		BQL		BQL	
Half-life (Days)	3.67		3.26		5.10		1.52	

BQL – Below Quantification Level, SD – Standard Deviation

residues reduced to 0.08 and 0.06 mg kg^{-1}on third and fifth day after spraying and showed 55.55 and 66.66 per cent dissipation. The residues reached below the quantification limit on seventh day after spraying. Half life of thiamethoxam in cabbage under plains was 3.67 days. However, initial deposit of thiamethoxam in hills was 0.12 mg kg^{-1} when applied at 37.5 g $a.ha^{-1}$. After one and third day, residue reduced to 0.07 and 0.06 mg kg^{-1} with a per cent dissipation of 41.66 and 50.00. Residue reached below quantification level after fifth days of spraying. The calculated half life of thiamethoxam in cabbage was 3.26 days.

Average initial deposit of thiamethoxam on cauliflower under plains at recommended dose was 0.46 mg kg^{-1}. It declined to 0.31 on first day with 32.60 per cent dissipation. Residues on third, fifth, seventh and tenth days were 0.22, 0.17, 0.16 and 0.10 with per cent dissipation of 52.17, 63.04, 65.21 and 78.26 respectively. Half life calculated was 5.10 days, while in hills residues of thiamethoxam was 0.83 mg kg^{-1} after two hrs of spraying. Subsequently residues were declined to 0.13, 0.08 and 0.06 mg kg^{-1} with a dissipation loss of 84.33, 90.36 and 92.77 respectively. Half life calculated was 1.52 days.

4.2.3.10 *Dimethoate*

Dissipation of dimethoate in cabbage and cauliflower under plains and hills are depicted in Table 22.

The initial deposits of dimethoate was 3.21 mg kg^{-1} on 2 hrs after application in plains which dissipated to 0.61 and 0.19 mg kg^{-1} on first and third day after spraying recording a dissipation loss of 80.99 and 94.08 per cent respectively. Average residues recorded on 5 days after spraying was 0.13 mg kg^{-1} with dissipation per cent of 95.95. However, in hills a mean deposit of 0.72 mg kg^{-1} after two hrs of spraying was recorded. Dimethoate residue dissipated to 0.43 mg kg^{-1} with a reduction of 40.27 per cent and on third day residues declined to 0.37 mg kg^{-1} with 48.61 per cent dissipation. About 75.00 per cent of residues were dissipated on fifth day after spraying. Residues reached below quantification

Table 22. Dissipation of dimethoate in cabbage and cauliflower under plains and hills

Days after spraying (DAS)	Dimethoate 30 % EC							
	Cabbage				Cauliflower			
	Plains		Hills		Plains		Hills	
	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)	Mean Residue ±SD(mg kg^{-1})	Dissipation (%)
0	3.21 ±0.010	-	0.72 ± 0.010	-	3.50±0.051	-	0.74±0.025	-
1	0.61 ± 0.012	80.99	0.43 ± 0.030	40.27	2.35±0.315	32.85	0.35±0.126	52.70
3	0.19 ± 0.010	94.08	0.37 ± 0.010	48.61	1.73±0.030	50.57	0.30±0.046	59.45
5	0.13 ±0.020	95.95	0.18 ± 0.020	75.00	1.31±0.067	62.57	0.25±0.036	66.21
7	BQL		BQL		0.77±0.033	78.00	0.09±0.011	87.83
10	BQL		BQL		0.44±0.027	87.42	BQL	
15	BQL		BQL		0.16±0.012	95.42	BQL	
20	BQL		BQL		BQL		BQL	
Half-life (Days)	1.14		2.75		3.39		2.77	

BQL – Below Quantification Level, SD - Standard Deviation

level on seventh day after spraying in plains and hills respectively. Half life of dimethoate calculated was 1.14 and 2.75 days in plains and hills respectively.

In cauliflower, initial mean concentration of dimethoate two hour after application was 3.50 mg kg^{-1} under plains. The residue estimated on first day was 2.35 mg kg^{-1} with a loss of 32.85 per cent. The residues were declined further to 1.73 and 1.31 mg kg^{-1} on third and fifth day with 50.57 and 62.57 per cent dissipation respectively. Residues were 0.77, 0.44 and 0.16 mg kg^{-1} on seventh, tenth and fifteenth days after spraying. Residues reached below quantification level on 20th days after spraying. Half life calculated was 3.39 days. Whereas, in hills initial deposit was 0.74 mg kg^{-1} at recommended dose after two hrs of spraying. On first day after spraying residues reached to 0.35 mg kg^{-1} with per cent dissipation of 52.70 and on third day it was 0.30 mg kg^{-1} with 59.45 per cent. Later residues were 0.25 and 0.09 mg kg^{-1} on cauliflower curds after fifth and seventh days after spraying with 66.21 and 87.83 per cent dissipation. On tenth day residue of dimethoate reached below quantification level in hills. Half life calculated was 2.77 days.

4.3 RISK ASSESSMENT OF INSECTICIDES

4.3.1 Chlorantraniliprole

The result on the risk assessment of chlorantraniliprole in cabbage and cauliflower under plains and hills are presented in Table 23.

The MPI of chlorantraniliprole was found to be 110000 μg $person^{-1}$ day^{-1}. The calculated TMRC values for cabbage under plains were 35.20, 17.60, 7.20 and 6.40 μg $person^{-1}$ day^{-1} under plains on 0, 1, 3 and 5 days after spraying respectively. While in hills, TMRC were 42.40, 30.40, 18.40 and 8.80 μg $person^{-1}$ day^{-1} on 0, 1, 3 and 5 days after spraying respectively. The derived TMRC values on all the days were found to be lower than the respective MPI values. Hence consumption of chlorantraniliprole treated cabbage even on the day of spraying at recommended dose was found to be safe.

Table 23. Risk assessment of chlorantraniliprole in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg person^{-1} d^{-1})	Average residue (µg g^{-1})				TMRC (µg person^{-1} d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
2	55	0	80	110000	0.44	0.53	1.51	1.39	35.20	42.40	120.80	111.20
2	55	1	80	110000	0.22	0.38	1.08	1.17	17.60	30.40	86.40	93.60
2	55	3	80	110000	0.09	0.23	1.07	0.72	7.20	18.40	85.60	57.60
2	55	5	80	110000	0.08	0.11	1.02	0.09	6.40	8.80	81.60	7.20
2	55	7	80	110000	-	-	0.99	-	-	-	79.20	-
2	55	10	80	110000	-	-	0.71	-	-	-	56.80	-
2	55	15	80	110000	-	-	0.16	-	-	-	12.80	-

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

TMRC values were 120.80, 86.40, 85.60, 81.60, 79.20, 56.80 and 12.80 μg person^{-1} day^{-1} in cauliflower under plains on 0, 1, 3, 5, 7, 10 and 15 days after spraying . Correspondingly in hills it was 111.20, 93.60, 57.60 and 7.20 μg person^{-1} day^{-1} respectively. When compared with MPI, TMRC values were much lower on all the days after spraying at recommended dose under plains and hills. Hence residues of chlorantraniliprole do not pose any harmful risk on human even on the day of spraying.

4.3.2 Flubendiamide

The result on the risk assessment of flubendiamide in cabbage and cauliflower under plains and hills are presented in Table 24.

The acceptable daily intake of flubendiamide on cabbage was 0.017 mg kg^{-1} bw^{-1} d^{-1}. The MPI was found to be 935 80 μg person^{-1} day^{-1} and obtained TMRC values in cabbage under plains were 29.60, 25.60, 21.60, 20.00, 16.80 and 12.80 80 μg person^{-1} day^{-1} respectively on 0, 1, 3, 5, 7, 10 and 15 days after spraying. While in hills, TMRC were 28.00, 22.40, 16.80, 8.00 and 7.20 80 μg person^{-1} day^{-1} respectively on 0, 1, 3, 5 and 7 days after spraying. Consumption of flubendiamide treated cabbage even on the day of spraying at recommended dose was found to be safe, since derived TMRC values on all the days interval on which residue studies had been conducted were found to be lower than the MPI value.

In cauliflower under plains, TMRC values were 116.80, 108.00, 90.40, 86.40, 80.80, 52.80 and 45.60 80 μg person^{-1} day^{-1} respectively on 0,1, 3, 5, 7, 10 and 15 days after spraying of flubendiamide on cabbage. While in hills TMRC were 123.20, 90.40, 78.40, 57.60, 52.00, 33.60 and 20.80 80 μg person^{-1} day^{-1} respectively on 0, 1, 3,5, 7, 10 and 15 days after spraying respectively. TMRC values were less than MPI, hence consumption of flubendiamide treated cauliflower even on the day of spraying at recommended dose was found to be safe.

Table 24. Risk assessment of flubendiamide in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg person^{-1} d^{-1})	Average residue (µg g^{-1})				TMRC (µg person^{-1} d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
0.017	55	0	80	935	0.37	0.35	1.46	1.54	29.60	28.00	116.80	123.20
0.017	55	1	80	935	0.32	0.28	1.35	1.13	25.60	22.40	108.00	90.40
0.017	55	3	80	935	0.27	0.21	1.13	0.98	21.60	16.80	90.40	78.40
0.017	55	5	80	935	0.25	0.10	1.08	0.72	20.00	8.00	86.40	57.60
0.017	55	7	80	935	0.21	0.09	1.01	0.65	16.80	7.20	80.80	52.00
0.017	55	10	80	935	0.16	-	0.66	0.42	12.80	-	52.80	33.60
0.017	55	15	80	935	0.13	-	0.57	0.26	10.40	-	45.60	20.80

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake; TMRC- Theoretical maximum residue concentration; * MPI= ADI x Average body weight x 1000

4.3.3 Indoxacarb

The result on the risk assessment of indoxacarb in cabbage and cauliflower under plains and hills are presented in Table 25.

ADI of indoxacarb was 0.01 mg kg^{-1} bw^{-1} day^{-1} and daily consumption of cabbage was considered as 80 g day^{-1}. Residues of indoxacarb were persisted upto 5 and 7 days in plains and hills respectively. MPI calculated was 550 80 µg person^{-1} day^{-1} and TMRC was 53.6 80 µg person^{-1} day^{-1}. On first and third day, TMRC were 39.20 and 29.60 80 µg person^{-1} day^{-1} whereas on fifth day it was 16 80 µg person^{-1} day^{-1} under plains. TMRC were 56.80, 50.40, 36.80 and 28.80 80 µg person^{-1} day^{-1} on 0, 1, 3 and 5 days after spraying at recommended dose under hills. When compared with MPI, TMRC values were much lower on all the days after spraying at recommended dose under plains and hills, hence the residues of indoxacarb do not pose any harmful risk on human even on the day of spraying.

In cauliflower under plains, TMRC values were 78.40, 58.40, 39.20 and 32.80 µg person^{-1} day^{-1} on 0, 1, 3 and 5 days after spraying, correspondingly in hills it was 81.60, 66.40, 49.60, 36.80 and 20.80 µg person^{-1} day^{-1} respectively on 0, 1, 3 , 5 and 7 days after spraying. When compared with MPI, TMRC values were much lower on all the days after spraying at recommended dose under plains and hills. Residues of indoxacarb do not pose any harmful risk on human even on the day of spraying.

4.3.4 Emamectin Benzoate

The result on the risk assessment of emamectin benzoate in cabbage and cauliflower under plains and hills are presented in Table 26.Since the residues of emamectin benzoate was below quantification level even on two hrs after spraying, there was no risk in the consumption of cabbage treated with emamectin benzoate at recommended dose.

The calculated ADI and MPI were 0.002 mg kg^{-1} and 27.5 80 µg person^{-1} day^{-1} respectively. TMRC value on 0 th day was 16.16 µg person^{-1}day^{-1} under

Table 25. Risk assessment of indoxacarb in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg person^{-1} d^{-1})	Average residue (µg g^{-1})				TMRC (µg person^{-1} d^{-1})			
					Cabbage		cauliflower		Cabbage		cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
0.01	55	0	80	550	0.67	0.71	0.98	1.02	53.60	56.80	78.40	81.60
0.01	55	1	80	550	0.49	0.63	0.73	0.83	39.20	50.40	58.40	66.40
0.01	55	3	80	550	0.37	0.46	0.49	0.62	29.60	36.80	39.20	49.60
0.01	55	5	80	550	0.2	0.36	0.41	0.46	16.00	28.80	32.80	36.80
0.01	55	7	80	550	-	-	-	0.26	-		-	20.80

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

Table 26. Risk assessment of emamectin benzoate in cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg $person^{-1}$ d^{-1})	Average residue (µg g^{-1})				TMRC (µg $person^{-1}$ d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
0.002	55	0	80	27.50	BQL	BQL	0.20	0.26	-	-	16.16	20.80
0.002	55	1	80	27.50	BQL	BQL	0.06	0.09	-	-	4.80	7.20

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

plains. In hills TMRC was 20.80 μg person^{-1}day^{-1} and it was less than MPI. In both locations TMRC was less than MPI, hence consumption of emamectin benzoate treated cauliflower was found to be safe.

4.3.5 Fipronil

The result on the risk assessment of fipronil in cabbage and cauliflower under plains and hills are presented in Table 27.

The acceptable daily intake of fipronil on cabbage was 0.0002 mg kg^{-1} bw^{-1}day^{-1}. The MPI was found to be 11 μg person^{-1}day^{-1} and obtained TMRC values in cabbage under plains were 6.63 and 5.59 μg person^{-1}day^{-1} respectively on 0th and 1st days after spraying. While in hills, TMRC were 72.80, 38.40, 13.60 and 10.40 μg person^{-1}day^{-1} respectively on 0, 1, 3 and 5 days after spraying. Consumption of fipronil treated cabbage was not safe up to 3 days under hills since derived TMRC values on the day's interval on which residue studies had been conducted were found to be higher than the MPI value.

In cauliflower, TMRC values under plains were 96.80, 95.20, 75.20, 49.60 and 16.00 μg person^{-1}day^{-1} on 0, 1, 3, 5 and 7 days after spraying. While in hills, corresponding TMRC were 108.80, 76.80, 60.80, 38.40 and 20. μg person^{-1}day^{-1} . Hence consumption of cauliflower under both plains and hills was not safe since derived TMRC values were found to be higher than the MPI values.

4.3.6 Quinalphos

The result on the risk assessment of quinalphos in cabbage and cauliflower under plains and hills are presented in Table 28.

MPI calculated was 550 μg person^{-1}day^{-1} and TMRC was 212.80 μg person^{-1}day^{-1} under plain. On first and third day, TMRC were 96.00 and 11.20 μg person^{-1}day^{-1}, whereas on fifth day it was 8.80 μg person^{-1}day^{-1} under plains. While in hills, TMRC were19.20, 16.80, 12.80 and 7.20 on 0, 1, 3 and 5 days after spraying.

Table 27. Risk assessment of fipronil in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg person^{-1} d^{-1})	Average residue (µg g^{-1})				TMRC (µg person^{-1} d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
0.0002	55	0	80	11	0.08	0.91	1.21	1.36	6.63	72.80	96.80	108.80
0.0002	55	1	80	11	0.07	0.48	1.19	0.96	5.59	38.40	95.20	76.80
0.0002	55	3	80	11	-	0.17	0.94	0.76	-	13.60	75.20	60.80
0.0002	55	5	80	11	-	0.13	0.62	0.48	-	10.40	49.60	38.40
0.0002	55	7	80	11	-	-	0.20	0.25	-	-	16.00	20.00

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

Table 28. Risk assessment of quinalphos in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg person^{-1} d^{-1})	Average residue (µg g^{-1})				TMRC (µg person^{-1} d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
0.01	55	0	80	550	2.66	0.24	3.70	3.80	212.80	19.20	296.00	304.00
0.01	55	1	80	550	1.2	0.21	2.07	2.50	96.00	16.80	165.60	200.00
0.01	55	3	80	550	0.14	0.16	1.69	1.64	11.20	12.80	135.20	131.20
0.01	55	5	80	550	0.11	0.09	1.54	1.54	8.80	7.20	123.20	123.20
0.01	55	7	80	550	-	-	0.46	1.13	-	-	36.80	90.40
0.01	55	10	80	550	-	-	0.16	0.66	-	-	12.80	52.80
0.01	55	15	-	-	-	-		0.33	-	-	-	26.40

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

In cauliflower, TMRC were 296.00, 165.60, 135.20, 123.20, 36.80 and 12.80 µg person^{-1}day^{-1} on 0, 1, 3, 5, 7 and 10 days after spraying under plains. While, in hills TMRC were 304.00, 200.00, 131.20, 123.20, 90.40, 52.80 and 26.40 µg person^{-1}day^{-1} on 0, 1, 3, 5 ,7, 10 and 15 days after spraying. TMRC values were much lesser than MPI values in cabbage and cauliflower under both locations. Hence consumption of quinalphos treated cabbage and cauliflower at recommended dose found to be safe for human health.

4.3.7 Cypermethrin

The result on the risk assessment of cypermethrin in cabbage and cauliflower under plains and hills are presented in Table 29.

Safety risk of cypermethrin on cabbage was evaluated by comparing TMRC obtained at recommended dose on 0, 1, 3, 5, 7 and 10 days with MPI. ADI of cypermethrin was 0.02 mg kg^{-1} bw^{-1}day^{-1}. From the field experiment mean residue of cypermethrin on 0 day was 0.26 and 0.34 mg kg^{-1} at plains and hills respectively. The MPI of cypermethrin was 1100 µg person^{-1}day^{-1} TMRC values obtained were 20.80 and 27.20 µg person^{-1}day^{-1} two hrs after spraying under plains and hills at recommended dose. TMRC values were 12.00, 8.80 and 7.20 µg person^{-1}day^{-1} on 1, 3 and 5 days after spraying under plains. TMRC values under hills were 24.00, 18.40, 14.40 and 5.60 µg person^{-1}day^{-1} on 1, 3, 5 and 7th days after spraying. Since TMRC values were lesser than MPI values in both locations consumption of cabbage was found to be safe on human health.

In cauliflower, TMRC values obtained were 18.40 and 75.20 µg person^{-1}day^{-1} two hrs after spraying of cypermethrin under plains and hills at recommended dose. TMRC values were 16.00, 12.00, 11.20 and 8.00 µg person^{-1}day^{-1} on 1, 3, 5 and 7th days after spraying under plains. TMRC values under hills were 32.80, 29.60, 28.00, 20.00 and 8.80 µg person^{-1}day^{-1} on 1, 3, 5, 7 and 10 days after spraying. Since TMRC values were lesser than MPI values in both locations after spraying of cypermethrin at recommended dose was found to be safe for human health.

Table 29. Risk assessment of cypermethrin in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg $person^{-1}$ d^{-1})	Average residue (µg g^{-1})				TMRC (µg $person^{-1}$ d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
0.02	55	0	80	1100	0.26	0.34	0.23	0.94	20.80	27.20	18.40	75.20
0.02	55	1	80	1100	0.15	0.30	0.20	0.41	12.00	24.00	16.00	32.80
0.02	55	3	80	1100	0.11	0.23	0.15	0.37	8.80	18.40	12.00	29.60
0.02	55	5	80	1100	0.09	0.18	0.14	0.35	7.20	14.40	11.20	28.00
0.02	55	7	80	1100	-	0.07	0.10	0.25	-	5.60	8.00	20.00
0.02	55	10	80	1100	-	-	-	0.11	-	-	-	8.80

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

4.3.8 Acetamiprid

The result on the risk assessment of acetamiprid in cabbage and cauliflower under plains and hills are presented in Table 30.

Dietary risk assessment of acetamiprid on cabbage was determined based on the comparison of TMRC and MPI values. Two hrs after spraying of acetamiprid at recommended dose, MPI calculated was 3850 μg person^{-1}day^{-1} and TMRC was 24.80 μg person^{-1} day^{-1} under plain. On first and third day, TMRC were 11.20 and 9.60 μg person^{-1}day^{-1}, whereas on fifth and seventh day it was 7.20 and 4.80 μg person^{-1} day^{-1} under plains. While in hills, TMRC were 6.40, 4.24 and 1.36 μg person^{-1} day^{-1} on 0, 1 and 3 days after spraying.

In cauliflower, TMRC of acetamiprid on 0 (two hrs after spraying), 1, 3, 5 and 7 days were 36.00, 27.20, 21.60, 17.60 and 11.20 μg person^{-1} day^{-1} respectively under plains. While, in hills TMRC were 51.20, 33.60, 19.20 and 12.80 μg person^{-1} day^{-1} on 0, 1, 3 and 5 days after spraying. TMRC values were much lesser than MPI values. Hence assumption of cabbage and cauliflower after spraying of acetamiprid at recommended dose found to be safe for human health.

4.3.9 Thiamethoxam

The result on the risk assessment of thiamethoxam in cabbage and cauliflower under plains and hills are presented in Table 31.

MPI of thiamethoxam was 4400 μg person^{-1} day^{-1}. TMRC of thiamethoxam on 0, 1, 3 and 5 were 14.40, 7.20, 6.40 and 4.80 μg person^{-1} day^{-1} respectively under plains. However, in hills TMRC were 9.60, 5.60 and 4.80 μg person^{-1} day^{-1} on 0, 1 and 3 days after spraying.

In cauliflower, TMRC of thiamethoxam on 0, 1, 3, 5, 7 and 10 days were 36.80, 24.80, 17.60, 13.60, 12.80 and 8.00 μg person^{-1} day^{-1} respectively under plains. While in hills TMRC were 66.40, 10.40, 6.40 and 4.80 μg person^{-1} day^{-1} on 0, 1, 3 and 5 days after spraying. TMRC values were much lesser than MPI values. Consumption of cabbage and cauliflower under both locations after

Table 30. Risk assessment of acetamiprid in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg person^{-1} d^{-1})	Average residue (µg g^{-1})				TMRC (µg person^{-1} d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
0.07	55	0	80	3850	0.31	0.08	0.45	0.64	24.80	6.40	36.00	51.20
0.07	55	1	80	3850	0.14	0.05	0.34	0.42	11.20	4.24	27.20	33.60
0.07	55	3	80	3850	0.12	0.02	0.27	0.24	9.60	1.36	21.60	19.20
0.07	55	5	80	3850	0.09	-	0.22	0.16	7.20	-	17.60	12.80
0.07	55	7	80	3850	0.06	-	0.14	-	4.80	-	11.20	-

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

Table 31. Risk assessment of thiamethoxam in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw^{-1} d^{-1})	Average body weight of Indian (kg^{-1})	DAS	Daily consumption (g d^{-1})	MPI* (µg person^{-1} d^{-1})	Average residue (µg g^{-1})				TMRC (µg person^{-1} d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
0.08	55	0	80	4400	0.18	0.12	0.46	0.83	14.40	9.60	36.80	66.40
0.08	55	1	80	4400	0.09	0.07	0.31	0.13	7.20	5.60	24.80	10.40
0.08	55	3	80	4400	0.08	0.06	0.22	0.08	6.40	4.80	17.60	6.40
0.08	55	5	80	4400	0.06	-	0.17	0.06	4.80	-	13.60	4.80
0.08	55	7	80	4400	-	-	0.16	-	-	-	12.80	-
0.08	55	10	80	4400	-	-	0.10	-	-	-	8.00	-

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

spraying of thiamethoxam at recommended dose found to be safe for human health.

4.3.10 Dimethoate

The result on the risk assessment of dimethoate in cabbage and cauliflower under plains and hills are presented in Table 32.

Dietary risk assessment of dimethoate on cabbage heads were determined based on the comparison of TMRC and MPI values. Two hrs after spraying of dimethoate at recommended dose, MPI calculated was 110 µg person^{-1} day^{-1} and TMRC was 256.80 µg person^{-1} day^{-1}. On first and third day, TMRC was 48.80 and 15.20 µg person^{-1} day^{-1} whereas on fifth day it was 10.40 µg person^{-1} day^{-1} under plains. While, in hills TMRC were 57.60, 34.40, 29.60 and 14.40 µg person^{-1} day^{-1} on 0, 1, 3 and 5 days after spraying.

In cauliflower, calculated TMRC values under plains were 280.00, 188.00, 138.40, 104.80, 61.60, 35.20 and 12.80 µg person^{-1} day^{-1} on 0, 1, 3, 5, 7, 10 and 15 days after spraying. While in hills, TMRC were 59.20, 28.00, 24.00, 20.00 and 7.20 µg person^{-1} day^{-1} on 0, 1, 3, 5 and 7 day after spraying. TMRC was much higher than MPI values for cabbage on the day of application in plains. While in cauliflower under plains showed higher TMRC values up to 3 days. Hence consumption of cabbage and cauliflower under plains upto 3 days after spraying can cause health problems.

4.4 EFFECT OF PESTICIDE RESIDUES ON SOIL MICROBIAL ACTIVITY IN CABBAGE AND CAULIFLOWER

4.4.1 Effect of Urease Activity under Plains

Urease activity under plains is represented in Table 33. Unit of urease activity is expressed as ppm of urea hydrolyzed g^{-1} soil hr^{-1}.

Significantly higher enzyme activity was recorded in control plots (116.23) which was on par with dimethoate (115.45) and flubendiamide (113.79)

Table 32.Risk assessment of dimethoate in cabbage and cauliflower under plains and hills

ADI (mg kg^{-1} bw d^{-1})	Average body weight of Indian (kg)	DAS	Daily consumption (g d^{-1})	MPI* (µg person^{-1} d^{-1})	Average residue (µg g^{-1})				TMRC (µg person^{-1} d^{-1})			
					Cabbage		Cauliflower		Cabbage		Cauliflower	
					Plains	Hills	Plains	Hills	Plains	Hills	Plains	Hills
2	55	0	80	110	3.21	0.72	3.5 0	0.74	256.80	57.60	280.00	59.20
2	55	1	80	110	0.61	0.43	2.35	0.35	48.80	34.40	188.00	28.00
2	55	3	80	110	0.19	0.37	1.73	0.30	15.20	29.60	138.40	24.00
2	55	5	80	110	0.13	0.18	1.31	0.25	10.40	14.40	104.80	20.00
2	55	7	80	110	-	-	0.77	0.09	8.80	-	61.60	7.20
2	55	10	80	110	-	-	0.44	-	-	-	35.20	-
2	55	15	80	110	-	-	0.16	-	-	-	12.80	-

DAS- Days after spraying; ADI- Acceptable daily intake; MPI- Maximum permissible intake;

TMRC- Theoretical maximum residue concentration;* MPI= ADI x Average body weight x 1000

Table 33. Effect of insecticides on urease activity in soils of cabbage and cauliflower in plains

Treatments	Urease at different intervals after spraying (ppm of urea hydrolyzed g $^{-1}$ soil hr $^{-1}$)							
	3 DAS		5 DAS		10 DAS		15 DAS	
	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower
Flubendiamide 39.35 % SC	113.79	109.73	103.07	107.33	77.97	69.41	69.25	60.42
Chlorantraniliprole 18.5 % SC	106.62	114.70	77.14	98.57	75.08	65.53	58.20	60.36
Indoxacarb 14.5 % SC	110.62	105.90	93.91	101.73	73.08	70.14	55.33	52.47
Dimethoate 30 % EC	115.45	109.62	89.91	108.59	72.25	73.30	58.75	62.45
Fipronil 5% SC	93.41	98.53	90.63	86.84	74.75	73.47	72.70	52.57
Thiamethoxam 25 % WG	106.13	106.51	90.02	102.07	86.19	79.87	69.41	61.85
Emamectin benzoate 5% SG	108.95	102.07	93.35	96.78	72.86	81.85	70.71	51.97
Acetamiprid 20 % SP	110.68	104.46	92.69	107.68	89.97	71.05	78.80	54.08
Quinalphos 25% EC	104.29	106.29	88.91	101.88	92.41	73.03	70.42	55.21
Cypermethrin 10 % EC	109.12	102.05	90.30	97.72	81.58	68.35	64.14	57.23
Control	116.23	116.70	116.23	116.70	116.23	116.70	116.23	116.70
CD (0.05)	4.153	1.136	5.045	3.135	8.358	2.085	3.405	7.726
SEM	1.407	0.385	1.710	1.062	2.833	0.706	1.154	2.618

DAS- Days after spraying

treated plots on three days after application of insecticides followed by acetamiprid (110.68), indoxacarb (110.62), cypermethrin (109.12), emamectin benzoate (108.95), chlorantraniliprole (106.62), thiamethoxam (106.13) and quinalphos (104.29). The lowest enzyme activity was recorded in fipronil treated cabbage plots (93.41).

In cauliflower field, three days after spraying, significantly highest urease enzyme activity was recorded in control plots (116.70) which were significantly different from others. The urease activity recorded in different insecticides *viz*; chlorantraniliprole (114.70), flubendiamide (109.73), dimethoate (109.62), thiamethoxam (106.51), quinalphos (106.29), indoxacarb (105.90) acetamiprid (104.46) and emamectin benzoate (102.07). The lowest enzyme activity was recorded in fipronil (98.53).

In cabbage, five days after spraying the highest enzyme activity was observed in control plots (116.23) and it was significantly differed from all other treatments *viz.,* flubendiamide (103.07), indoxacarb (93.91), emamectin benzoate (93.35), acetamiprid (92.69), fipronil (90.63), cypermethrin (90.30), thiamethoxam (90.02), dimethoate (89.91) and quinalphos (88.91). The lowest enzyme activity was recorded for chlorantraniliprole (77.14).

After five days of spraying in cauliflower, all treatments were significantly different from control (116.70). Higher enzyme activity was reported in the plots treated with dimethoate (108.59) which was on par with acetamiprid (107.68) and flubendiamide (107.33) followed by thiamethoxam (102.07), quinalphos (101.88), indoxacarb (101.73), chlorantraniliprole (98.57), cypermethrin (97.72) and emamectin benzoate (96.78). The lowest enzyme activity was recorded for fipronil (86.84).

On tenth day after spraying in cabbage, the highest urease enzyme activity in ppm of urea hydrolyzed g^{-1} soil hr^{-1} was recorded in control plots (116.23) which differed significantly from all other treatments. Higher enzyme activity was recorded for quinalphos (92.41), acetamiprid (92.41), thiamethoxam (89.97) and thiamethoxam (86.19) which were on par with each other followed by cypermethrin (81.58), flubendiamide (77.97), chlorantraniliprole (75.08), fipronil (74.75), indoxacarb (73.08) and emamectin benzoate (72.86). The lowest enzyme activity was recorded for dimethoate (72.25)

On tenth day after spraying in cauliflower, the highest urease activity in was recorded in control plot (116.70) which was significantly different from all other treatments. Higher enzyme activity was recorded for emamectin benzoate (81.85) and thiamethoxam (79.87) and they were on par with each other followed by fipronil (73.47), dimethoate (73.30), quinalphos (73.03), acetamiprid (71.05), indoxacarb (70.14), flubendiamide (69.41) and cyprmethrin (68.35). The lowest enzyme activity was recorded for chlorantraniliprole (65.53).

After fifteen days of spraying in cabbage, all treatments were significantly different from control (116.70). Higher enzyme activity was reported in the plots treated with acetamiprid (78.80) followed by fipronil (72.70), emamectin benzoate (70.71), quinalphos (70.42). thiamethoxam (69.41), flubendiamide (69.25), cypermethrin (64.14), dimethoate (58.75) and chlorantraniliprole (58.20). The lowest enzyme activity was recorded for indoxacarb (55.33).

After fifteen days of spraying in cauliflower, the highest urease activity in was recorded in control plot (116.70) which was significantly different from all other treatments. Higher enzyme activity was recorded for dimethoate (62.45), thiamethoxam (61.85), flubendiamide (60.42), chlorantraniliprole (60.36), cypermethrin (57.23) and quinlaphos (55.21) which were on par with each other followed by acetamiprid (54.08), fipronil (52.57), indoxacarb (52.47). The lowest activity was recorded for emamectin benzoate (51.97).

4.4.2 Effect of Urease Activity under Hills

Urease activity in cabbage and cauliflower under hills are represented in Table 34. Unit of urease activity is expressed as ppm of urea hydrolyzed g^{-1} soil hr^{-1}.

Table 34. Effect of insecticides on urease activity in soils of cabbage and cauliflower grown under hills

Treatments	Urease at different intervals after spraying (ppm of urea hydrolyzed g^{-1} soil hr^{-1})							
	3 DAS		5 DAS		10 DAS		15 DAS	
	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower
Flubendiamide 39.35 % SC	116.06	80.35	110.57	47.78	69.31	62.09	64.86	63.13
Chlorantraniliprole 18.5 % SC	114.90	65.50	102.35	44.52	70.25	63.61	60.14	66.69
Indoxacarb 14.5 % SC	108.57	54.16	106.73	38.83	76.03	33.26	59.98	28.30
Dimethoate 30 % EC	117.12	70.80	110.62	67.37	78.30	58.10	63.64	48.75
Fipronil 5% SC	100.13	68.39	96.19	51.01	93.68	44.54	57.09	35.05
Thiamethoxam 25 % WG	108.84	89.78	103.13	74.21	86.47	67.14	67.52	56.52
Emamectin benzoate 5% SG	106.51	77.97	101.96	58.56	87.85	48.50	60.43	42.86
Acetamiprid 20 % SP	106.57	63.51	108.01	60.55	75.42	57.69	60.32	49.01
Quinalphos 25% EC	105.51	48.95	102.63	34.57	77.81	28.68	55.65	20.20
Cypermethrin 10 % EC	110.24	100.18	105.62	75.58	72.75	62.27	58.58	57.51
Control	120.28	101.36	120.28	101.35	120.28	101.36	120.28	101.35
CD (0.05)	4.912	1.518	2.884	0.960	3.356	2.419	5.081	1.148
SEM	1.665	0.514	0.977	0.325	1.137	0.820	1.722	0.389

DAS- Days after spraying

In cabbage, three days after spraying significantly the highest urease enzyme activity was recorded in control plots (120.28), dimethoate (117.12), flubendiamide (116.06) which were on par with each other followed by chlorantraniliprole (114.90), cypermethrin (110.24), thiamethoxam (108.84), indoxacarb (108.57), acetamiprid (106.57), emamectin benzoate (106.51) and quinalphos (105.51). The lowest activity was recorded in fipronil treated plots (100.13).

After three days of spraying in cauliflower, the highest urease activity was recorded in control plot (101.36) and cypermethrin (100.18) which was significantly different from all other treatments followed by thiamethoxam (89.78), flubendiamide (80.35), emamectin benzoate (77.97), dimethoate (70.80), fipronil (68.39), chlorantraniliprole (65.50), acetamiprid (63.51). The lowest activity was recorded in and quinalphos (48.95) treated soil followed by indoxacarb (54.16).

On fifth day after spraying in cabbage, the highest urease enzyme activity was recorded in control plots (120.28) which differed significantly from all other treatments. Higher enzyme activity was recorded for dimethoate (110.62), flubendiamide (110.57) and acetamiprid (108.01) which were on par with each other followed by indoxacarb (106.73), cypermethrin (105.62), thiamethoxam (103.13), quinalphos (102.63), chlorantraniliprole (102.35), emamectin benzoate (101.96). The lowest enzyme activity was recorded in fipronil (96.19) treated plots.

On fifth day after spraying in cauliflower, the highest urease enzyme activity was recorded in control plots (101.35) which differed significantly from all other treatments. Higher enzyme activity was recorded for cypermethrin (75.58) followed by thiamethoxam (74.21), dimethoate (67.37), acetamiprid (60.55), emamectin benzoate (58.56), fipronil (51.01), flubendiamide (47.78), chlorantraniliprole (44.52) and indoxacarb (38.83). The lowest activity was recorded in quinalphos (34.75) treated plots.

After ten days of spraying in cabbage plots, all treatments were significantly different from control (120.28). Higher urease enzyme activity was reported in the plots treated with fipronil (93.68) followed by emamectin benzoate (87.85), thiamethoxam (86.47), dimethoate (78.30), quinalphos (77.81), indoxacarb (76.03), acetamiprid (75.42), cypermethrin (72.75), chlorantraniliprole (70.25). The lowest enzyme activity was observed in flubendiamide (69.31) treated plots.

After ten days of spraying in cauliflower plots, all treatments were significantly different from control (101.36). Higher urease enzyme activity was reported in the plots treated with thiamethoxam (67.14) followed by chlorantraniliprole (63.61), cypermethrin (62.27), flubendiamide (62.09), dimethoate (58.10), acetamiprid (57.69), emamectin benzoate (48.50), fipronil (44.54). Lower enzyme activity was observed in indoxacarb (33.26) and quinalphos (28.68) treated cauliflower plots.

On fifteenth day after spraying in cabbage, the highest urease enzyme activity was recorded in control plots (120.28) which differed significantly from all other treatments. Higher enzyme activity was recorded in thiamethoxam (67.52), flubendiamide (64.86) and dimethoate (63.64) treated soils and they were on par with each other followed by emamectin benzoate (60.43), acetamiprid (60.32), chlorantraniliprole (60.14), indoxacarb (59.98), cypermethrin (58.58) and fipronil (57.09). The lowest enzyme activity was recorded in quinalphos (55.65) treated plots.

On fifteenth day after spraying in cauliflower, the highest urease enzyme activity was recorded in control plots (101.35) which differed significantly from all other treatments. Higher enzyme activity was recorded for chlorantraniliprole (66.69) followed by flubendiamide (63.13), cypermethrin (57.51), thiamethoxam (56.52), acetamiprid (49.01), dimethoate (48.75), emamectin benzoate (42.86), fipronil (35.05), indoxacarb (28.30). The lowest activity was recorded in quinalphos (20.20) treated plots.

4.4.3 Effect of Phosphatase Activity under Plains

Phosphatase activity in cabbage and cauliflower under plains are represented in Table 35. Phosphatase activity is expressed in µg P-NP g^{-1} soil hr^{-1}

Significantly higher phosphatase enzyme activity was recorded in control plots (101.17) in cabbage plots on 3 days after application of insecticides. Higher enzyme activity was observed for thiamethoxam (99.96) followed by cypermethrin (97.87), flubendiamide (80.64), emamectin benzoate (77.45), dimethoate (71.03), chlorantraniliprole (61.31), acetamiprid (58.52), fipronil (51.88) and indoxacarb (43.44). The lowest enzyme activity was recorded in quinalphos (42.95) treated plots which was on par with indoxacarb (43.44).

On third day after spraying in cauliflower, highest enzyme activity was recorded in control plots (118.48) which differed significantly from all other treatments. Higher enzyme activity was recorded for flubendiamide (113.03) which was significantly different from dimethoate (110.46), thiamethoxam (104.51), acetamiprid (104.18), emamectin benzoate (104.13), cypermethrin (103.36), quinalphos (98.88), chlorantraniliprole (97.63) and indoxacarb (95.70). The lowest activity recorded in fipronil (95.65) treated plots.

After five days of spraying in cabbage plots, all treatments were significantly different from control (101.17). Higher enzyme activity was reported in the plots treated with dimethaote (74.43) followed by acetamiprid (61.64), thiamethoxam (57.35), fipronil (49.73), emamectin benzoate (40.35), chlorantraniliprole (38.31), flubendiamide (36.36), indoxacarb (31.64) and cypermethrin (25.79) and these were significantly different from each other. The lowest enzyme activity was recorded in quinalphos treated plots (25.67).

In cauliflower, all treatments were significantly different from control (118.47) after five days of spraying. Higher enzyme activity was reported in the plots treated with cypermethrin (98.47), flubendiamide (98.13) and they were on par with each other followed by quinalphos (93.57), dimethoate (90.81), indoxacarb (88.35), thiamethoxam (88.27), acetamiprid (86.63), fipronil (86.44),

Table 35. Effect of insecticides on phosphatase activity in soils of cabbage and cauliflower grown under plains

Treatments	Phosphatase at different intervals after spraying (µg P-NP g^{-1} soil hr^{-1})							
	3 DAS		5 DAS		10 DAS		15 DAS	
	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower
Flubendiamide 39.35 % SC	80.64	113.03	36.36	98.13	59.54	69.44	66.40	52.79
Chlorantraniliprole 18.5 % SC	61.31	97.63	38.31	81.24	63.51	73.45	68.08	60.68
Indoxacarb 14.5 % SC	43.44	95.70	31.64	88.35	28.66	72.14	21.30	58.17
Dimethoate 30 % EC	71.03	110.46	74.43	90.81	21.34	59.28	17.43	55.33
Fipronil 5% SC	51.88	95.65	49.73	86.44	57.25	74.19	62.97	70.37
Thiamethoxam 25 % WG	99.96	104.51	57.35	88.27	45.92	82.14	37.88	64.04
Emamectin benzoate 5% SG	77.45	104.13	40.35	84.97	35.72	74.08	23.07	69.27
Acetamiprid 20 % SP	58.52	104.18	61.64	86.63	38.56	80.28	37.49	76.19
Quinalphos 25% EC	42.95	98.88	25.67	93.57	15.87	85.24	13.09	72.40
Cypermethrin 10 % EC	97.87	103.36	25.79	98.47	35.60	86.01	40.31	72.94
Control	101.17	118.48	101.17	118.48	101.17	118.48	101.17	118.48
CD (0.05)	0.870	1.723	0.584	1.615	0.729	0.766	0.842	0.699
SEM	0.294	0.584	0.197	0.547	0.247	0.259	0.285	0.236

DAS- Days after spraying

emamectin benzoate (84.97). The lowest enzyme activity was recorded in chlorantraniliprole treated plots (81.24)

On tenth day after spraying in cabbage, the highest phosphatase enzyme activity was recorded in control plots (101.17) which differed significantly from all other treatments. Higher enzyme activity was recorded for chlorantraniliprole (63.51), flubendiamide (59.54), fipronil (57.25), thiamethoxam (45.92), acetamiprid (38.56), emamectin benzoate (35.72), cypermethrin (35.60), indoxacarb (28.66) and dimethoate (21.34) which was significantly different from each other. The lowest enzyme activity was recorded in quinalphos treated plots (15.87).

In cauliflower, the highest phosphatase enzyme activity was recorded in control plots (118.48) which differed significantly from all other treatments. Significantly higher enzyme activity was observed for cypermethrin (86.01) and quinalphos (85.24) and they were on par with each other followed by thiamethoxam(82.14), acetamiprid (80.28), fipronil (74.19), emamectin benzoate (74.08), chlorantraniliprole (73.45), indoxacarb (72.14), flubendiamide (69.44). The lowest activity was recorded for dimethoate (59.28) which was significantly different from all other treatments.

After fifteen days of spraying in cabbage, all treatments were significantly different from control. Higher enzyme activity was reported in the plots treated with chlorantraniliprole (68.08) followed by flubendiamide (66.40), fipronil (62.97), cypermethrin (40.31), thiamethoxam (37.88), acetamiprid (37.49), emamectin benzoate (23.07), indoxacarb (21.30) and dimethaote (17.43). The lowest enzyme activity was recorded in quinalphos treated plots (13.09) which were significantly different from all other treatments.

After fifteen days of spraying in cauliflower plots, all treatments were significantly different from control. Significantly higher enzyme activity was reported in the plots treated with acetamiprid (76.19) followed by cypermethrin (72.94), quinalphos (72.40), fipronil (70.37), emamectin benzoate (69.27), thiamethoxam (64.04), chlorantraniliprole (60.68), indoxacarb (58.17), dimethaote (55.33). Significantly the lowest enzyme activity was recorded in flubendiamide (52.79) treated plot.

4.4.4 Effect of Phosphatase Activity under Hills

Phosphatase enzyme activity in cabbage and cauliflower under hills are represented in Table 36. Phosphatase enzyme activity is expressed in μg P-NP g^{-1} soil hr^{-1}.

Significantly higher phosphatase activity was recorded in control plots of cabbage (110.28). Significantly higher enzyme activity was recorded for cypermethrin (95.73) and thiamethoxam (95.34) which was on par with each other followed by flubendiamide (90.23), emamectin benzoate (80.41), dimethoate (75.63), chlorantraniliprole (65.31), acetamiprid (63.63), quinalphos (58.46), fipronil (55.63) and the lowest enzyme activity was recorded for indoxacarb (48.15) treated cabbage plots.

In cauliflower plots, all treatments were significantly different from control (101.71) after three days of spraying. Significantly higher enzyme activity was reported in the plots treated with cypermethrin (95.67) followed by thiamethoxam (82.07), emamectin benzoate (73.74), dimethoate (69.22), flubendiamide (62.19), acetamiprid (59.23), chlorantraniliprole (58.23), fipronil (53.02) and indoxacarb (50.75). The lowest enzyme activity was recorded in quinalphos (46.48) treated plot.

In cabbage, after five days of spraying, all treatments were significantly different from control (110.28). Higher enzyme activity was recorded in dimethoate (73.75) followed by thiamethoxam (63.40), cypermethrin (62.10), emamectin benzoate (54.24), acetamiprid (53.65), fipronil (47.09), flubendiamide (45.30), chlorantraniliprole (40.55), quinalphos (36.98). The lowest enzyme activity was recorded in indoxacarb (34.88) treated plot.

Table 36. Effect of insecticides on phosphatase activity in soils of cabbage and cauliflower grown under hills

Treatments	Phosphatase at different intervals after spraying (µg P-NP g^{-1} soil hr^{-1})							
	3 DAS		5 DAS		10 DAS		15 DAS	
	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower
Flubendiamide 39.35 % SC	90.23	69.19	45.30	39.22	65.40	59.50	70.31	61.47
Chlorantraniliprole 18.5 % SC	65.31	58.23	40.55	41.95	55.59	60.18	67.36	61.78
Indoxacarb 14.5 % SC	48.15	50.75	34.88	35.41	30.40	32.84	23.71	26.63
Dimethoate 30 % EC	75.63	69.22	73.75	67.22	29.94	57.55	20.32	48.38
Fipronil 5% SC	55.63	53.02	47.09	49.29	53.51	42.49	60.24	33.47
Thiamethoxam 25 % WG	95.34	82.07	63.40	66.70	53.68	63.47	42.14	53.04
Emamectin benzoate 5% SG	80.41	73.74	54.24	48.38	44.75	46.45	33.74	45.98
Acetamiprid 20 % SP	63.63	59.23	53.65	57.52	48.08	54.39	35.18	47.46
Quinalphos 25% EC	58.46	46.48	36.98	32.46	34.38	27.78	25.21	23.25
Cypermethrin 10 % EC	95.73	93.81	62.10	73.19	33.55	66.75	22.83	57.79
Control	110.28	95.67	110.28	95.67	110.28	95.67	110.28	95.67
CD (0.05)	0.966	0.301	1.240	0.383	1.799	1.242	1.395	0.375
SEM	0.327	0.102	0.420	0.129	0.609	0.421	0.472	0.127

DAS- Days after spraying

After five days of spraying, all treatments were significantly different from control (95.67) in cauliflower. Higher enzyme activity was recorded in cypermethrin (73.19) followed by dimethoate (67.22), thiamethoxam (66.70), acetamiprid (57.52), fipronil (49.29), emamectin benzoate (43.38), chlorantraniliprole (41.95), flubendiamide (39.22) and indoxacarb (35.41). The lowest enzyme activity was recorded in quinalphos (32.46) treated plot.

Phosphatase activity in cabbage after ten days of spraying showed that, all treatments were significantly different from control (110.28 μg P-NP g^{-1} soil hr^{-1}). Higher enzyme activity was reported in the plots treated with flubendiamide (65.40) followed by chlorantraniliprole (55.59), thiamethoxam (53.68), fipronil (53.51), acetamiprid (48.08), emamectin benzoate (44.75), quinalphos (34.38), cypermethrin (33.55), indoxacarb (30.40) and the lowest enzyme activity was recorded in dimethoate (29.94) treated plot.

In cauliflower plots, all treatments were significantly different from control (95.67) after ten days of spraying. Higher enzyme activity was reported in the plots treated with cypermethrin (66.75) followed by thiamethoxam (63.47), chlorantraniliprole (60.18), flubendiamide (59.50), dimethoate (57.55), acetamiprid (54.39), emamectin benzoate (46.45), fipronil (42.49), indoxacarb (32.84) and the lowest activity was recorded for quinalphos (27.78) and it was statistically different from all others.

More or less similar trend was observed after fifteenth day of spraying in cabbage. The highest phosphatase enzyme activity was recorded in control plots (110.28) which differed significantly from all other treatments. Higher enzyme activity was recorded for flubendiamide (70.31), chlorantraniliprole (67.36), fipronil (60.24), thiamethoxam (42.14), acetamiprid (35.18), emamectin benzoate (33.74), quinalphos (25.21), indoxacarb (23.71) and cypermethrin (22.83). The lowest enzyme activity was recorded in dimethoate (20.32) treated plots.

In cauliflower, all treatments were significantly different from control (95.67). Higher enzyme activity was reported in the plots treated with chlorantraniliprole (61.78) and flubendiamide (61.47) which were on par with each other followed by cypermethrin (57.79), thiamethoxam (53.04), dimethoate (48.38), acetamiprid (47.46), emamectin benzoate (45.98), fipronil (33.47) and indoxacarb (26.63). The lowest enzyme activity was recorded in quinalphos (23.25).

4.4.5 Effect of Dehydrogenase Activity under Plains

Dehydrogenase enzyme activity in cabbage and cauliflower under plains are represented in Table 37. Dehydrogenase enzyme activity is expressed in µg TPF hydrolyzed g^{-1}soil 24 hr^{-1}.

Significantly the highest dehydrogenase enzyme activity was recorded in control plots (46.26) in cabbage plots on three days after application of insecticides which was on par with acetamiprid (46.10) followed by flubendiamide (45.55), cypermethrin (45.48), dimethoate (45.06), chlorantraniliprole (41.62), emamectin benzoate (39.48), fipronil (37.61), quinlaphos (36.44) and thiamethoxam (35.68). The lowest enzyme activity was recorded in treated plot indoxacarb (35.28) treated plot.

On third day after spraying in cauliflower, the highest dehydrogenase enzyme activity was recorded in control plots (46.63) which differed significantly from all other treatments. Higher enzyme activity was recorded for acetamiprid (43.98) and cypermethrin (43.31) which was on par with each other followed by thiamethoxam (40.78), chlorantraniliprole (40.65), flubendiamide (40.49), dimethoate (40.47), quinalphos (40.32), emamectin benzoate (39.15), fipronil (37.74). The lowest enzyme activity was recorded in indoxacarb (36.19) treated plots.

In cabbage, after five days of spraying, all treatments were significantly different from control (46.26). Higher enzyme activity was recorded in acetamiprid (40.64) followed by cypermethrin (39.32), dimethoate (39.31), flubendiamide (38.54), emamectin benzoate (36.55), thiamethoxam (34.33),

Table 37. Effect of insecticides on dehydrogenase activity in soils of cabbage and cauliflower grown under plains

Treatments	Dehydrogenase at different intervals (µg TPF hydrolyzed g^{-1} soil $24hr^{-1}$)							
	3 DAS		5 DAS		10 DAS		15 DAS	
	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower
Flubendiamide 39.35 % SC	45.55	40.49	38.54	37.45	34.37	30.10	23.85	22.10
Chlorantraniliprole 18.5 % SC	41.62	40.65	33.68	35.15	31.13	32.48	19.05	21.77
Indoxacarb 14.5 % SC	35.28	36.19	32.36	30.74	26.36	23.81	14.72	18.13
Dimethoate 30 % EC	45.06	40.47	39.31	33.70	37.71	28.27	19.60	18.35
Fipronil 5% SC	37.61	37.74	31.52	31.17	24.58	25.74	15.80	19.54
Thiamethoxam 25 % WG	35.68	40.78	34.33	36.06	25.23	28.84	18.34	21.56
Emamectin benzoate 5% SG	39.48	39.15	36.55	33.29	33.70	25.68	26.19	20.24
Acetamiprid 20 % SP	46.10	43.98	40.64	38.35	32.38	32.45	30.40	28.36
Quinalphos 25% EC	36.44	40.32	32.51	35.33	29.60	25.13	20.26	22.32
Cypermethrin 10 % EC	45.48	43.31	39.32	40.06	37.27	34.91	31.32	29.67
Control	46.26	46.63	46.26	46.63	46.26	46.63	46.26	46.63
CD (0.05)	0.589	1.270	0.359	0.661	0.414	1.460	0.396	0.777
SEM	0.199	0.430	0.121	0.224	0.140	0.494	0.134	0.263

DAS- Days after spraying

chlorantraniliprole (33.68), quinalphos (32.51) and indoxacarb (32.36). The lowest enzyme activity was recorded in fipronil (31.52).

After five days of spraying, all treatments were significantly different from control (46.63) in cauliflower. Higher enzyme activity was recorded in cypermethrin (40.06) followed by acetamiprid (38.35), flubendiamide (37.45), thiamethoxam (36.06), quinalphos (35.33), chlorantraniliprole (35.15), dimethoate (33.70), emamectin benzoate (33.29), fipronil (31.17). The lowest enzyme activity was recorded in and indoxacarb (30.74) treated plot.

More or less similar trend was observed on tenth day after spraying in cabbage, highest dehydrogenase enzyme activity was recorded in control plots (46.26) which differed significantly from all other treatments. Higher enzyme activity was recorded for dimethoate (37.71) followed by cypermethrin (37.27), flubendiamide (34.37), emamectin benzoate (33.70), acetamiprid (32.38), chlorantraniliprole (31.13), quinalphos (29.60), indoxacarb (26.36) and thiamethoxam (25.23). The lowest enzyme activity was recorded in fipronil (24.58).

The highest dehydrogenase enzyme activity was recorded in control plots (46.63) which differed significantly from all other treatments on tenth day after spraying in cauliflower. Higher enzyme activity was recorded for cypermethrin (34.91), chlorantraniliprole (32.48), acetamiprid (32.45), flubendiamide (30.10), thiamethoxam (28.84), dimethoate (28.27), fipronil (25.74), emamectin benzoate (25.68) and quinalphos (25.13). The lowest enzyme activity was recorded in indoxacarb (23.81) treated plots.

After fifteenth days of spraying in cabbage plots, all treatments were significantly different from control (46.26). Significantly higher enzyme activity was reported in the plots treated with cypermethrin (31.32) followed by acetamiprid (30.40), emamectin benzoate (26.19), flubendiamide (23.85), quinalphos (20.26), dimethoate (19.60), chlorantraniliprole (19.05), thiamethoxam

(18.34) and fipronil (15.80). The lowest enzyme activity was recorded in indoxacarb (14.72).

In cauliflower, all treatments were significantly different from control (46.63) after 15 days of spraying. Higher enzyme activity was reported in the plots treated with cypermethrin (29.67) followed by acetamiprid (28.36), quinalphos (22.32), flubendiamide (22.10), chlorantraniliprole (21.77), thiamethoxam (21.56), emamectin benzoate (20.24) and fipronil (19.54) and which was on par with dimethoate (18.35). The lowest enzyme activity was recorded in indoxacarb (18.13).

4.4.6 Effect of Dehydrogenase Activity under Hills

Dehydrogenase enzyme activity in cabbage and cauliflower under hills are represented in Table 38 Dehydrogenase enzyme activity is expressed in µg TPF hydrolyzed g^{-1}soil 24 hr^{-1}.

After third day of spraying in cabbage plots, all treatments were significantly different from control (48.56). Significantly higher enzyme activity was reported in the plots treated with dimethoate (46.16) and acetamiprid (46.09) which were on par with each other followed by cypermethrin (44.16), flubendiamide (43.44), quinalphos (43.02), emamectin benzoate (42.63), fipronil (41.15), chlorantraniliprole (38.90), indoxacarb (38.90). The lowest enzyme activity was recorded in thiamethoxam (38.85).

The highest dehydrogenase enzyme activity was recorded in control plots (43.65) which differed significantly from all other treatments third day after spraying in cauliflower. Higher enzyme activity was recorded for acetamiprid (41.82) and flubendiamide (41.41) which were on par with each other followed by cypermethrin (41.10), chlorantraniliprole (39.95), dimethoate (37.06), emamectin benzoate (36.53), thiamethoxam (36.44), quinalphos (35.84) and fipronil (34.61), The lowest enzyme activity was recorded in indoxacarb (33.12) treated plots.

In cabbage, after five days of spraying, all treatments were significantly different from control (48.56). Higher enzyme activity was recorded in

Table 38. Effect of insecticides on dehydrogenase activity in soils of cabbage and cauliflower grown under hills

Treatments	Dehydrogenase at different intervals (µg TPF hydrolyzed g^{-1} soil $24hr^{-1}$)							
	3 DAS		3 DAS		3 DAS		3 DAS	
	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower	Cabbage	Cauliflower
Flubendiamide 39.35 % SC	43.44	41.41	34.88	35.36	27.69	28.70	20.15	20.12
Chlorantraniliprole 18.5 % SC	38.90	39.95	35.33	33.34	33.51	31.15	22.37	20.38
Indoxacarb 14.5 % SC	38.90	33.12	33.25	28.25	28.67	20.44	17.51	13.48
Dimethoate 30 % EC	46.16	37.06	40.67	29.47	36.97	26.30	21.45	18.22
Fipronil 5% SC	41.15	34.61	33.19	30.19	25.73	25.09	19.26	17.40
Thiamethoxam 25 % WG	38.85	36.44	35.32	33.43	26.36	27.05	20.75	19.27
Emamectin benzoate 5% SG	42.63	36.53	36.53	34.69	32.37	31.75	28.78	27.25
Acetamiprid 20 % SP	46.09	41.82	43.36	38.22	35.33	33.65	31.16	28.55
Quinalphos 25% EC	43.02	35.84	34.64	30.02	30.45	27.24	23.83	19.51
Cypermethrin 10 % EC	44.16	41.10	37.05	40.26	33.99	36.21	29.06	29.73
Control	48.56	43.65	48.56	43.65	48.56	43.65	48.56	43.65
CD (0.05)	1.051	0.545	1.041	0.395	0.652	0.427	0.791	0.516
SEM	0.356	0.184	0.352	0.133	0.221	0.144	0.268	0.174

DAS- Days after spraying

acetamiprid (43.36) followed by dimethoate (40.67), cypermethrin (37.05), emamectin benzoate (36.53), chlorantraniliprole (35.33), thiamethoxam (35.32), flubendiamide (34.88), quinalphos (34.64), indoxacarb (33.25). The lowest enzyme activity was recorded in fipronil (33.19).

After five days of spraying, all treatments were significantly different from control (43.65). Higher enzyme activity was recorded in cypermethrin (40.26), acetamiprid (38.22), flubendiamide (35.36), emamectin benzoate (34.67), thiamethoxam (33.43), chlorantraniliprole (33.34), fipronil (30.19). The lowest enzyme activity was recorded in followed by quinalphos (29.47) treated plot.

After tenth day of spraying in cabbage plots, all treatments were significantly different from control (48.56). Higher enzyme activity was reported in the plots treated with dimethoate (36.97) followed by acetamiprid (35.33), cypermethrin (33.99) chlorantraniliprole (33.51), emamectin benzoate (31.75), quinalphos (30.45), indoxacarb (28.67), flubendiamide (27.69), thiamethoxam (26.36). The lowest enzyme activity was recorded in fipronil (25.73).

All treatments were significantly different from control (43.65) in cauliflower after tenth day of spraying. Higher enzyme activity was reported in the plots treated with cypermethrin (36.21) followed by acetamiprid (33.65), emamectin benzoate (33.65), chlorantraniliprole (31.15), flubendiamide (28.70), quinalphos (27.24), thiamethoxam (27.05), dimethoate (26.30), fipronil (25.09). The lowest enzyme activity was recorded in indoxacarb (20.44).

After fifteenth days of spraying in cabbage plots, all treatments were significantly different from control (48.56). Higher enzyme activity was reported in the plots treated with acetamiprid (31.16) followed by cypermethrin (29.06), emamectin benzoate (28.78), quinalphos (23.83), chlorantraniliprole (22.37), dimethoate (21.45), thiamethoxam (20.75), flubendiamide (20.15) and fipronil (19.26). The lowest enzyme activity was recorded in indoxacarb (17.51).

In cauliflower, all treatments were significantly different from control (43.65) after fifteen days of spraying. Higher enzyme activity was reported in the plots treated with cypermethrin (29.73), acetamiprid (28.55), emamectin benzoate (27.25), chlorantraniliprole (20.38), flubendiamide (20.12), quinalphos (19.51), thiamethoxam (19.27), dimethoate (18.22), and fipronil (17.40).The lowest enzyme activity was recorded in indoxacarb (13.48).

4.5 ESTIMATION OF PESTICIDE RESIDUES IN COOKED SAMPLES OF CABBAGE AND CAULIFLOWER

Insecticides selected for experiment on extent of removal of residues through cooking in cabbage and cauliflower are presented in Table 39.

Table 39. Insecticides selected for estimation of pesticide residues in cooked samples

Cabbage		Cauliflower	
Plains	Hills	Plains	Hills
Quinalphos	Quinalphos	Chlorantraniliprole	Flubendiamide
Acetamiprid	Cypermethrin	Flubendiamide	Cypermethrin
Flubendiamide	Flubendiamide	Dimethoate	Quinalphos

The results on the effect of cooking in removal of pesticide residues from cabbage and cauliflower under plains and hills are presented in Table 40 and 41.

4.5.1 Cabbage

4.5.1.1 *Plains*

The highest per cent removal of pesticide residues after cooking was recorded in cabbage treated with quinalphos (54.79) followed by flubendiamide (51.54) and acetamiprid (38.91) and they were significantly different from each other.

The highest removal of pesticides was recorded in cabbage after 15 min. of cooking (54.78%) followed by 10 min. (47.97 %) and 5 min. (42.48 %) after cooking and they were significantly different.

The data on interactive effect of insecticides in different cooking time revealed that flubendiamide and quinalphos treated cabbage cooked for 15 min showed the higher percentage removal of 60.11 and 58.33 respectively which were on par with each other followed by quinalphos after 10 min. of cooking (56.24%). Per cent removal of quinalphos after 5 min. and flubendiamide after 10 min. of cooking recorded 49.80 and 49.30 and which were found to be on par with eachother. The lowest per cent removal was recorded in acetamiprid (32.44) treated cabbage after 5 min. of cooking. The per cent removal of acetamiprid after 15 min. (45.90), flubendiamide after 5 min. of cooking (45.20) and acetamiprid 10 min. cooking (38.39) were statistically on par with each other.

4.5.1.2 *Hills*

The highest removal of pesticide residues after cooking was observed in cabbage in hills treated with cypermethrin (66.47 %) which was significantly higher than all others. It was followed by flubendiamide (55.34%) and quinalphos (41.76 %) and they were significantly different.

By considering the time taken for the removal of pesticides, the highest removal of pesticides was recorded in cabbage after 15 min. of cooking (62.16 %) followed by 10 min. (53.93%) and 5 min. (47.47%) after cooking and they were significantly different.

The results of the interaction effect showed that the highest percentage removal of pesticide was noticed in cabbage treated with cypermethrin for 15 min. (71.16) after cooking which was significantly different from flubendiamide after 15 min. (67.57) of cooking followed by cypermethrin cooked for 10 min. (65.39) . The lowest per cent removal was recorded in quinalphos cooked for 5 min. (32.30) followed by 10 min of cooking (45.24). per cent removal of pesticides after cooking showed that 5 min. cooking removed 62.85 per cent of

Table 40. Effect of cooking in removal of pesticide residues from cabbage under plains and hills

Plains		Hills	
Treatments	Removal of pesticide residues (%)	Treatments	Removal of pesticide residues (%)
Quinalphos (A1)	54.79	Quinalphos (C1)	41.76
Acetamiprid (A2)	38.91	Cypermethrin (C2)	66.47
Flubendiamide (A3)	51.54	Flubendiamide (C3)	55.34
CD 0.05	2.100	CD 0.05	0.998
SEM	0.701	SEM	0.333
5 min. cooking (B1)	42.48	5 min. cooking (D1)	47.47
10 min. cooking (B2)	47.97	10 min. cooking (D2)	53.93
15 min. cooking (B3)	54.78	15 min. cooking (D3)	62.16
CD 0.05	2.100	CD 0.05	0.998
SEM	0.701	SEM	0.333
A1B1	49.80	C1D1	32.30
A1B2	56.24	C1D2	45.24
A1B3	58.33	C1D3	47.73
A2B1	32.44	C2D1	62.85
A2B2	38.39	C2D2	65.39
A2B3	45.90	C2D3	71.16
A3B1	45.20	C3D1	47.27
A3B2	49.30	C3D2	51.17
A3B3	60.11	C3D3	67.57
CD 0.05	3.637	CD 0.05	1.728
SEM	1.215	SEM	0.577

cypermethrin, 10 mn. Cooking removed 51.17 per cent of flubendiamide, 15 min. cooking removed 47.73 per cent of quinalphos and 5 min. cooking removed 47.27 per cent of flubendiamide in cabbage.

4.5.2 Cauliflower

4.5.2.1 *Plains*

The highest per cent removal of pesticide was noticed in cauliflower treated with chlorantraniliprole (44.78) followed by flubendiamide (43.65) and dimethoate (41.34) and they were significantly differed from each other.

The data on removal of insecticides after different time of cooking revealed that the highest removal of pesticides was recorded in cauliflower curds after 15 min. of cooking (56.35 %) followed by 10 min. (43.30 %) and 5 min. (30.13 %) of cooking and they were significantly different.

The data on the interactive effects of insecticides and time of cooking revealed that cooking at 15 min. removed 59.33 per cent of chlorantraniliprole followed by dimethoate at 15 min. cooking (57.93 %) and they were statistically on par. 15 min. cooking removed 51.79 per cent of flubendiamide. 10 min cooking removed 44.59 per cent of flubendiamide, 44.02 per cent dimethoate and 41.28 per cent chlorantraniliprole. However, 5 min. cooking removed only 34.58 per cent of flubendiamide, 33.73 per cent of chlorantraniliprole and 22.67 per cent of dimethoate in cauliflower.

Per cent removal of pesticide after cooking showed that 5 min. cooking removed 62.85 of cypermethrin, 10 min. cooking removed 51.17 of flubendiamide, 15 min. cooking removed 47.73 of quinalphos and 5 min. cooking removed 47.27 of flubendiamide in cabbage.

4.5.2.2 *Hills*

The highest per cent removal of pesticide was noticed in cauliflower treated with cypermethrin (52.32) followed by quinalphos (47.43), flubendiamide (44.59) and they were significantly different.

Table 41. Effect of cooking in removal of pesticide residues from cauliflower under plains and hills

Plains		Hills	
Treatments	Removal of pesticide residues (%)	Treatments	Removal of pesticide residues (%)
Chlorantraniliprole (E1)	44.78	Flubendiamide (G1)	44.59
Flubendiamide (E2)	43.65	Cypermethrin (G2)	52.32
Dimethoate (E3)	41.34	Quinalphos (G3)	47.43
CD 0.05	1.313	CD 0.05	0.966
SEM	0.438	SEM	0.322
5 min. cooking (F1)	30.13	5 min. cooking (H1)	38.43
10 min. cooking (F2)	43.30	10 min. cooking (H2)	47.96
15 min. cooking (F3)	56.35	15 min. cooking (H3)	57.95
CD 0.05	1.313	CD 0.05	0.966
SEM	0.438	SEM	0.322
E1F1	33.73	G1H1	36.33
E1F2	41.28	G1H2	43.42
E1F3	59.33	G1H3	54.02
E2F1	34.58	G2H1	42.49
E2F2	44.59	G2H2	52.24
E2F3	51.79	G2H3	62.23
E3F1	22.67	G3H1	36.48
E3F2	44.02	G3H2	48.22
E3F3	57.93	G3H3	59.60
CD 0.05	2.274	CD 0.05	1.672
SEM	0.759	SEM	0.559

Considering time of cooking, the highest removal of pesticides was recorded in cauliflower after 15 min. of cooking (57.95 %) followed by 10 min. (47.96 %) and 5 min. (38.43 %) of cooking and they were significantly different.

The data on interactive effect in removal of insecticides and time of cooking showed that the highest percentage removal of pesticide was noticed in cauliflower treated with cypermethrin cooked at 15 min. (62.23) followed by quinalphos at 15 min. (59.60) , flubendiamide at 15 min. (54.02), cypermethrin at 10 min. (52.24), quinalphos at 15 min. (48.22), cypermethrin at 5 min. (54.02). Lower per cent removal was recorded in quinalphos (36.48) and flubendiamide (36.33) cooked at 5 min. which were on par with each other.

4.6 EVALUATION OF "VEGGIE WASH" FOR THE REMOVAL OF PESTICIDE RESIDUES IN CABBAGE AND CAULIFLOWER

4.6.1 Cabbage

The result on the removal of pesticide residue from cabbage after treating with "Veggie Wash" at different intervals is presented in Table 42

On first day after spraying, the highest per cent removal was recorded in flubendiamide treated cabbage (41.09) dipped in Veggie Wash for 10 min. followed by flubendiamide treated cabbage dipped in water for 10 min. (36.33) and they were significantly different. Per cent removal of chlorantraniliprole after Veggie Wash treatment was 34.46 as compared to water dip (31.23). Significantly higher removal of indoxacarb was observed in Veggie Wash dipped cabbage (32.15) than water dipped cabbage (30.23 %). Per cent removal of fipronil was 31.46 after treating with Veggie Wash and it was 25.22 when treated with water. Per cent removal of quinalphos after Veggie Wash treatment was 38.60 as compared to water dip (36.94). Per cent removal of cypermethrin was 34.52 after treating with Veggie Wash and it was 29.98 when treated with water wash. Per cent removal of acetamiprid after Veggie Wash treatment was 38.79 as compared to water dip (34.52). Per cent removal of thiamethoxam after Veggie Wash treatment was 35.24 as compared to water dip (28.11). Significantly higher

Table 42. Evaluation of Veggie Wash in removal of pesticide residues from cabbage at different intervals

Treatments	Removal of insecticides (%)									
	1DAS		3DAS		5DAS		7DAS		10DAS	
	Veggie wash	Water washing	Veggie wash	Water washing	Veggie wash	Water washing	Veggie wash	Water washing	Veggie wash	Water washing
Chlorantraniliprole	34.46	31.23	35.82	26.55	32.29	25.86	*	*	*	*
Flubendiamide	41.09	36.33	39.21	35.24	37.46	32.95	38.09	32.29	41.78	35.24
Indoxacarb	32.15	30.23	33.88	31.07	32.83	29.00	*	*	*	*
Fipronil	31.46	25.22	29.98	21.75	*	*	*	*	*	*
Quinalphos	38.60	36.94	41.39	37.41	42.04	39.09	39.54	36.99	*	*
Cypermethrin	34.52	29.98	33.97	29.98	33.19	27.96	*	*	*	*
Acetamiprid	38.79	34.52	36.43	32.82	33.67	28.69	*	*	*	*
Thiamethoxam	35.24	28.11	36.67	27.55	35.24	29.61	*	*	*	*
Dimethoate	40.47	38.38	40.41	36.20	42.01	38.67	41.53	36.85	*	*
CD (0.05)	0.598									
SEM	0.214									

DAS - Days after spraying, * Residues of insecticide residue was BDL removal of dimethoate was observed in Veggie Wash dipped cabbage (40.47) than water dipped cabbage (38.38 per cent).

After three days of spraying, the highest per cent removal was recorded in quinalphos treated cabbage (41.39) dipped in Veggie Wash for 10 min. followed by quinalphos treated cabbage dipped in water for 10 min. (37.41) and they were significantly different. Per cent removal of chlorantraniliprole after Veggie Wash treatment was 35.82 as compared with water dip (26.55). Significantly higher removal of indoxacarb was observed in Veggie Wash dipped cabbage (33.88) than water dipped cabbage (31.07 per cent). Per cent removal of fipronil after Veggie Wash treatment was 29.98 as compared with water dip (21.75). Per cent removal of cypermethrin after Veggie Wash treatment was 33.97 as compared with water dip (29.98). Significantly higher removal of acetamiprid was observed in Veggie Wash dipped cabbage (36.43) than water dipped cabbage (32.82 per cent). Significantly higher removal of thiamethoxam was observed in Veggie Wash dipped cabbage (36.67) than water dipped cabbage (27.55 per cent). Per cent removal of dimethoate after Veggie Wash treatment was 40.41 as compared with water dip (36.20).

On fifth days after spraying, the highest per cent removal was recorded in quinalphos treated cabbage (42.04) dipped in Veggie Wash for 10 min. followed by quinalphos treated cabbage dipped in water for 10 min. (39.09) and they were significantly different. Per cent removal of chlorantraniliprole after Veggie Wash treatment was 32.29 as compared with water dip (25.86). Significantly higher removal of flubendiamide was observed in Veggie Wash dipped cabbage (37.46) than water dipped cabbage (32.95 per cent). Significantly higher removal of indoxacarb was observed in Veggie Wash dipped cabbage (32.83) than water dipped cabbage (29.00 per cent). Per cent removal of cypermethrin after Veggie Wash treatment was 33.19 as compared with water dip (27.96). Per cent removal of acetamiprid after Veggie Wash treatment was 33.67 as compared with water dip (28.69). Significantly higher removal of thiamethoxam was observed in Veggie Wash dipped cabbage (35.24 %) than water dipped cabbage (29.61 %).

Significantly higher removal of dimethoate was observed in Veggie Wash dipped cabbage (42.01) than water dipped cabbage (38.67 per cent).

After seven days of spraying, the highest per cent removal was recorded in dimethoate treated cabbage (41.53) dipped in Veggie Wash for 10 min. followed by dimethoate treated cabbage dipped in water for 10 min. (36.85) and they were significantly different. Per cent removal of quinalphos after Veggie Wash treatment was 39.54 as compared with water dip (36.99). Significantly higher removal of flubendiamide was observed in Veggie Wash dipped cabbage (38.09 %) than water dipped cabbage (32.29 %).

On tenth days after spraying, the per cent removal was recorded in chlorantraniliprole treated cabbage (41.78) dipped in Veggie Wash for 10 min. followed by chlorantraniliprole treated cabbage dipped in water for 10 min. (35.24) and they were significantly different.

The consolidated results on the evaluation of Veggie Wash in removal of residues from cabbage over different intervals are presented in Table 43.

The result showed that per cent removal of insecticides after dipping in Veggie Wash was in the range of 12.29 to 39.35 per cent. However, the per cent removal of insecticides after dipping in water was in the range of 9.39 to 34.41.

The highest per cent removal was recorded in flubendiamide treated cabbage (39.35) after dipped in Veggie Wash for 10 min. followed by flubendiamide treated cabbage dipped in water for 10 min. (34.41) and they were significantly different. Statistically higher removal of chlorantraniliprole was observed in Veggie Wash treated cabbage (20.51 %) than water dipped cabbage (16.73 %) Significantly higher removal of indoxacarb was observed in Veggie Wash dipped cabbage (19.77) than water dipped cabbage (16.73 %). Similar trend was observed in fipronil sprayed cabbage. Per cent removal of fipronil was 12.29 after treated with Veggie Wash and it was 9.39 after wash. In quinalphos sprayed cabbage, per cent removal was 32.32 in Veggie Wash followed by water wash (30.08). Per cent removal of cypermethrin after Veggie Wash treatment was 20.33

Table 43 Evaluation of veggie wash in removal of residues from cabbage

Treatments	Removal of insecticides (%)	
	Dipping in veggie wash for 10 min.	Dipping in water for 10 min.
Chlorantraniliprole	20.51	16.73
Flubendiamide	39.53	34.41
Indoxacarb	19.77	18.06
Fipronil	12.29	9.39
Quinalphos	32.32	30.08
Cypermethrin	20.33	17.58
Acetamiprid	21.77	19.20
Thiamethoxam	21.43	17.05
Dimethoate	32.88	30.02
CD	0.267	
SEM	0.068	

as compared with water dip (17.58). Significantly higher removal of acetamiprid was observed in Veggie Wash treated cabbage (21.77) than water wash (19.20) and they were significantly different. Per cent removal of thiamethoxam was 21.43 after treating with Veggie Wash and it was 17.05 when treated with water wash. Statistically higher removal of dimethoate was observed in Veggie Wash treated cabbage (32.88) than water dipped cabbage (30.02).

4.6.2 Cauliflower

The result on the removal of pesticide residue from cauliflower after treating with "Veggie Wash" at different intervals is presented in Table 44.

On first day after spraying, the highest per cent removal was recorded in quinalphos treated cauliflower (38.86) after dipped in Veggie Wash followed by after dipped in water for 10 min. (36.15) and they were significantly different. Per cent removal of chlorantraniliprole was 33.54 after treating with Veggie Wash and it was 31.19 when treated with water wash. Statistically higher removal of flubendiamide was observed in Veggie Wash treated cauliflower (32.50 %) than water dipped cauliflower (31.00 %). Per cent removal of indoxacarb after Veggie Wash treatment was 34.77 as compared with water dip (31.87). Significantly higher removal of fipronil was observed in Veggie Wash dipped cauliflower (34.68 %) than water dipped cauliflower (32.96 %). Statistically higher removal of cypermethrin was observed in Veggie Wash treated cauliflower (36.85 %) than water dipped cabbage (31.93 %). Per cent removal of acetamiprid was 37.74 after treating with Veggie Wash and it was 33.97 when treated with water wash. Statistically higher removal of thiamethoxam was observed in Veggie Wash treated cauliflower (36.54 %) than water dipped cauliflower (30.51 %). Per cent removal of dimethoate was 36.10 after treating with Veggie Wash and it was 27.33 when treated with water wash.

After three days of spraying, the highest per cent removal was recorded in thiamethoxam treated cauliflower (38.70) dipped in Veggie Wash followed by after dipped in water for 10 min. (36.12) and they were significantly different.

Significantly higher removal of chlorantraniliprole was observed in Veggie Wash dipped cauliflower (37.06 %) than water dipped cauliflower (34.00 %). Per cent removal of flubendiamide was 32.55 after treating with Veggie Wash and it was 30.74 when treated with water wash. Per cent removal of indoxacarb was 35.04 after treating with Veggie Wash and it was 32.82 when treated with water wash. Statistically higher removal of fipronil was observed in Veggie Wash treated cauliflower (37.07 %) than water dipped cauliflower (32.90 %). Statistically higher removal of cypermethrin was observed in Veggie Wash treated cauliflower (38.55 %) than water dipped cauliflower (31.78 %). Per cent removal of acetamiprid was 35.87 after treating with Veggie Wash and it was 32.00 when treated with water wash. Per cent removal of dimethoate was 34.96 after treating with Veggie Wash and it was 31.19 when treated with water wash.

After five days of spraying the highest per cent removal was recorded in thiamethoxam treated cauliflower (38.56) dipped in Veggie Wash followed by after dipped in water for 10 min. (31.78) and they were significantly different. Per cent removal of chlorantraniliprole was 33.08 after treating with Veggie Wash and it was 29.27 per cent when treated with water wash. Per cent removal of flubendiamide was 31.95 after treating with Veggie Wash and it was 30.38 when treated with water wash. Statistically higher removal of indoxacarb was observed in Veggie Wash treated cauliflower (33.19 %) than water dipped cauliflower (31.16 %). Per cent removal of fipronil after Veggie Wash treatment was 35.57 as compared with water dip (33.59). Statistically higher removal of quinalphos was observed in Veggie Wash treated cauliflower (34.96 %) than water dipped cauliflower (31.54 %). Per cent removal of cypermethrin after Veggie Wash treatment was 36.68 as compared with water dip (32.29). Per cent removal of acetamiprid was 37.46 after treating with Veggie Wash and it was 32.95 per cent when treated with water wash. Per cent removal of dimethoate was 34.05 after treating with Veggie Wash and it was 31.12 when treated with water wash.

After 7 days of spraying, the highest per cent removal was recorded in thiamethoxam treated cauliflower (37.78) dipped in Veggie Wash followed by

Table 44. Evaluation of Veggie Wash in removal of pesticide residues from cauliflower at different intervals

Treatments	Removal of insecticides (%)									
	1DAS		3DAS		5DAS		7DAS		10DAS	
	Veggie wash	Water washing	Veggie wash	Water washing	Veggie wash	Water washing	Veggie wash	Water washing	Veggie wash	Water washing
Chlorantraniliprole	33.54	31.19	37.06	34.00	33.08	29.27	34.47	30.91	33.97	29.98
Flubendiamide	32.50	31.00	32.55	30.74	31.95	30.38	33.97	32.01	34.89	31.66
Indoxacarb	34.77	31.87	35.04	32.82	33.19	31.16	*	*	*	*
Fipronil	34.68	32.96	37.07	32.90	35.57	33.59	34.17	30.84	*	*
Quinalphos	38.86	36.15	35.66	32.48	34.96	31.54	37.06	34.31	39.89	30.95
Cypermethrin	36.85	31.93	38.55	31.78	36.68	32.29	35.24	28.10	*	*
Acetamiprid	37.74	33.97	35.87	32.00	37.46	32.95	37.74	32.95	*	*
Thiamethoxam	36.54	30.51	38.70	36.12	38.56	31.78	37.78	33.97	38.14	31.46
Dimethoate	36.10	27.33	34.96	31.19	34.05	31.12	33.54	30.59	37.80	36.29
CD 0.05	0.693									
SEM	0.248									

DAS- Days after spraying, * Residues of insecticide residue was BDL after dipped in water for 10 min. (33.97) and they were significantly different. Per cent removal of chlorantraniliprole after Veggie Wash treatment was 34.47 as compared with water dip (30.91). Statistically higher removal of flubendiamide was observed in Veggie Wash treated cauliflower (33.97 %) than water dipped cauliflower (32.01 %). Per cent removal of fipronil after Veggie Wash treatment was 34.17 as compared with water dip (30.84). Statistically higher removal of quinalphos was observed in Veggie Wash treated cauliflower (37.06 %) than water dipped cauliflower (34.31 %). Per cent removal of cypermethrin was 35.24 after treating with Veggie Wash and it was 28.10 when treated with water wash. Significantly higher removal of acetamiprid was observed in Veggie Wash treated cauliflower (37.74 %) than water wash (32.95 %) and they were significantly different. Per cent removal of dimethoate was 33.54 after treating with Veggie Wash and it was 30.59 when treated with water wash.

On tenth day after spraying, the highest per cent removal was recorded in quinalphos treated cauliflower (39.89) dipped in Veggie Wash followed by after dipped in water for 10 min. (30.95) and they were significantly different. Per cent removal of chlorantraniliprole was 33.97 after treating with Veggie Wash and it was 29.98 when treated with water wash. Per cent removal of flubendiamide was 34.89 after treating with Veggie Wash and it was 31.66 when treated with water wash. Significantly higher removal of thiamethoxam was observed in Veggie Wash treated cauliflower (38.14 %) than water wash (31.46 %) and they were significantly different. Per cent removal of dimethoate was 37.80 after treating with Veggie Wash and it was 36.29 when treated with water wash.

The overall results on the evaluation of Veggie Wash in removal of residues from cauliflower over different intervals is presented in Table 45

The highest per cent removal was recorded in thiamethoxam treated cauliflower after dipped in Veggie Wash (37.94) followed by thiamethoxam treated cauliflower dipped in water for 10 min. (32.77) and they were significantly different. Per cent removal of chlorantraniliprole after Veggie Wash treatment was 34.57 as compared with water dip (31.07). Significantly higher removal of

Table 45. Evaluation of Veggie Wash in removal of residues from cauliflower

Treatments	Removal of insecticides (%)	
	Dipping in veggie wash for 10 min.	Dipping in water for 10 min.
Chlorantraniliprole	34.57	31.07
Flubendiamide	33.17	31.16
Indoxacarb	20.60	19.26
Fipronil	28.29	26.06
Quinalphos	37.29	33.09
Cypermethrin	29.46	24.82
Acetamiprid	29.76	26.58
Thiamethoxam	37.94	32.77
Dimethoate	35.29	31.30
CD	0.310	
SEM	0.111	

flubendiamide was observed in Veggie Wash treated cauliflower (33.17 %) than water wash (31.16 %) and they were significantly different. Significantly higher removal of indoxacarb was observed in Veggie Wash dipped cauliflower (20.60 %) than water dipped cauliflower (19.26 %). Per cent removal of fipronil was 28.29 after treating with Veggie Wash and it was 26.06 when treated with water wash. Per cent removal of quinalphos after Veggie Wash treatment was 37.29 as compared to water dip (33.09). Significantly higher removal of cypermethrin was observed in Veggie Wash dipped cauliflower (29.46 %) than water dipped cauliflower (24.82 %). Per cent removal of acetamiprid was 29.76 after treating with Veggie Wash and it was 26.58 when treated with water wash. Statistically higher removal of dimethoate was observed in Veggie Wash treated cauliflower (35.29 %) than water dipped cabbage (31.30 %).

DISCUSSION

5. DISCUSSION

Increase in agricultural productivity can be associated with the use of fertilizers and plant protection chemicals. However, there is ample evidence that agricultural use of pesticides has a major impact on serious environmental consequences. Exposure to pesticides, both occupationally and environmentally pose a range of adverse effects. When pesticides are applied not as per the Good Agricultural Practices (GAP), pesticide residues can pose significant health risks to consumers. Among the different sources of exposure of pesticides, food appears to be the most significant, as pesticide residues are consistently detected in some food materials. Apart from spices, vegetables get maximum exposure to pesticides. Some of these residues find their way into terrestrial and aquatic food chains where they may undergo concentration and in certain cases appear to exert undesirable effects. Hence, it is essential to explore the strategies that address this situation affecting food safety, especially for the developing countries where pesticide contamination is wide spread due to indiscriminate usage. Analysis of pesticide residues differs from analysis of other chemical compounds since the residues exist in minute quantities, varying parts per million (ppm). Their concentration is likely to decline further on account of degradation, volatilization, leaching and absorption by plant and animal tissues and they may change their chemical nature inside the plants either to a more toxic or less toxic metabolites than their parent compounds.

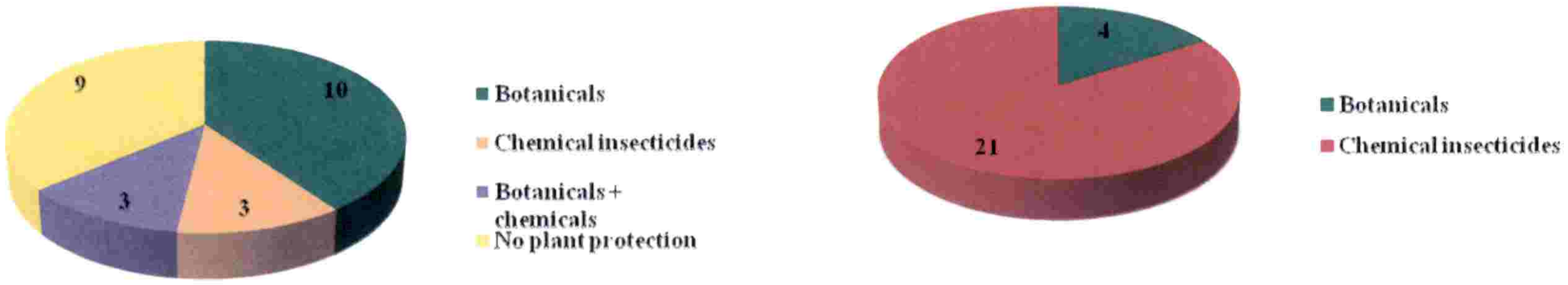
Cabbage (*B. oleracea* var. *capitata*) and cauliflower (*B. oleracea* var. *botrytis*) are the two major cole vegetables produced and consumed in India. Over the years, they have been cultivated more intensively in Kerala especially in the hilly tracts of Idukki and Wayanad districts. Of late, the cultivation of cabbage and cauliflower has extended to the plain regions of Kerala owing to the development of tropical varieties. As both these cruciferous vegetables are highly pest prone, farmers apply insecticides injudiciously to achieve the targeted yield. This often culminates in less effective management of the pests as well as deterioration of the environment. The CIBRC (Central Insecticide Board and Registration Committee), has recommended several newer pesticides with novel modes of action against the pests of cabbage and cauliflower (CIBRC, 2015). However, information on the dissipation of these insecticides on cabbage and cauliflower cultivated in different agro climatic zones *viz.*, plains and hilly regions and their impact on soil enzymes in Kerala are meagre.

5.1. PESTICIDE USE PATTERN IN CABBAGE AND CAULIFLOWER

Survey conducted among cabbage and cauliflower growers in the plains (Thiruvananthapuram district) and hills (Idukki district) of Kerala to study the extent of consumption of pesticides and their use pattern revealed that pest infestation was higher in the hills than in plains. Five species of pests *viz.*, Tobacco caterpillar (*S. litura*), diamond back moth (DBM) (*P. xylostella*), painted bug (*B. hilaris*), cabbage aphid (*L.erysimi*) and flea beetles (*P. chotanica*) were the major pests in both cabbage and cauliflower in hilly areas. The pests recorded from the crucifers in plains were Tobacco caterpillar (*S. litura*), pierid butterfly (*A. lyncida*) and painted bug (*B. hilaris*). The diamond back moth and cabbage aphids could not be detected in the plains. More or less similar findings were observed in another study conducted by GOK (2018) in Kerala. Twenty pest species were found to infest cabbage and cauliflower grown in plains and hills. *S. litura, Plusia signata, Pericallia ricini, Spilosoma obliqua, Dasychira mendosa, A. lyncida, P. chotanica, Plusia orichalia, P. brassica, H. undalis, L. erysimi* were the pest reported in this study from Thiruvananthapuram district during 2014-2018. They reported that *S. litura* was the major pest in plains and *P. xylostella* was the major pest in hills.

Cabbage and cauliflower were introduced in plains only recently but much before that they were so popular in Idukki, Wayanad and high altitudes of Palakkad districts where mild sub tropical climate conducive for the cultivation of these vegetables are available. With the development of tropical varieties of cabbage and cauliflower which can resist high temperature and humidity, their cultivation has spread to non-traditional areas of Kerala also. Agro ecosystem available in high ranges is more conducive to pests of cabbage and cauliflower since these vegetables have been cultivating for a longer period in hilly areas. Whereas in plains, the micro environment available is not favorable for the development of pests as these plants introduced recently. This may be the reason for less number of pests in plains. Sachan and Srivastava (1972) reported that high build up of larval population of DBM has been reported during February and March (late-winter) and April-August (summer and mild rainy season). However, in plains of Kerala the cultivation of cole crops will be started on August- September in plains and extended up to January- February. Hence the conducive environmental factors for the fast development of DBM do not coincide with the cultivation period in plains. Other studies showed that DBM can be found on crucifers throughout the year provided that the host crop is planted continuously. Heavy rain is also one of the important factors affecting DBM's abundance (Leu and Lee, 1984; Talekar and Lee, 1985). Ahmed and Ansari (2010) reported that favourable temperature and humidity for the development of *P. xylostella* were in the range of 24.15 to 32.91° C and 68.60 to 91.30 per cent, respectively. This temperature zone is prevailing mostly in hills than in plains.

Current study revealed that more number of farmers (10 and 12) were using botanicals in plains and less number using chemicals (3 and 2) in cabbage and cauliflower respectively. However, 21 farmers were using chemical insecticides in cabbage and cauliflower in Idukki (figure 1). Cultivation of these two cole crops has started years back in Idukki and farmers are cultivating cabbage and cauliflower as commercial crops. Hence farmers are widely using insecticides for containing pest infestation in Idukki. As these crops are the recently introduced in plain, cultivation is restricted to small holdings such as in terrace garden or in grow bags. Therefore, usage of botanicals is more prevalent in plains than in hills. Synthetic pyrethroid, fenvalerate (90.47 and 95.23 % farmers) was the most used insecticide in both

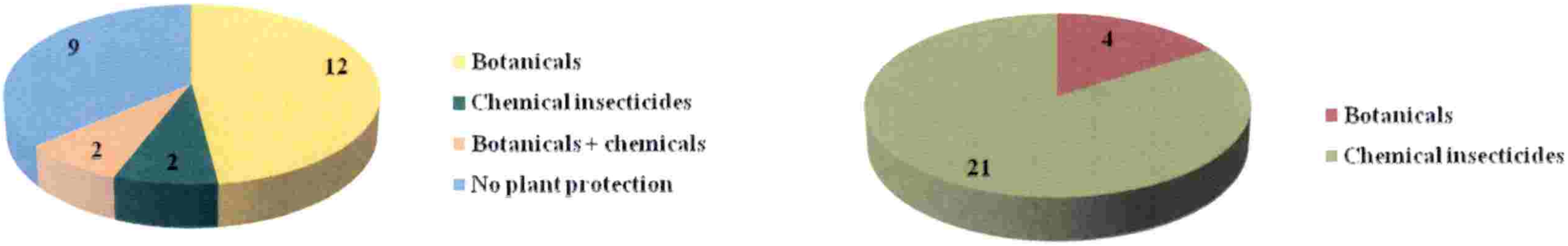


Number of farmers surveyed- 25

Number of farmers surveyed- 25

a. Cabbage farmers in Thiruvananthapuram district

b. Cabbage farmers in Idukki district



Number of farmers surveyed- 25

Number of farmers surveyed- 25

c. Cauliflower farmers in Thiruvananthapuram district

d. Cauliflower farmers in Idukki district

Figure 1. Plant protection methods adopted by farmers in surveyed areas

cabbage and cauliflower in hilly areas. This was evident from the occurrence of fenvalerate residues in cabbage and cauliflower during monitoring studies conducted at PRRAL, College of Agriculture, Vellayani (PAMSTEV, 2017). About 33.33 and 16.66 per cent farmers responded that they were using flubendiamide and chlorantraniliprole respectively for the management of insect pests in cole crops in plains. Whereas, less number of farmers in hilly areas under survey were using new generation insecticides. This may be due to the strong extension service in Thiruvananthapuram (plain) than in hilly areas and also the easy availability of new generation insecticides in plains.

In the present study, 81.25-87.50 per cent of farmers responded that the dose of the chemicals they had taken as "approximate". Hence the quantity of insecticide that has fallen on the plants might not be accurate and the residues estimated will be high in the harvested produce. This may be one of the reasons for high level of insecticide residues in harvested produce.

5.2 DISSIPATION OF INSECTICIDES IN CABBAGE AND CAULIFLOWER

Cabbage and cauliflower are the most important cruciferous vegetables and around 37 insect pests have been reported to infest cabbage and the pest attack resulted in severe yield loss. To achieve the desired yield, farmers apply insecticides frequently at rates higher than the recommended dose resulting in high level of pesticide residues in harvested produce. The monitoring data of CSS ON MPR (2015) portrayed frequent occurrence of pesticide residues in these crops.

Present studies on dissipation of recommended insecticides (CIBRC, 2015) in Thiruvananthapuram (plains) and Idukki (hill) district revealed that the degradation of insecticides varied with crop, agro climatic zones and chemistry of the insecticides. The insecticides that persisted more in cabbage under plain were flubendiamide (20 days), acetamiprid and quinalphos (10 days each), while in hills, higher persistence was observed for flubendiamide, cypermethrin and quinalphos (10 days each). The lowest persistence was observed in fipronil (3 days) in cabbage under plains and acetamiprid (3 days) in hills. In cauliflower, higher persistence was observed for flubendiamide, chlorantraniliprole and dimethoate in plains and flubendiamide, quinalphos (20 days each) and cypermethrin (15 days) in the hills. The lowest persistence was observed for emamectin benzoate (3 days) in cauliflower under plains and hills.

In the current study, flubendiamide is the chemical persisted more in both cabbage and cauliflower (20 days). Studies on comparison of persistence of flubendiamide in different agro climatic zones are so meagre. Studies conducted by Mohapatra *et al.* (2010) and Paramasivam and Banerjee, (2013) revelaed that flubendiamide persisted upto 10 and 7 days respectively.

However, several studies are available on the persistence of flubendiamide in single locations on various crops. Flubendiamide residues persisted up to 3 days in tomato (Kooner *et al.*, 2009), 5 days in chilli (Sahoo *et al.*, 2009), 20 days in tomato (Mohapatra *et al.*, 2011), 7 days in chilli (Sharma *et al.*, 2011), 3 days in brinjal (Takkar *et al.*, 2012), 5 days in okra (Das *et al.*, 2012) and 5 days in tomato (Paramasivam and Banerjee, 2012). This reveals the variation in persistence of flubendiamide in different crops in different locations.

In the present study half life of flubendiamide 39.5 % SC @ 18. 24 g a.i ha^{-1} in cabbage under plains and hills were 9.93 and 3.30 days respectively, while in cauliflower it was 10.66 and 6.08 days. Half life of flubendiamide was 0.96 days in chilli (Sahoo *et al.*, 2009), 3.90 days in cabbage (Mohapatra *et al.*, 2010), 2.68 days in brinjal (Chawla *et al.*, 2011), 3.90 days in tomato (Mohapatra *et al.*, 2011), 4.70 days in okra (Das *et al.*, 2012), 1.64 days in tomato (Paramasivam and Banerjee, 2012), 0.62 days in brinjal (Takkar *et al.*, 2012), 3.40 days in cabbage (Paramsivam and Banerjee, 2013) and 3.51 days in chilli (Chen *et al.*, 2014) at recommended dose. Multi locational study conducted by Sharma *et al.* (2014) reported the persistence of flubendiamide on different agro climatic zones *viz.*, Bangalore, Rahuri, Ludhiana and Durgapura. Initial deposits of flubendiamide on cabbage on all these locations varied greatly. Initial deposits of 0.84, 0.38, 0.08 and 0.37 mg kg^{-1} reported respectively at Bangalore, Rahuri, Ludhiana and Durgapura at a dose of 48 g a.i ha^{-1}. Residues were reached below its detectable level on 20, 5, 3 and 5 days respectively at the above places. Flubendiamide is stable to hydrolysis under laboratory conditions, but direct aqueous photolysis appears to be a main route of degradation. Flubendiamide degrades to des-iodo flubendiamide under field soil photolysis. It has longer persistence and is also reported to form toxic metabolites in soil. It has also shown groundwater contamination potential if the soil is porous and sandy (Das *et al.*, 2017).

In the current study, higher persistence of quinalphos 25 % EC was observed in cabbage under both locations (10 days). In cauliflower 15 and 20 days persistence were observed in plains and hills, Studies on the persistence of quinalphos at different parts of India showed that the degradation of quinalphos is slower in Kerala as compared to other parts of India. Quinalphos residues were persisted upto 7 and 4 days in main and spring cauliflower at the dose of 250 g a.i ha^{-1}(Chawla *et al.*, 1979), 7 days in yard long bean (Kabir *et al.*, 2008), 7 days in cabbage (Chahil *et al.*, 2011), 15 days in cauliflower (Mohapatra and Deepa, 2013), 7 days in chilli (Raut *et al.*, 2016), 10, 7 and 5 days respectively in cabbage, egg plant and yard long bean (Prodhan *et al.*, 2018). These studies showed more or less similar trend with current study.

Half-lives of quinalphos 25 % EC @ 375 g a.i ha^{-1} were 1.38 and 3.37 days in cabbage under plains and hills, while in cauliflower it was 2.34 and 4.52 days respectively in the present study. Half life of quinalphos was 3.02 days in cabbage (Chahil *et al.*, 2011), 4.80 days in cauliflower (Mohapatra and Deepa, 2013) 1.99

days in chilli (Raut *et al.*, 2016) and 1.61 days in cauliflower (Gupta and Parihar, 1989).

Cypermethrin 10 % EC @ 70 g a.i ha^{-1} residues persisted up to 7 and 10 days in cabbage under plains and hills while it was 10 and 15 days in cauliflower under plains and hills in the present study. Studies conducted in different parts are in confirmation with present study. Persistence of cypermethrin was 11 days in cauliflower (Rai *et al.*, 1986), 15 days in chickpea (Kumar *et al.*, 1998), 10 days in okra (Khan *et al.*, 1999), 10 days in soybean (Abdullah *et al.*, 2001), 7 days in chilli (Jyot *et al.*, 2013) were recorded.

Half life of cypermethrin was 3.52 and 3.30 days respectively in cabbage under plains and hills, however in cauliflower it was 6.14 and 3.99 days respectively. Half lives were 8.36 days in chick pea green pods (Kumar *et al.*, 1998), 2.25 days in okra (Samriti *et al.*, 2010) and 2.51 days in chilli (Jyot *et al.*, 2013),

Present study revealed that, residues of acetamiprid 20 % SP @ 10 g. a.i ha^{-1} persisted up to 10 and 3 days in cabbage under plains and hills respectively. While in cauliflower it was 10 and 7 day respectively. More or less similar results were observed in studies conducted in different crops *viz.,* 3 days in mustard (Pramanik *et al.*, 2006), 7 days on chilli (Sanyal *et al.*, 2008), 10 days in tomato and cucumber (Shams *et al.,* 2012), 5 days in brinjal (Romeh *et al.*, 2013). In Kerala, Pratheeshkumar and Chandran (2015) reported the persistence of acetamiprid residues on fresh and dry cardamom samples as 21 days after spraying at single dose. Lazic *et al.* (2017) reported the persistence of acetamiprid up to 14 days on sweet cherry.

Half- lives of acetamiprid in cabbage in the current study were 3.46 and 2.16 days in plains and hills. While in cauliflower these were 4.50 and 2.50 days respectively. Half-life of acetamiprid was reported as 3 days in mustard (Pramanik *et al.*, 2006), 4.84 days in chilli (Sanyal *et al.*, 2008), 1.04 days in tomato and cucumber

(Shams *et al.*, 2012), 1.96 days in brinjal (Romeh *et al.*, 2013) and 3.65 days in sweet cherries (Lazic *et al.*, 2017). These results are in confirmation with present study.

Residues of chlorantraniliprole 18.5 % SC @ 30 g a.i ha^{-1} persisted up to 7 days in cabbage both in the plains and hills. In cauliflower, the residues persisted up to 15 and 5 days respectively. Half lives of chlorantraniliprole in cabbage were 2.01 and 2.22, whereas in cauliflower it was 5.50 and 1.28 days respectively in plains and hills. Studies on persistence and dissipation of chlorantraniliprole in cabbage and cauliflower in different agro climatic zones are meagre. Kar *et al.* (2013) found that chlorantraniliprole when sprayed @ 9.25 and 18.50 g a.i ha^{-1} on cauliflower persisted up to 3 and 5 days respectively at both the doses. Detailed studies have been done on the persistence and dissipation of chlorantraniliprole in several other crops. Malhat *et al.* (2012) reported the persistence of the insecticide up to 15 days and residues reached below detectable level on 21st day on tomato fruit. Malhat (2012) reported the persistence of chlorantraniliprole on grapes, which was 21 days. Vijayasree *et al.* (2013) studied the persistence of chlorantraniliprole in Kerala and they reported an average initial deposit of 0.55 mg kg^{-1} and which persisted up to 10 days in cowpea which was almost similar with the average initial deposit of chlorantraniliprole detected on cabbage in plains (0.44 mg kg^{-1}) and hills (0.53 mg kg^{-1}) in the present study. Recently, Reddy (2018) reported 7 days persistence of chlorantraniliprole in cowpea in the plains of Kerala. This result was in confirmation with present study.

Half life of chlorantraniliprole was studied by several authors as 3.30 days in tomato (Malhat *et al.*, 2012), 2.70 days in grapes (Malhat, 2012), 0.62 days in cowpea (Vijayasree *et al.*, 2013) and 1.36 days in cauliflower (Kar *et al.*, 2013) and 1.66 days in cowpea (Reddy, 2018).

Dimethoate 30 % EC @ 200 g a.i ha^{-1} residues were persisted up to 7 days in cabbage under plains and hills, while in cauliflower it was 20 and 10 days respectively. Dimethoate was persisted up to 49 days in citrus (Hadjidemetrious *et* *al.*, 1985), 10 days in mango (Awasthi, 1993), 25 days in papaya (Ahuja *et al.*, 2005), 15 days in chilli (Varghese *et al.*, 2011), 21 days in chilli and okra (Waghulde *et al.*, 2011), 14 days in tomato and cucumber (Shiboob *et al.*, 2012) and 10 days in mango (Bhattacherjee and Dikshit, 2016). As compared to new generation insecticides, old generation insecticides *viz.*, dimethoate also showed more or less similar trend of dissipation.

In the present study, half life of dimethoate in cabbage was 1.14 and 2.75 days in plains and hills. Correspondingly in cauliflower it was 3.39 and 2.77 days. As compared to the results of present study, all other studies showed much higher persistence and half life in various other crops. Half life of dimethoate was 7 days in citrus (Hadjidemetrious *et al.*, 1985), 3.1 days in mango (Awasthi, 1993), 2.8 to 3.3 days in guava (Khan *et al.*, 2009), 3.7 days in papaya (Ahuja *et al.*, 2005), 1.94 days in chilli (Varghese *et al.*, 2011), 4.7 days in chilli and 5.21 days in okra (Waghulde *et al.*, 2011) , 1.69 days in tomato and 1.92 days in cucumber (Shiboob *et al.*, 2012).

Results of the present study revealed that the degradation of insecticides varied with crop, chemistry of the insecticides and environmental factors. Plant factors like varieties and growth rate, physical and chemical properties of pesticides and their dosage etc. environmental conditions like temperature, climate, humidity and light, influence the dissipation of toxicants (Magallona, 1994; Ariaz-Estevez *et al.*, 2006; Khay *et al.*, 2008). In the current study, the dissipation of insecticides *viz.,*chlorantraniliprole, flubendiamide, acetamiprid, thiamethoxam, and dimethoate was faster in hills than in plains. High rainfall (Appendix II) and slight morning drizzle during the experimental period in hills may be the reason for fast degradation of insecticide from cabbage and cauliflower.

The structure of a pesticide molecule determines its physical and chemical properties and inherent biodegradability. The introduction of substituents on a benzene ring influences its degradation. Minor alterations in structure frequently cause a drastic change in the susceptibility of a compound to biotransformations (Cork and Krueger, 1991). Stability of pesticides range from unstable to extremely stable and their basic structure is fundamental in influencing their persistence in plants. A readily metabolizable pesticide breaks down rapidly in plants irrespective of environmental factors. Some pesticides can be partially broken down, and then become extremely persistent. The breakdown products are being more stable than the parent compound. Hence, recommendations for the use of a pesticide on a crop cannot be made until studies of its persistence have been carried out. Information on degradation rate also helps to assess and predict the environmental behaviour of the pesticide (Laskowski *et al.*, 1983).

5.3 RISK ASSESSMENT OF INSECTICIDES IN CABBAGE AND CAULIFLOWER

After the application of pesticides, target compounds will degrade within a certain period of time. However certain amount of residues will lapse on plant, leaves, fruits, water, soil etc. Since pesticides are biologically active compounds, it has adverse effects on human ranging from short term effects to chronic effects (Berrada *et al.*, 2010; Claeys *et al.*, 2011). Dietary intake of vegetables and fruits acts as a predominant route of pesticides to human. The route of pesticides through dietary intake is much higher than other means such as air and drinking water (Claeys *et al.*, 2011). Hence there is a necessity to assess the potential risk of the insecticides on human health. There are food and health authorities to monitor pesticide residues in food. Government and international organisations such as Food Safety Standards Authority of India (FSSAI), European Union (EU) and Codex alimentarius plays an important role in fixing MRL, the limit for international trade. In India FSSAI is the authority to fix MRL for each insecticide in each crop.

Risk assessment studies revealed that consumption of cabbage and cauliflower treated with chlorantraniliprole, flubendiamide, indoxacarb, quinalphos, cypermethrin, acetamiprid and thiamethoxam both from plains and hills were safe. However, consumption of fipronil and dimethoate treated cabbage and cauliflower can cause deleterious health impact on human. MPI values obtained for fipronil in cabbage plots under plains was 11µg person^{-1} day^{-1}. TMRC values obtained were 72.8, 38.4 and 13.6 11 µg person^{-1} day^{-1} on 0, 1 and 3 days after spraying at recommended dose. Similar observations were recorded in cauliflower treated with fipronil too. Consumption of cauliflower treated with fipronil under plains and hills was not safe for human health.

There are several studies indicating the higher toxicity implications by fipronil application. Environmental fate of fipronil is unique and different metabolites are produced through different degradation pathways. Fipronil may be converted into fipronil- desulfinyl, which is an extremely stable and more toxic form than parent compound (Hainzl *et al*., 1998). It was found that fipronil formulation can cause risk to bird, fish, aquatic and marine invertebrate. Though fipronil plays a major role in suppression of several insect pest, it can exhibit harmful impact on non- target organisms (Tingle *et al*., 2000). High risk and toxicity of fipronil was studied by scientists in water, soil and food samples and toxicity to bees also reported. Estimation of residues even in honey, pollen and honey bees were carried out (Morzycka, 2002; Kadar and Faucon, 2006). Due to high toxicity, countries like USA, France, Uruguay restricted or prohibited the usage of fipronil and it is permitted for seed treatment alone in China (GMOAC, 2008). Contradictory to the present study, Bhardwaj *et al*. (2012) revealed that fipronil treated cabbage do not cause any health impact.

Dimethoate residues in cabbage and cauliflower grown under plains too proved harmful to humans. MPI of dimethoate was 110 µg person^{-1} day^{-1}and TMRC values were 280, 188, 138.4 µg person^{-1} day^{-1}on 0, 1 and 3 days after spraying at recommended dose on cauliflower. In cabbage TMRC value was 256.8 µg person^{-1}

day^{-1} on the day of spraying. Hence consumption of cabbage and cauliflower treated with dimethoate was not safe up to 5 days after spraying at recommended dose.

Sanyal *et al* (2008) conducted risk assessment of acetamiprid in chilli revealed that TMRC values were lesser than MPI values and hence acetamiprid application in chilli does not make any potential impact on human health. Chauhan (2011) also assessed the risk of bifenthrin and lamda cyhalothrin residues in tomato. In both insecticides TMRC values were much lower than MPI values. It was indicated that bifenthrin and lamda cyhalothrin treated tomatoes are safer to humans. These findings are in agreement with present study. While, thiacloprid treated egg plant was not safe even on 3 days after spraying since TMRC values were more than MPI values (Saimandir *et al.*, 2009). Hence it was recommended that safety measures should be considered while applying thiacloprid.

The result of the present study was in line with studies conducted by Aktar *et al.* (2010). They revealed that permissible dietary intake of quinalphos in cabbage was far below the ADI, indicated that dietary intake of quinalphos treated cabbage had no appreciable risk on human health. Similarly Takkar *et al.* (2011) studied the risk assessment in cauliflower after the application of indoxacarb. MPI and TMRC values obtained from the study were 550 and 20.8 μg person^{-1}day^{-1}. Since the TMRC values were much lower than MPI, consumption was safe from the consumer point of view. Consumption of thiamethoxam treated tomato was found to be safe at 50 g a.i ha^{-1} in a study conducted by Malhat *et al.* (2014). The risk assessment study of flubendiamide on gherkin reveals the safety of the insecticide in a consumer point of view (Paramasivam *et al.*, 2014).

Increasing need to address the potential risks associated with exposure to pesticide residues in dietary intake has instigated the risk assessment of pesticides in consumable products. Recently it is mandatory to conduct risk assessment studies of all insecticides before giving field level application along with dissipation studies.

5.4 EFFECT OF PESTICIDES ON SOIL ENZYME ACTIVITY

Soil is an active agile framework containing diverse liberated enzymes and soil enzymes reveal the quality of the soil. It is well known that enzymes in soil contribute to the total biological activities in the soil environment because they are intimately involved in catalyzing reactions necessary for organic matter decomposition, nutrient cycling, energy transfer and environmental quality (Dick, 1994). Enzymes mediate many processes occurring in soil and play an important role in the organic matter turnover and degradation of xenobiotics. Soil enzymes are therefore, useful in describing and understanding the ecosystem quality. During a cropping season more than one type of pesticide may go into the soil and act on non target microorganisms. Hence, examination of such interaction effect of the various pesticides or individual effect of these pesticides is warranted as the biochemical transformations are of paramount importance in maintaining the soil fertility (Bam, 2008).

Despite the role of insecticides in pest management, there is no information on impact of insecticides recommended in cabbage and cauliflower against soil enzymes. Hence the present study on effect of chlorantraniliprole, flubendiamide, indoxacarb, emamectin benzoate, fipronil, quinalphos, cypermethrin, acetamiprid, thiamethoxam and dimethoate in cabbage and cauliflower on soil enzyme *viz.,* urease, phosphatase and dehydrogenase was undertaken in two different agro climatic zones of Kerala *viz.,* plains (Thiruvananthapuram) and hills (Idukki). Insecticides were sprayed at recommended doses under plains and hills. Soil samples were collected from each plot on 3, 5, 10 and 15 days after spraying and evaluated the urease, phosphatase and dehydrogenase activity. Soil enzymes such as urease, phosphatase and dehydrogenase were found to be in a decreasing trend after application of all insecticides up to 15 days after spraying.

Lower reduction in urease activity was observed in flubendiamide, dimethoate and thiamethoxam treated plot and higher reduction was recorded in fipronil and quinalphos treated plots both in cabbage and cauliflower. However, lower reduction in phosphatase activity was recorded in flubendiamide, thiamethoxam and cypermethrin and higher reduction was observed in indoxacarb and fipronil treated plots over control. Lower reduction in dehydrogenase activity was recorded in cypermethrin, acetamiprid and thiamethoxam treated plots and higher reduction was recorded in indoxacarb and fipronil treated plots over contol in both cabbage and cauliflower.

Urease is an enzyme that catalyses the hydrolysis of urea into carbon dioxide and ammonia and is a key component in the nitrogen cycle in soils. In the present study, urease activity was decreased upto 15 days after spraying at recommended dose. (Figure 2-5). There are several reports on the inhibition of urease activity by several old generation insecticides *viz.*, malathion and thimet in a sandy loam @1000 mg kg^{-1} to an extent of 40 to 50 per cent (Lethbridge and Burns, 1975), carbofuran and quintezone (Basavaraj, 1984), quinalphos @ 100 ppm (Basavaraj and Siddaramappa,1991), imidacloprid, amitraz and tebupirimiphos @ 10 µg a.i g^{-1} soil (Tu, 1995), carbofuran @ 1.5 kg ha^{-1} (Kennedy *et al.,* 1999), fenvalerate, quinalphos and endosulfan (Laksmikantha, 2000), diazinon @ 0.79 and 1.59 g m^{-2} (Ingram *et al.,* 2005) and acetamiprid (Punitha *et al.,* 2012).

Contradictory to the present findings, some studies proved that certain insecticides at different doses did not inhibit the activity of urease enzymes *viz.*, pyrethroids (Tu, 1980), chlorfenvinphos, chlorpyriphos, diazinon, ethion, ethoprop, fensulfothion, fonophos, leptophos, malathion, parathion, phorate, thionazin, triaziophos, trichloronat, terbufos, chlordane, dieldrin, lindane and carbofuran @ 5 µg g^{-1} in clay loam soil (Tu, 1981), cyfluthrin @ 10 µg g^{-1} (Tu, 1995), acetamiprid at 0.50, 5.00 and 50 mg kg^{-1} (Yao *et al.*, 2006), imidacloprid @ 0.66 and 0.13 g m^{2} (Ingram *et al.,* 2005), fenamiphos @ 100 mg kg^{-1} (Caceres *et al.*, 2009),

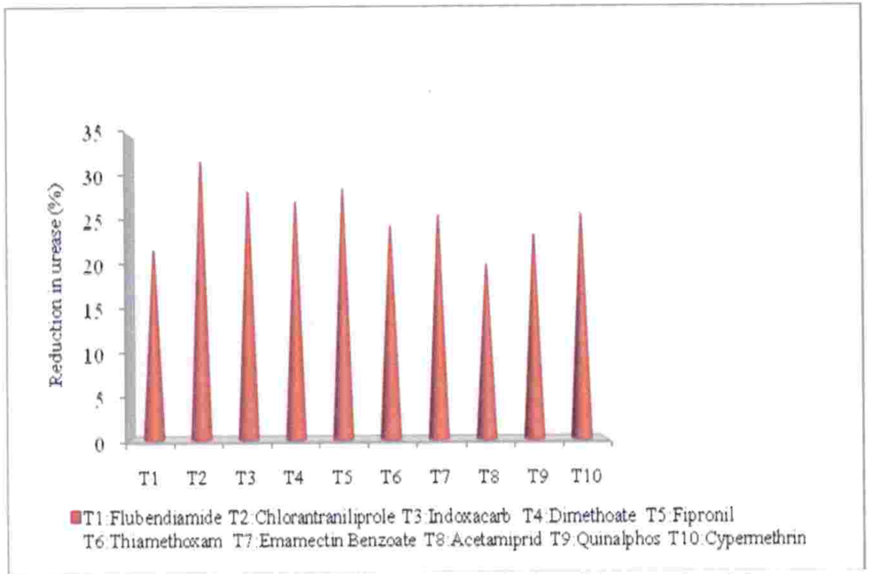


Figure 2. Percentage reduction in urease activity in cabbage under plains

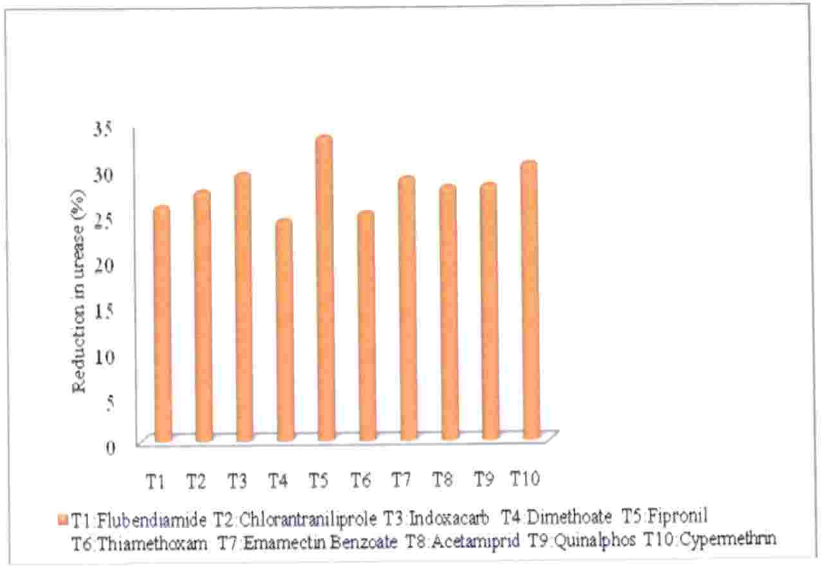


Figure 3. Percentage reduction in urease activity in cauliflower under plains

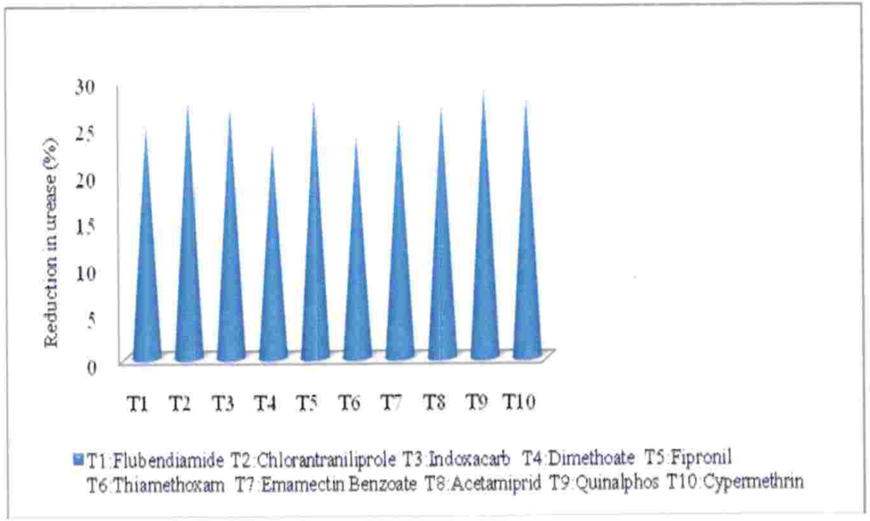


Figure 4. Percentage reduction in urease activity in cabbage under hills

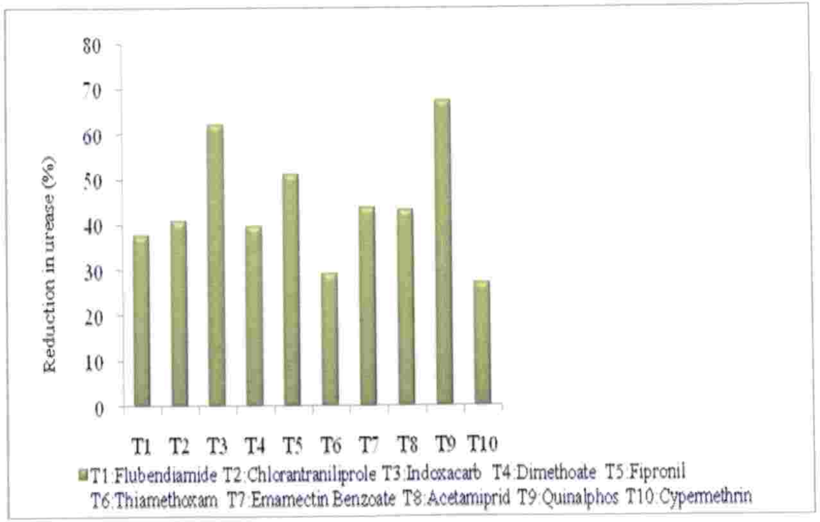


Figure 5. Percentage reduction in urease activity in cauliflower under hills

thiamethoxam @ 2.1 and 8.4 g a.i ha^{-1} (Jyot *et al.*, 2015). However in the present study, cypermethrin, thiamethoxam and acetamiprid reduced the urease activity 3, 5, 10 and 15 days after spraying.

Phosphatase enzyme plays a major role in conversion of organic phosphorus to inorganic phosphorus which can easily taken by the plants. Application of insecticides can hamper the release of phosphatase enzymes by micro organisms in the soil. Phosphatase enzymes catalyses the hydrolysis of ester-phosphate bond and prompting the plant or microbes to discharge phosphate which can be used by plants. Insecticide application can lead to decrease the number of soil bacteria in the transformation of organic phosphorus (Speir and Ross 1978; Malcom 1983; Tabatabai 1994).

In the current study, phosphatase activity was decreased upto 15 days after spraying at recommended dose. Lower reduction in phosphatase activity was recorded in flubendiamide, thiamethoxam and cypermethrin and higher reduction was observed in indoxacarb and fipronil treated plots over control (Figure 6-9). There are several literature available which reports the effect of pesticides on phosphatase activity. Phosphatase activity was inhibited by several insecticides *viz.,* cartap hydrochloride @1000 ppm (Endo *et al*., 1982), fenvalerate (Krishnamurthy, 1989), chlorpyriphos (Pozo *et al*., 1995), amitraz, tebupirimiphos and azet (Tu,1995), endosulfan (Lal and Yadav, 2000), carbofuran at 1 and 1.5 kg a.i ha^{-1} up to 30 days,while carbofuran at recommended dose (0.5 kg a.i ha^{-1}) do not pose any changes in the activity (Kennedy and Arathan, 2004). Studies on effect of neonicotinoides on phosphatase activity revealed the inhibition of activity by the application of acetamiprid at 5 and 50 mg kg^{-1} (Yao *et al*., 2006), thiamethoxam @ 2.10 and 8.40 g a.i kg^{-1} in cotton soil (Jyot *et al*., 2015). This is in confirmation with present findings.

Contradictory to the present findings, Madhuri and Rangaswami, (2002) reported increased phosphatase enzyme activity after application of insecticides *viz.,*

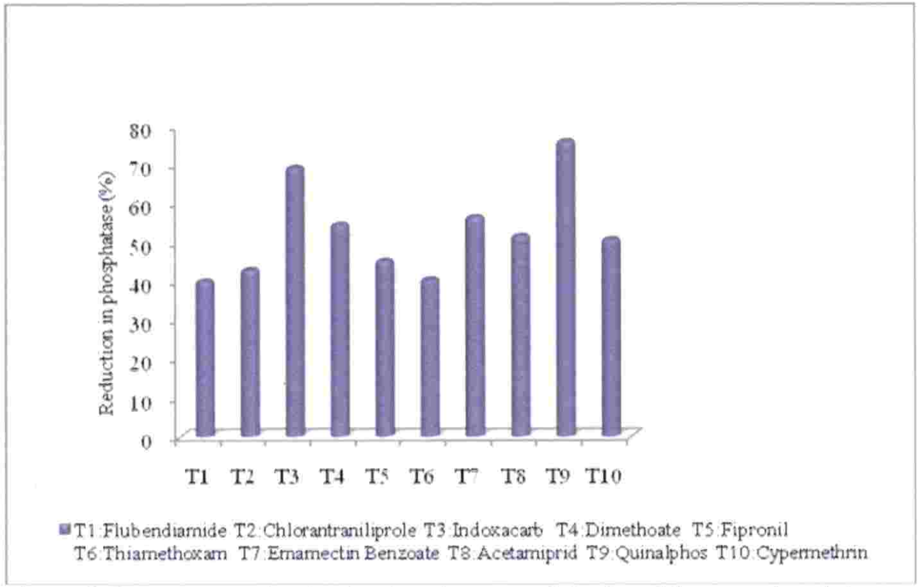


Figure 6. Percentage reduction in phosphatase activity in cabbage under plains

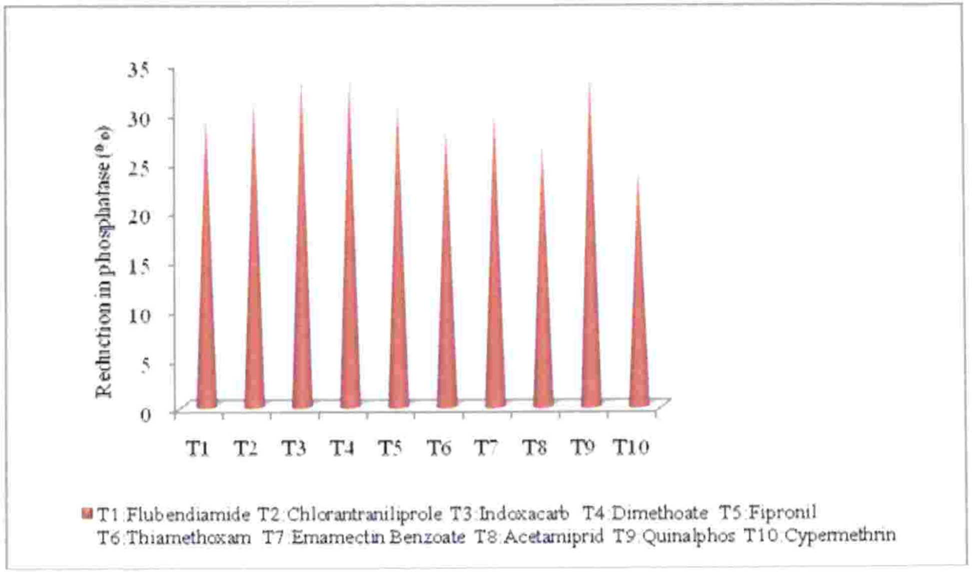


Figure 7. Percentage reduction in phosphatase activity in cauliflower under plains

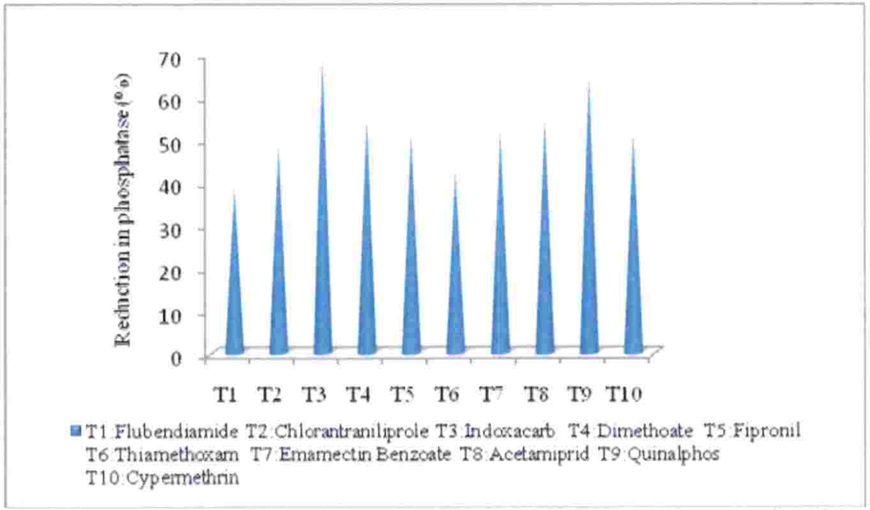


Figure 8. Percentage reduction in phosphatase activity in cabbage under hills

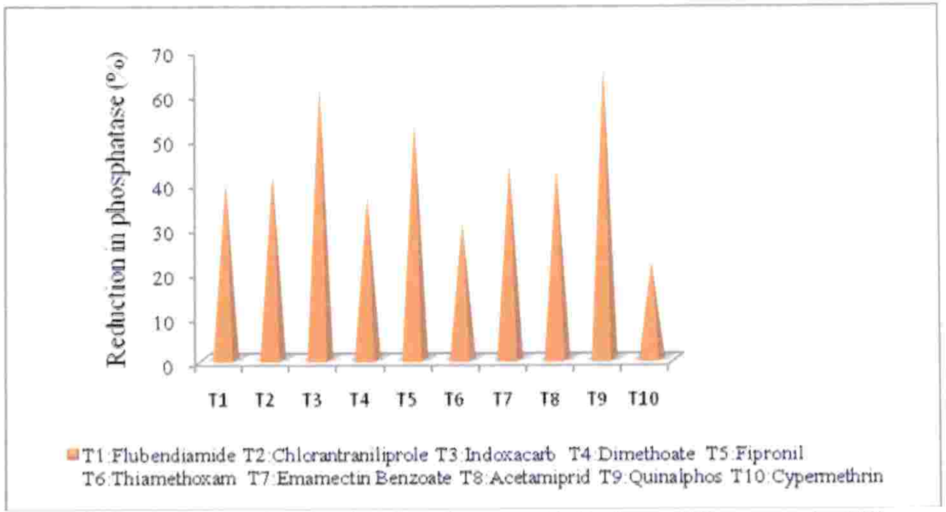


Figure 9. Percentage reduction in phosphatase activity in cauliflower under hills

dichlorovos, phorate and methomyl at 2.5 kg ha^{-1}, chlorpyriphos and methyl parathion at 5 kg ha^{-1} after 20 days. No changes in the enzyme activity was observed after the application of endosulfan over a period of 30 days, but after 60 days, an inhibitory action was recorded @1010 μg g^{-1} (Defo *et al*., 2011). Similarly, application of malathion did not inhibit enzymes at different concentrations (10 to 1000 ppm) on the same day of application. However, after seventh day of spraying, activity was decreased according to increase in concentration and from second week onwards activity was increased (Walia *et al*., 2018).

Dehydrogenase enzyme occurs in all living microbial cells, and it is linked with microbial respiratory processes (Bolton *et al*,. 1985). This intracellular enzyme is an indicator of overall microbial activity of soils. Unlike other enzymes, dehydrogenase does not accumulate extra cellular in soil and are invariably linked to the viability of intact cells. Hence, its quantification has been recommended as a useful indicator for testing the side effects of agrochemicals. Dehydrogenase is considered to play very essential role in the process of organic matter oxidation, particularly in the electron transfer reactions (Bam, 2008). In the current study dehydrogenase activity was decreased upto 15 days after spraying at recommended dose. Lower reduction in dehydrogenase activity was recorded in cypermethrin, acetamiprid and thiamethoxam treated plots and higher reduction was recorded in indoxacarb and fipronil treated plots over contol in both cabbage and cauliflower (Figure 10-13). Dehydrogenase activity was also inhibited several older generation insecticides *viz.,* cytrolane (Purushothaman *et al.,* 1974), HCH and carbaryl @ 100 μg g^{-1} (Chendrayan and Sethunathan, 1980), bromophos (Srimathi *et al.,* 1986), profenophos @ 100 ppm (Kalam *et al.,* 2004), quinalphos (Mayanglambam *et al.,* 2005), fenamiphos @ 100 mg kg^{-1} (Caceres *et al.,* 2009) and endosulfan @ 1, 10 and 100 ppm (Kalyani *et al.,* 2010) and chlorpyriphos @ 100 mg kg^{-1} (Sharma *et al.,* 2010)

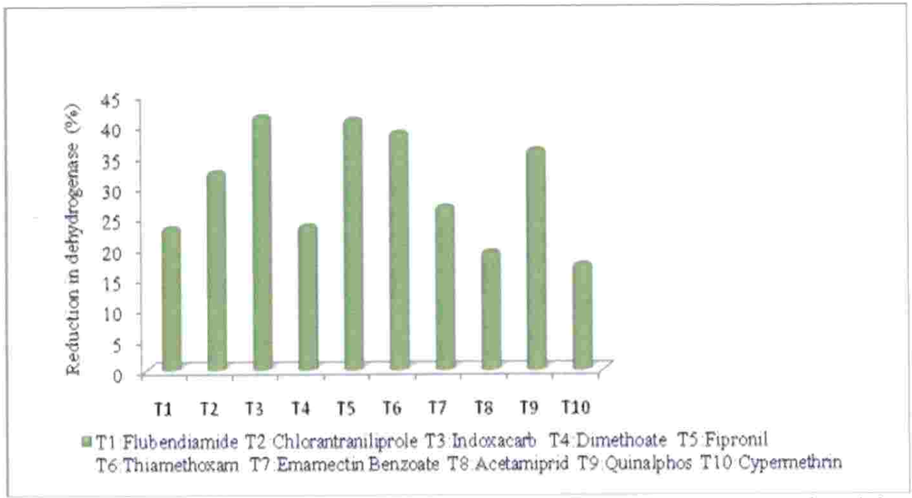


Figure 10.Percentage reduction in dehydrogenase activity in cabbage under plains

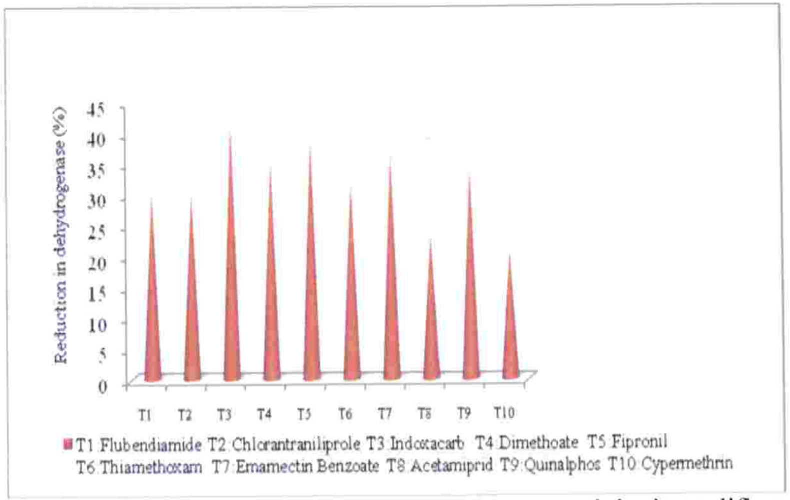


Figure 11.Percentage reduction in dehydrogenase activity in cauliflower under plains

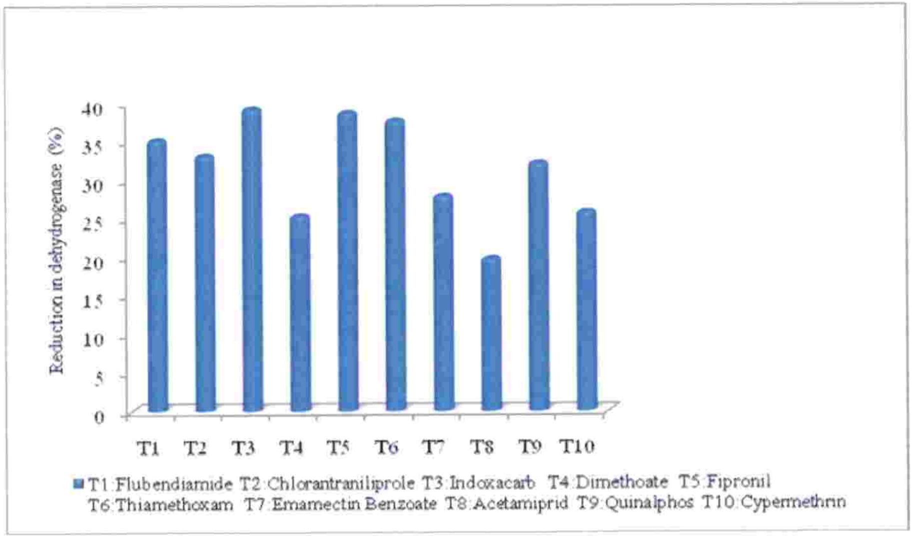


Figure 12. Percentage reduction in dehydrogenase activity in cabbage under hills

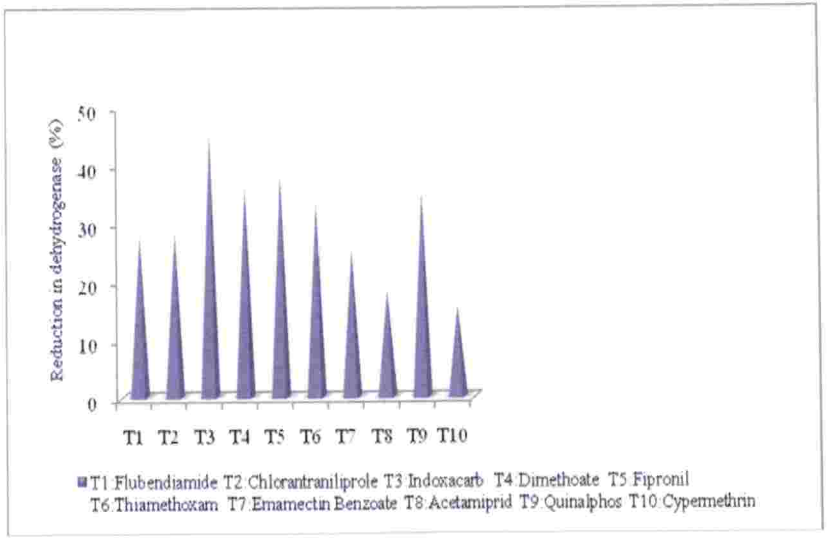


Figure 13. Percentage reduction in dehydrogenase activity in cauliflower under hills

Contradictory to present study, Yao *et al.* (2006) reported that dehydrogenase activity was increased by the application of acetamiprid @ 0.50, 5.00 and 50 mg kg^{-1} for two weeks. Other insecticides *viz.,* fenamiphos @ 100 mg kg^{-1} (Caceres *et al.,* 2009), monocrotophos and chlorpyriphos (Srinivasulu and Rangaswamy, 2013) did not inhibit the activity of dehydrogenase. Generally, whatever the dose considered, fungicides, herbicides and insecticides show inhibitory effects or no effects on the dehydrogenase activity, except endosulfan and mancozeb (Bam, 2008).

The effect of insecticides on soil fertility is complex. However, in the present study, all insecticides reduced soil enzyme in varying degree. Fipronil affected all three enzymes *viz.*, urease, phosphatase and dehydrogenase badly, while indoxacarb affected phosphatase and dehydrogenase more. The most serious problem in interpreting measurements of enzyme activities in soil is to decide which activity or combination of activities has been influenced by a certain factor. It is almost impossible to explain a change in enzyme activity in response to an application of a pesticide to soil, or to establish the cause-and-effect relationship between a pesticide and enzyme activity. Pesticides can be adsorbed on soil minerals, organic matter and organo-mineral complexes, depending on several factors such as structural and surface properties of the soil components, molecular structures and physico-chemical properties of pesticides and associated environmental factors. (Khan, 1978; Huang, 1990; Cheng, 1990). Even if pesticides are applied at recommended rates may cause slight and transient changes to populations or activities of soil microorganisms, it is obvious that long-term recurrent applications of pesticides are known to interfere with the biochemical balance, which can reduce soil fertility and productivity by affecting local metabolism and enzymatic activities.

5.5 EFFECT OF COOKING IN REMOVAL OF PESTICIDE RESIDUE FROM CABBAGE AND CAULIFLOWER UNDER PLAINS AND HILLS

The concern of food safety is an area of rising apprehension in its implication to human fitness all around the world. Processing results in creditable reductions in residue levels within the prepared food, especially through washing, peeling and cooking processes (Soliman, 2001; Zohair, 2001; Nair, 2013; Aaruni, 2016). Hence it is pertinent to study the effect of household techniques in the removal of pesticide residues from contaminated food and vegetables.

In the present investigation, on the effect of cooking at different intervals on the removal of pesticide residues from cabbage and cauliflower it was seen that 15 min cooking removed more residues (Figure 14 and 15) and the highest removal was observed for quinalphos (54.79 %) in cabbage under plains and cypermethrin (66.47 %) in hills. However, in cauliflower the highest percentage removal was observed for chlorantraniliprole (44.78) in plains and cypermethrin (52.32) in hills. The results are in agreement with the findings of Nagesh and Verma, (1997) who reported the removal of quinalphos residues to an extent of 39.06 to 44 per cent from cabbage. Aktar *et al.,* 2010 recorded 41.30 to 45.20 per cent removal of quinalphos from cabbage through cooking. Padmanabhan (2015) reported that washing + cooking of cauliflower can reduce the pesticide residues to an extent of 81.97 per cent.

Several authors studied the removal of organophosphate compounds through cooking *viz.,* cent per cent from brinjal (Kumari *et al.,* 2008), 66.34 per cent removal of triazophos from okra (Parmar *et al*., 2012), 42.90 per cent removal of profenophos from tomato (Harinathareddy *et al*., 2014), 42.97 per cent chlorpyrifos from garden pea (Joshi *et al.,* 2015).

Several factors such as the chemical properties of pesticide, the nature of the food commodity, the processing steps adopted and the length of time the compound

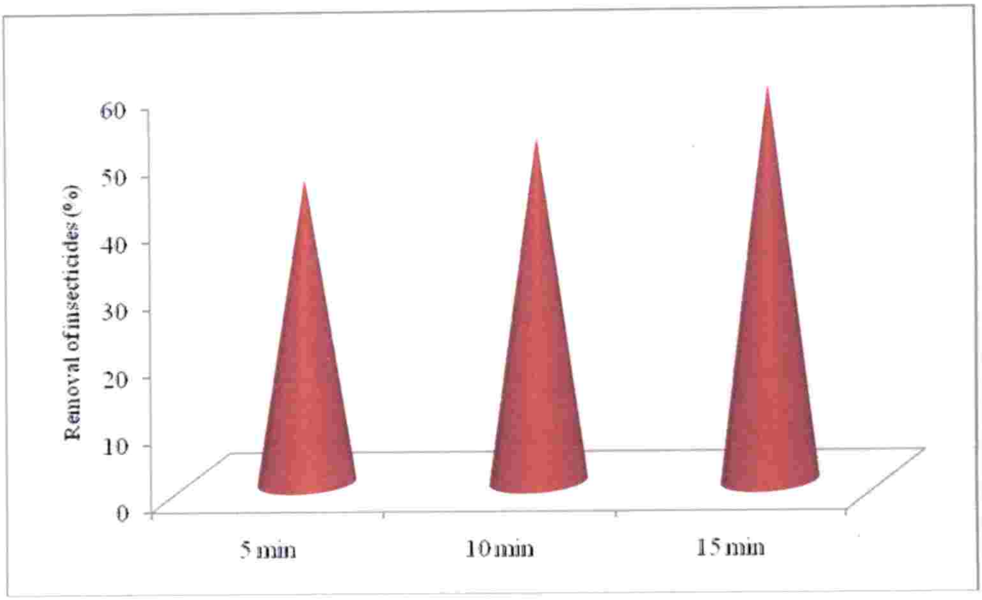


Figure 14. Percentage removal of insecticide residues from cabbage by cooking at different time interval

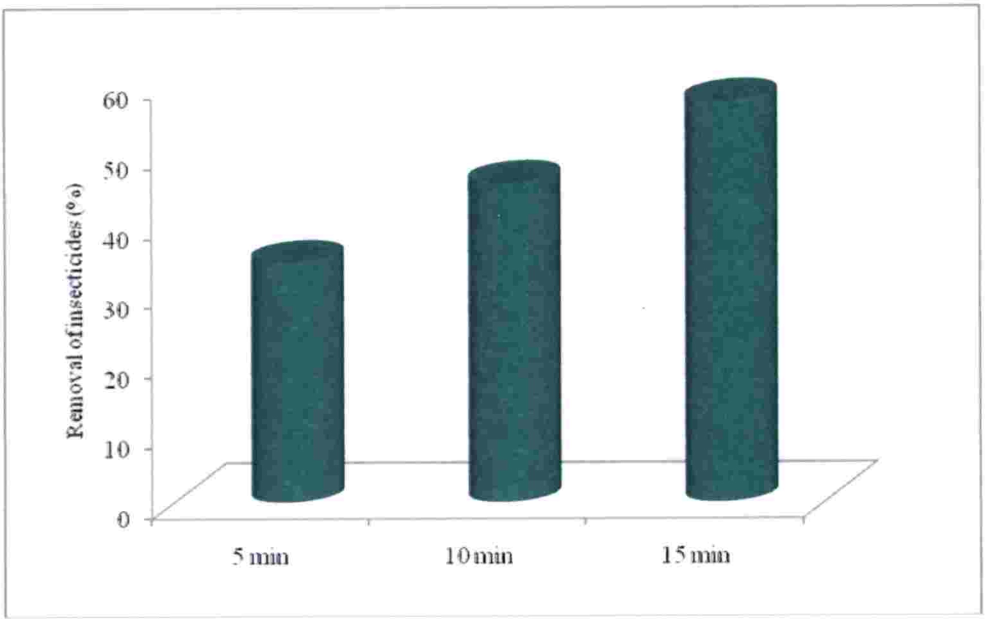


Figure 15. Percentage removal of insecticide residues from cauliflower by cooking at different time interval

has been in contact with food influence the degree to which the pesticide residues can be removed (Farris *et al*., 1992; Holland *et al*., 1994).

The literatures on cooking in removal of cypermethrin residues are meagre. However, studies on effect of cooking on removal of other compounds in synthetic pyrethroid group are available. Hotellier (1982) reported that deltamethrin residues abridged considerably in cooking. Elkins (1989) reported that cooking reduced the synthetic pyrethriods residues from different crops such as brinjal, cauliflower and okra to an extent of 37, 40 and 42 per cent respectively. In a study conducted by Sharma and Kumar (1993) also reported the reduction of fenvalerate residues to an extent of 27 to 56 per cent in brinjal. According to Malik *et al*. (1999) cooking deducted the alphamethrin residues to an extent of 12 to 17 per cent in cauliflower. Reduction of alphamethrin in the range of 25 to 32 per cent in brinjal was reported by Gill *et al*. (2001), In tomato reduction of pesticide residues were almost similar in the case of washing and cooking (11 to 30 %) (Gill *et al*., 2001). About 15 to 33 per cent of residues of cypermethrin reduced by cooking of tomato, okra, bottle gourd and ridge gourd (Kadian *et al*. 2001).

In the present study, the highest per cent removal was noticed in cauliflower curds treated with chlorantraniliprole (59.33) and dimethoate (57.93) after 15 min of cooking and they were on par with each other followed by flubendiamide for 15 min (51.79). Based on the study conducted by Kar *et al*. (2012), complete removal of chlorantraniliprole was recorded when chlorantraniliprole treated cabbage were boiled after 1 hr. of spraying. Initial deposit recorded were 0.12 and 0.20 mg kg^{-1} at 9.25 and 18.50 g a.i. ha^{-1}. Similar trend was observed after one day. Residues of chlorantraniliprole reached below detectable level and thereby recording 100 per cent reduction in residues by boiling. When chorantraniliprole treated cauliflower boiled after one hr. and 1 day after spraying, residues were reached to below detectable level at the application rate of 9.25 and 18.50 g a.i. ha^{-1}, thereby accounting a complete removal of residues. The removal rate is affected by the physicochemical properties of the pesticides. Higher solubility of chlorantraniliprole may be the reason for fast removal of residues after cooking. Chlorantraniliprole may be leached into cooking water thereby achieving fast removal of residues.

During cooking, extent of removal of insecticides varies greatly. Since cooking involves thermal energy, degradation of pesticides can occur variably according to the nature and stability of the pesticides, type of pesticides and length of treatment. During cooking pesticide residues may passed into cooking water from the commodity based on their solubility. Pesticide stability also might be contributing in reduction of residues from fruits and vegetables by various food processing (El-Nabarawy *et al.*, 2002). The loss of pesticide residue during heat processing may be due to evaporation, co-distillation, thermal degradation which vary with the chemical nature of the individual pesticide (Sharma *et al.*, 2005). A number of reports are available in literature on the effect of thermal treatment on pesticides.

5.6 EVALUATION OF VEGGIE WASH TECHNOLOGY IN REMOVAL OF PESTICIDE RESIDUES

Comparison of the efficacy of "Veggie Wash" with water wash revealed that dipping of cabbage and cauliflower in one per cent "Veggie wash" solution for 10 min. followed by water wash removed 12-40 per cent of treated insecticides while water wash alone removed 9 -35 per cent (Figure16 and 17).

Aaruni (2016) reported that dipping of chilli fruits in "Veggie Wash" for five minutes followed by three normal washing was very effective in removing organo phosphate molecules. However, she also reported that "Veggie Wash" was not effective in both cumin and fennel. Another study revealed that "Veggie Wash" removed 44-100 per cent of insecticides *viz.,* chlorpyriphos (61.00 %), cypermethrin (66.00 %), malathion (100 %), fenvalerate (64.00 %), ethion (70.00 %) and bifenthrin (63.00 %) from chilli, chlorpyriphos (52.00 %), cypermethrin (64.00 %),

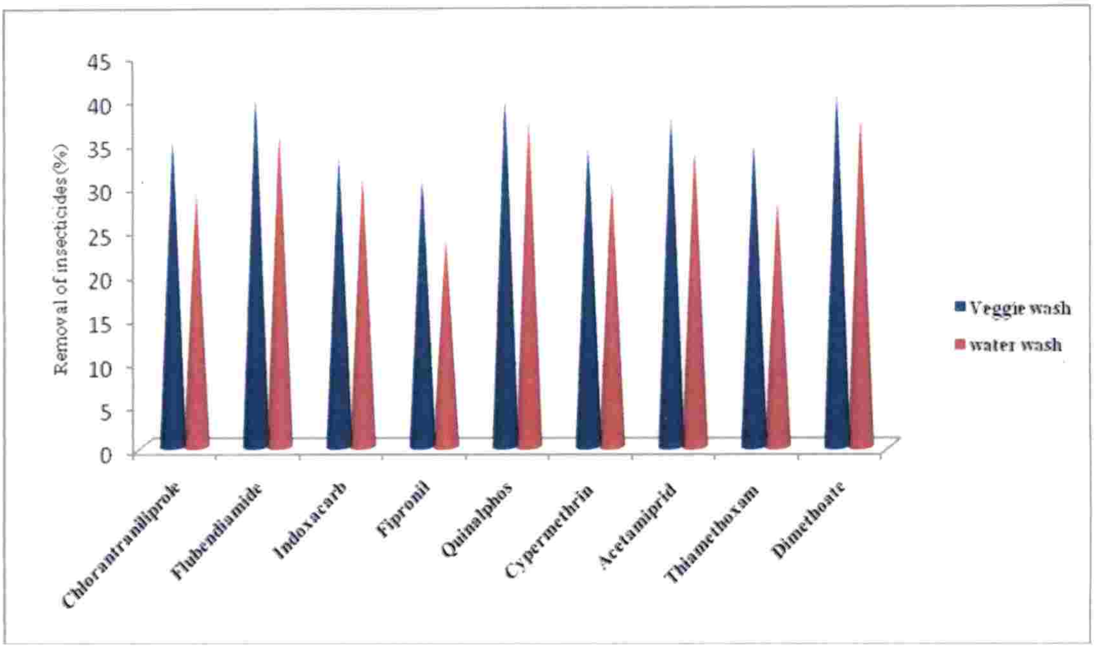


Figure 16. Effect of Veggie Wash and water wash in removal of pesticides from cabbage

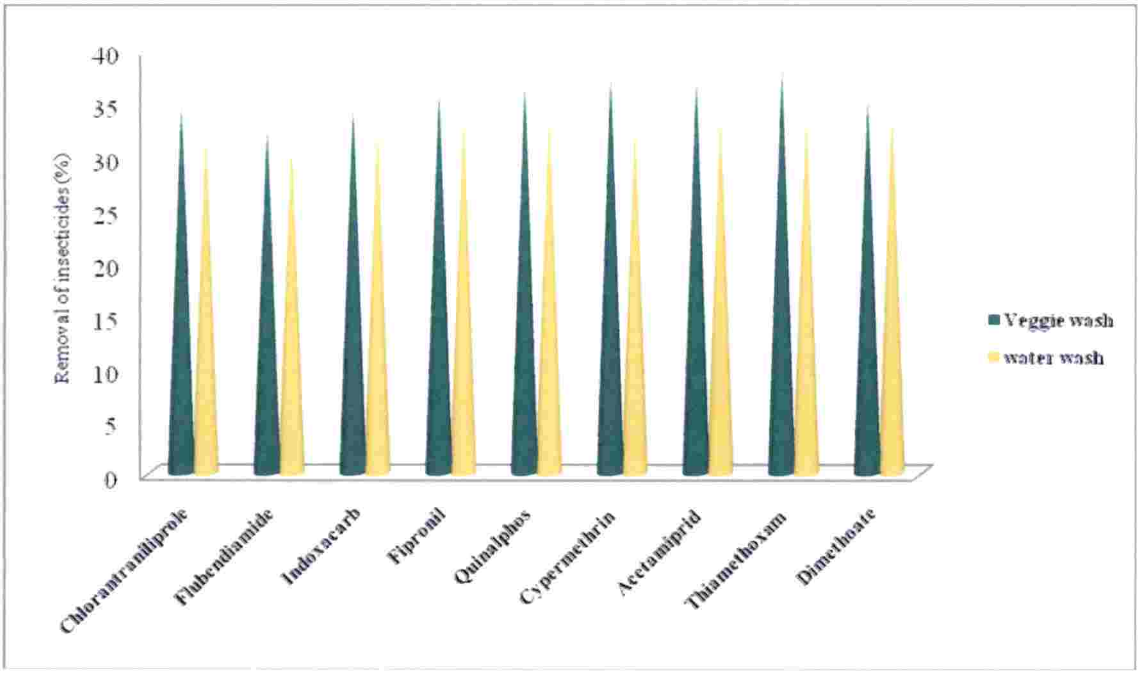


Figure 17. Effect of Veggie Wash and water wash in removal of pesticides from cauliflower

profenophos(56.00 %), quinalphos (44.00 %), dimethoate (74.00 %), ethion (55.00 %), malathion (75.20 %), methyl parathion (69.00 %), fenvalerate (44.00 %) and lamda cyhalothrin (82.00 %) from curry leaf (PAMSTEV, 2017). The current study concentrated on the removal of new generation insecticides from cabbage and cauliflower by "Veggie Wash". Whereas most of the earlier studies on "Veggie Wash" were conducted on conventional insecticides *viz.*, organo phosphates and synthetic pyrethroids. Hence further studies are required to test the efficacy of "Veggie Wash" to decontaminate new generation insecticides in crops other than cabbage and cauliflower.

Overall, the study revealed that the degradation of insecticides varied with nature of crop, chemistry of the insecticides and agro climatic variations. Among insecticides recommended against leaf eating and chewing pests of cabbage and cauliflower by CIBRC, flubendiamide was found to be the best with less risk to the consumers even though its persistence was more and had less impact on soil enzymes. Though, thiamethoxam having no label claim in CIBRC against sucking pests of cabbage and cauliflower, the present study revealed its less persistence in harvested produce and more safety to soil enzyme. Risk assessment study showed that fipronil and dimethoate posed high risk to human health at the recommended dose. The soil enzyme activity was inhibited by fipronil and indoxacarb having label claim in cabbage and cauliflower.

After the formation of World Trade Organisation (WTO), presence of pesticide residues above the permissible level is a major tailback in the acceptance of food commodities by the importing countries. To conquer the trade barriers at the international level with respect to food safety issues, it is important to know the status of pesticide residues in the produce. Present study urged the need to study the dissipation pattern of all insecticides in diverse agro ecological zones, to assess their effect on soil micro flora and to evaluate the new generation insecticides carefully, by considering safety to environment and human health. The risk assessment studies of all insecticides should be done before going for field level recommendations.

SUMMARY

6. SUMMARY

Cultivation of cabbage and cauliflower are recently popularized in Kerala since drought tolerant varieties were developed. The crop suffers from severe pest incidence especially in hilly areas as a result of which farmers apply insecticides indiscriminately to combat these pest problems. The present study was under taken to know the pesticide use pattern among cabbage and cauliflower growing farmers of Thiruvananthapuram and Idukki districts representing two different agro climatic conditions *viz.*, plains and hills of Kerala and the dissipation study of selected insecticides used for pest management in cabbage and cauliflower, to assess the risk of these insecticides on human health, effect of insecticides on soil microbial activity and to evaluate different house hold techniques in removal of insecticide residues. The results obtained are summarized hereunder.

- Survey conducted among 25 each of cabbage and cauliflower growing farmers of plain (Thiruvananthapuram) and hill (Idukki) revealed that tobacco leaf eating caterpillar, *S. litura* and painted bug, *B. hilaris* were observed in both plains and hills. Pierid butterfly, *A. lyncida* was recorded only from plains and cabbage aphid, *L .erysimi* and flea beetle, *P. chotanica* were recorded from hills.

- Regarding usage of pesticides, in Thiruvananthapuram district, the percentage of farmers applying botanicals for pest management was 40 to 48 per cent, while 8 to 12 per cent farmers applied insecticides and botanicals + chemicals together. Farmers in Thiruvananthapuram district (34 %) did not adopt any plant protection practices at all. In Idukki district it was recorded that the dependency on chemical insecticides was at an extent of 84 per cent in both crops, whereas only 16 per cent farmers depended on botanicals for pest management.

- Farmers in Thiruvananthapuram district relied on flubendiamide, chlorantraniliprole and quinalphos to an extent of 33.33, 16.66 and 50.00 per cent respectively. In Idukki district, the percentage of farmers applying fenvalerate, dimethoate, quinalphos, cypermethrin and mancozeb was recorded 90.47 to 95.23, 71.42 to 76.19, 76.19 to 95.23, 47.61 to 57.14 and 57.14 to 71.42 respectively.

- Dissipation studies of insecticides in cabbage and cauliflower in two agroclimatic conditions of Kerala *viz.*, Thiruvananthapuram and Idukki showed that the degradation of insecticides varied with crop and chemistry of the insecticides. Insecticides persisted more in cabbage under plain were flubendiamide (20 days), acetamiprid and quinalphos (10 days each), while in hills, higher persistence was observed in flubendiamide, cypermethrin and quinalphos (10 days each). The lowest persistence was observed in fipronil (3 days) in cabbage under plains and acetamiprid (3 days) in hills. In cauliflower higher persistence was observed for flubendiamide, chlorantraniliprole and dimethoate in plains and flubendiamide, quinalphos (20 days each) and cypermethrin (15 days) treated plots in hills. The lowest persistence was observed for emamectin benzoate (3 days) in cauliflower under plains and hills.

- Risk assessment carried out in all insecticides selected under study in cabbage and cauliflower revealed that dimethoate and fipronil treated cabbage and cauliflower were found to be harmful for consumers. All other insecticides *viz.*, chlorantraniliprole, flubendiamide, indoxacarb, emamectin benzoate, quinalphos, cypermethrin, acetamiprid and thiamethoxam at their recommended dose were safe even on the day of application.

- Effect of pesticides on soil microbial activity was studied through the activity of urease, phosphatase and dehydrogenase enzyme. Higher urease activity in plains was recorded in flubendiamide, dimethoate and thiamethoxam treated plots and lower activity was recorded for fipronil and quinalphos. Higher phosphatase activity was recorded for flubendiamide, thiamethoxam and cypermethrin and lower activity was recorded for indoxacarb and fipronil. Higher dehydrogenase activity was recorded for cypermethrin and acetamiprid and lower activity was recorded for fipronil.

- Based on the dissipation study, the insecticides which had more persistence were selected for the cooking experiment. In cabbage under plains, quinalphos, acetamiprid and flubendiamide were selected for cooking experiment. Similarly quinalphos, cypermethrin and flubendiamide were selected under hills. Chlorantraniliprole, flubendiamide and dimethoate were persisted more days in cauliflower under plains. While flubendiamide, cypermethrin and quinalphos was the more persisted insecticides in cauliflower under hills.

- Cabbage and cauliflower samples were cooked for 5, 10 and 15 min and pesticide residues were calculated. Results of the study revealed that 15 min cooking removed more insecticides from cabbage (54.78 to 62.16 %) and cauliflower (56.35 to 57.95 %). The highest per cent removal was observed for quinalphos (54.79) followed by flubendiamide (51.54) and acetamiprid (38.91) in cabbage under plains. Whereas the highest per cent removal was observed for cypermethrin (66.47) followed by flubendiamide (55.34) and quinalphos (41.76) in cabbage under hills. In cauliflower under plains, highest per cent removal was observed for chlorantraniliprole (44.78), followed by flubendiamide (43.65) and dimethoate (41.34). In hills, highest per cent removal of insecticides was recorded for cypermethrin (52.32) followed by quinalphos (47.43) and flubendiamide (44.59).

- "Veggie Wash" technology was evaluated in the cabbage and cauliflower after application of insecticides at recommended doses revealed that dipping of cabbage and cauliflower in one per cent "Veggie Wash" solution for 10 min. followed by water wash removed 12-40 per cent of treated insecticides while water wash alone removed 9 -35 per cent.

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DISSIPATION AND RISK ASSESSMENT OF SELECT INSECTICIDES USED FOR PEST MANAGEMENT IN CABBAGE AND CAULIFLOWER

By

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KERALA, INDIA

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ABSTRACT

Studies on "Dissipation and risk assessment of select insecticides used for pest management in cabbage and cauliflower" was conducted in College of Agriculture, Vellayani, Cardamom Research Station, Pampadumpara and farmers field at Kalliyoor during 2015-2018. The present research work was under taken to study the dissipation of select insecticides *viz.,* chlorantraniliprole 18.5 % SC, flubendiamide 39.35 % SC, indoxacarb14.5 % SC, emamectin benzoate 5 % SG, fipronil 5 % SC, quinalphos 25 % EC, cypermethrin 10% EC, acetamiprid 20% SP, thiamethoxam 25 % WG and dimethoate 30 % EC in cabbage and cauliflower, to assess their potential risks to human health, to determine their effect on soil microbial activity, to estimate the residues in cooked samples and to evaluate the efficacy of "Veggie Wash" to eliminate residues.

Survey conducted among 25 each of farmers cultivating cabbage and cauliflower in plain (Thiruvananthapuram) and hill (Idukki) representing two agro climatic conditions revealed that pest infestation was more in hills when compared with plains. Accordingly, pesticide usage was higher in Idukki (84 % each) than in Thiruvananthapuram district (12 and 8 %) in cabbage and cauliflower respectively.

Dissipation studies of insecticides having label claim for cabbage and cauliflower under CIB & RC in two agroclimatic regions of Kerala *viz.*, Thiruvananthapuram and Idukki showed that the degradation of insecticides varied with crop and chemistry of the insecticides. Insecticides persisted more in cabbage under plain were flubendiamide (20 days) followed by acetamiprid and quinalphos (10 days each), while in hills, higher persistence was observed in flubendiamide, cypermethrin and quinalphos (10 days each). The lowest persistence was observed in fipronil (3 days) in cabbage under plains and acetamiprid (3 days) in hills. In cauliflower higher persistence was observed for flubendiamide, chlorantraniliprole and dimethoate in plains and flubendiamide, quinalphos (20 days each) and cypermethrin (15 days) treated plots in hills. The lowest persistence was observed for emamectin benzoate (3 days) in cauliflower under plains and hills.

Risk assessment study was carried out in cabbage and cauliflower using selected insecticides under plains and hills by comparing the values of Theortical Maximum Residue Concentration (TMRC) and Maximum Permissible Intake (MPI). The result revealed that consumption of dimethoate and fipronil treated cabbage and cauliflower were found to be risky to the end users. However, all other insecticides are safe even on the same day of insecticide application.

Effect of insecticides on soil microbial activity was studied in cabbage and cauliflower through the activity of urease, phosphatase and dehydrogenase enzymes. Lower reduction in urease activity was observed in flubendiamide, dimethoate and thiamethoxam treated plot and higher reduction was recorded in fipronil and quinalphos treated plots over control both in cabbage and cauliflower. However, lower reduction in phosphatase activity was recorded in flubendiamide, thiamethoxam and cypermethrin and higher reduction was observed in indoxacarb and fipronil treated plots over control. Lower reduction in dehydrogenase activity was recorded in cypermethrin, acetamiprid and thiamethoxam treated plots and higher reduction was recorded in indoxacarb and fipronil treated plots over contol in both cabbage and cauliflower.

Study on extent of removal of insecticides through cooking from cabbage and cauliflower was conducted with insecticides which had more persistence revealed that 15 min cooking removed more residues and the highest removal was observed for quinalphos (54.79 %) in cabbage under plains and cypermethrin (66.47 %) in hills. However, in cauliflower the highest per cent removal was observed for chlorantraniliprole (44.78) in plains and cypermethrin (52.32 %) in hills. "Veggie wash" technology was evaluated in the cabbage and cauliflower after application of insecticides at recommended doses revealed that dipping of cabbage and cauliflower in one per cent "Veggie Wash" solution for 10 min. followed by water wash removed 12-40 per cent of treated insecticides while water wash alone removed 9 -35 per cent.

The present study revealed that the dissipation pattern of insecticides varied with crop, agro climatic areas, and chemistry of the molecules. Risk assessment study shown that insecticides *viz.*, fipronil and dimethoate posed risk on human health even at recommended dose. Studies on effect of insecticides on soil enzyme revealed that except fipronil and indoxacarb, all other insecticides under present study have less impact on soil enzymes. Decontamination studies showed that cooking at 15 min. removed 50-60 per cent of insecticides and "Veggie Wash" removed 12-40 per cent of treated insecticides. Present study urged the need to evaluate the new insecticides carefully, by considering safety to environment and human health. The risk assessment studies of all insecticides should be done before going for field level recommendations.

APPENDIX

APPENDIX I

SURVEY ON PESTICIDE USE PATTERN IN CABBAGE/ CAULIFLOWER IN KERALA

Date of the survey:

Name of the area:

I.GENERAL INFORMATION

Sl. No	Particulars	Response of farmers
1	Name &Address of the farmer	
2	Phone No	
3	Age	
4	Education	
5	Location	
6	Panchayat	
7	Block	
8	Taluk	
9	District	

II. INFORMATION ON CROP PRODUCTION

1	Area of cabbage (ha)			
3	Details of cabbage under cultivation	Crop	Variety	Yield
4	Cropping pattern			
5	Season			
6	Spacing			

7	Crop duration	
8	Type of irrigation	
9	Details on fertilizer usage	

III. INFORMATION ON CROP PROTECTION

1. Details of pests infesting cabbage

Sl. No	Stage of the crop	Pest observed
I	Vegetative stage	
II	Reproductive stage	

2	Details of plant protection practices followed		
a	Botanicals		
b	Bio control agents		
c	Chemical insecticides		
Sl. No	Pesticide applied	Dose	Frequency of application
3	Insecticide appliances used		
4	Volume of spray fluid used/acre		

IV. INFORMATIONON GENERAL AWRENESS ON PESTICIDE USE:

1	Since how long you are growing the crop (Cabbage	
2	Are you aware about recommended pesticides on cabbage	Yes/ No
3	Do you follow the safety methods while mixing/storing /spraying pesticide	
4	How do you measure the chemical	Bottle cap/approximate/others
5	When do you spray the chemicals	Morning/afternoon/ evening
6	Source of information for recommended pesticides	
7	How frequently you apply the pesticides	Week/fortnight
8	Are you aware of pesticide residues are found on vegetables	
9	From where you receiving technical advice for the adoption of plant protection operations	Follow farmers/Agrl. Officer/KAU

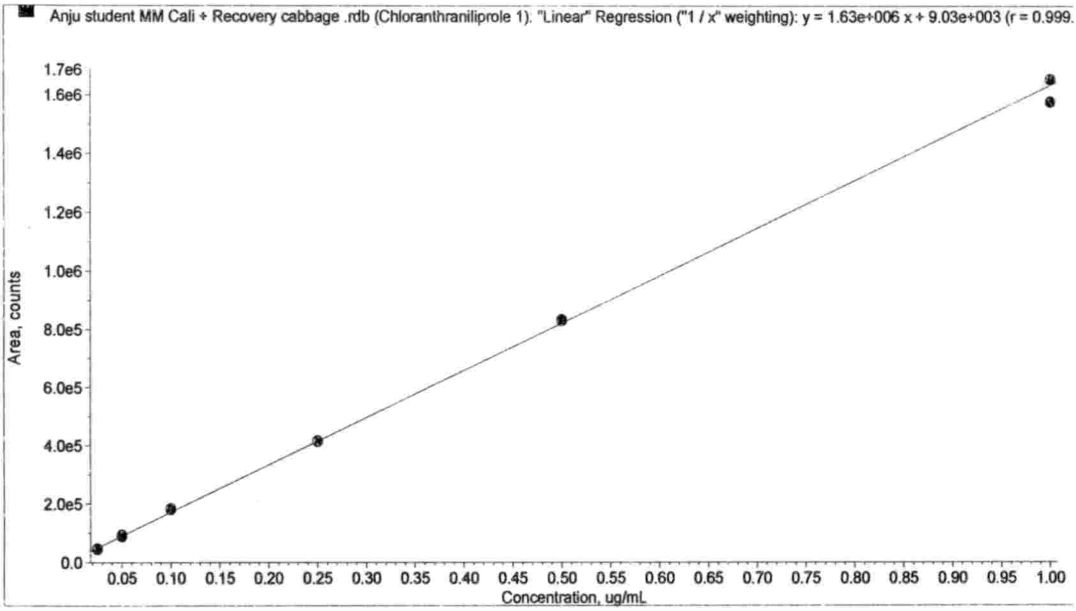
Signature of the farmer

APPENDIX II

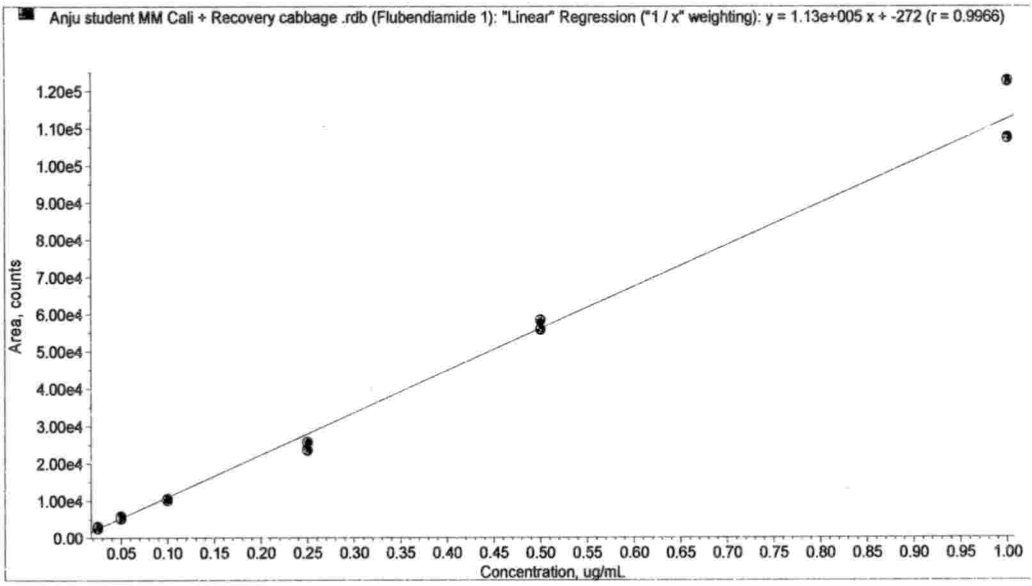
Weather Parameters	Farmers field, Kalliyoor, Thiruvananthapuram	Cardamom Research Station, Pampadumpara, Idukki
Temperature		
Maximum temperature	31.86 ° C	21.74 ° C
Minimum Temperature	23.19 ° C	18.74 ° C
Humidity	92.67	-
Rainfall	28.33 mm	55.06 mm

Weather data during the experimental period

APPENDIX III

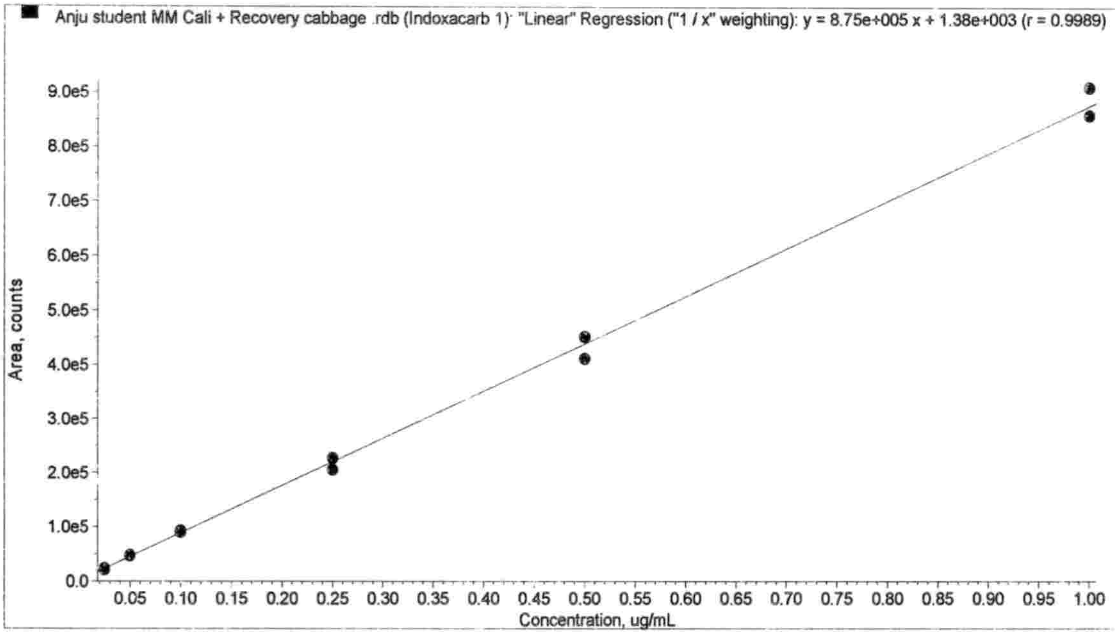


Calibration curve of chlorantraniliprole in LCMS/MS

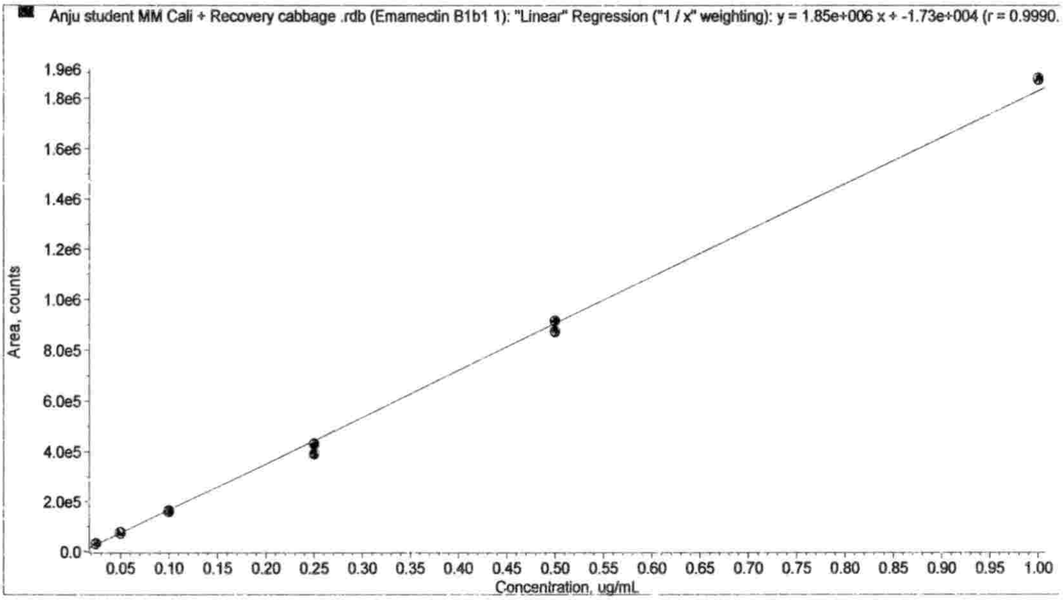


Calibration curve of flubendiamide in LCMS/MS

APPENDIX IV

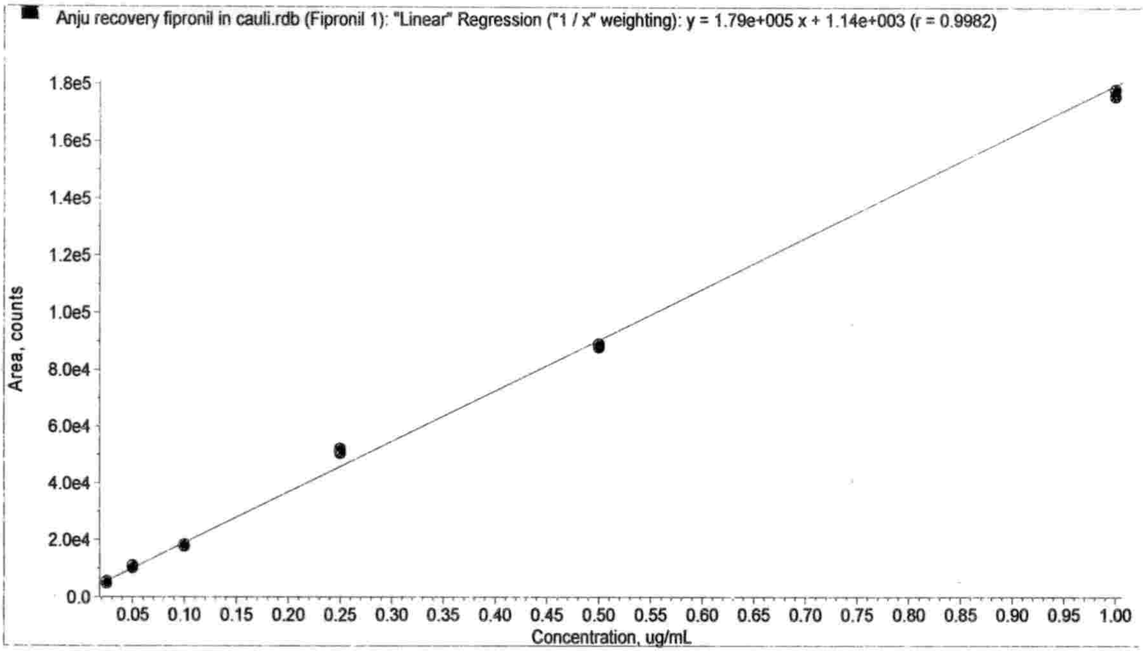


Calibration curve of indoxacarb in LCMS/MS

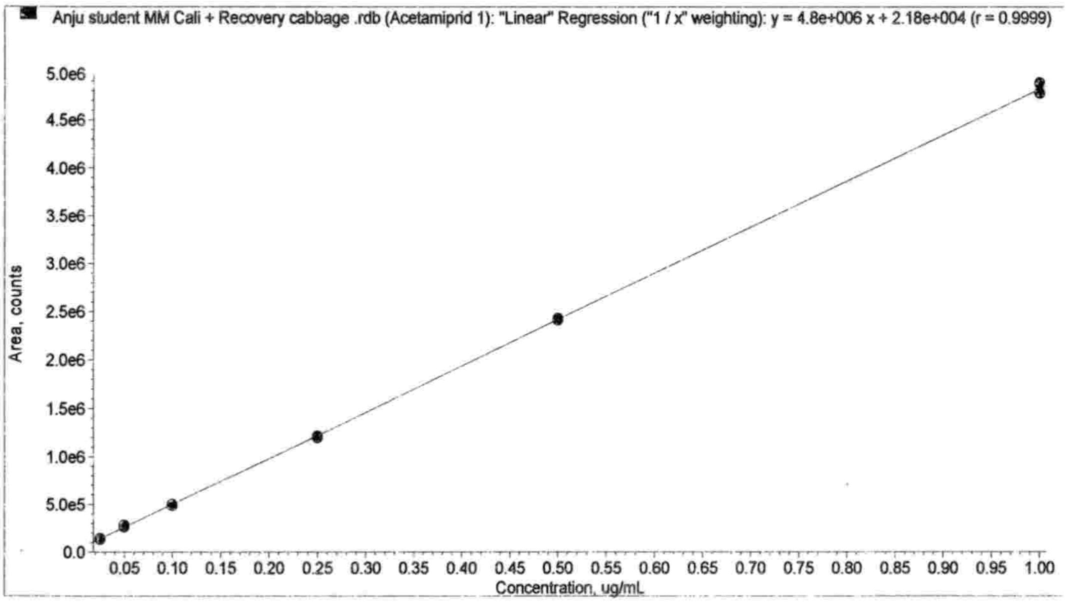


Calibration curve of emamectin benzoate in LCMS/MS

APPENDIX V

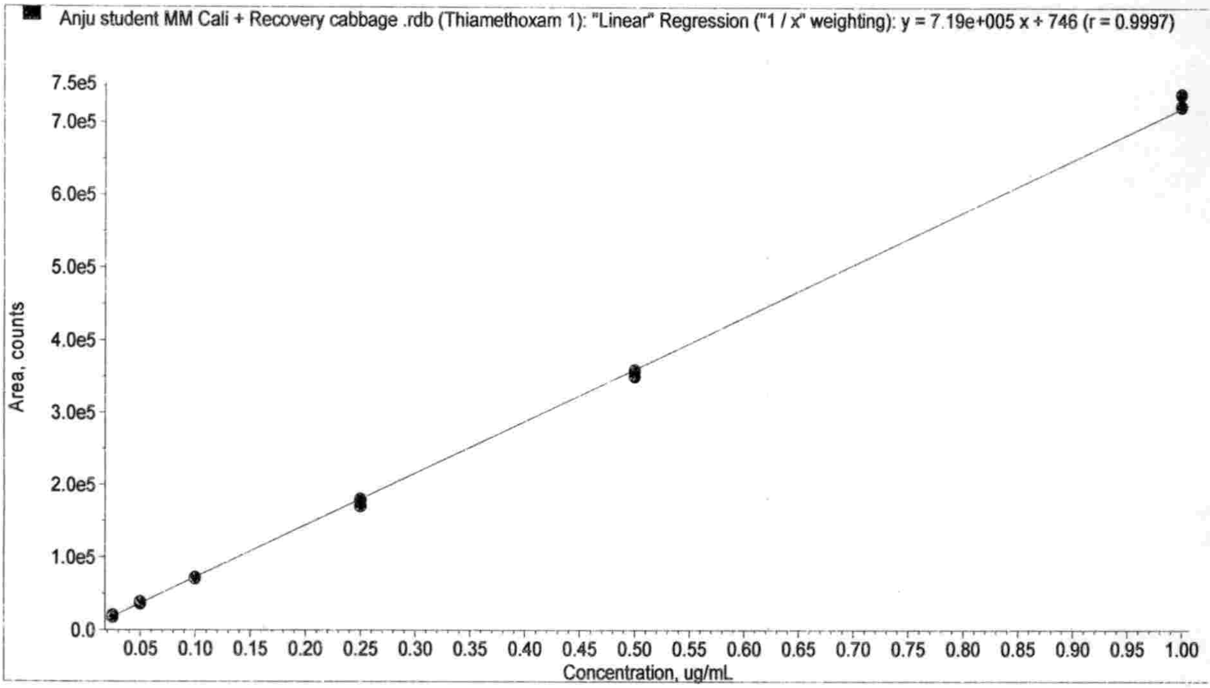


Calibration curve of fipronil in LCMS/MS



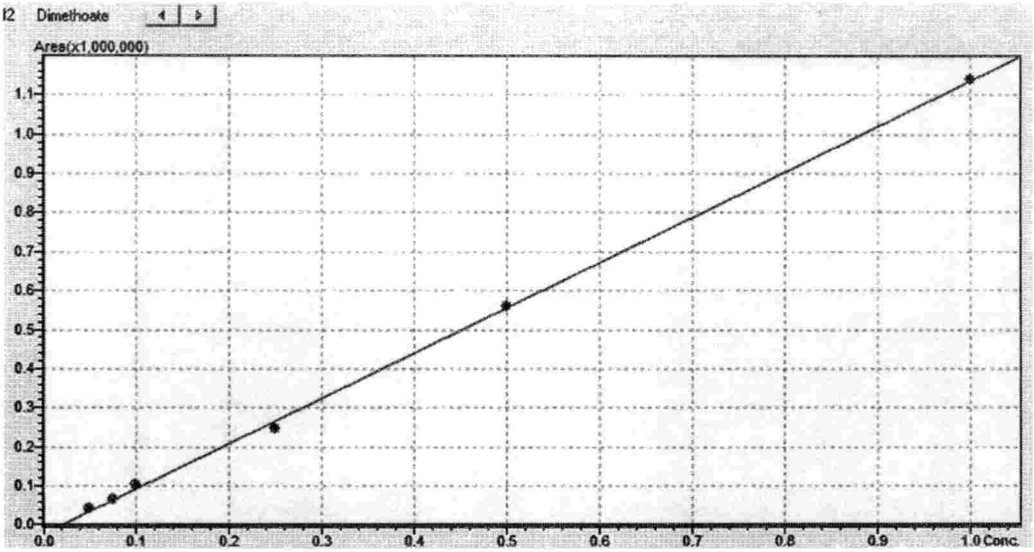
Calibration curve of acetamiprid in LCMS/MS

APPENDIX VI

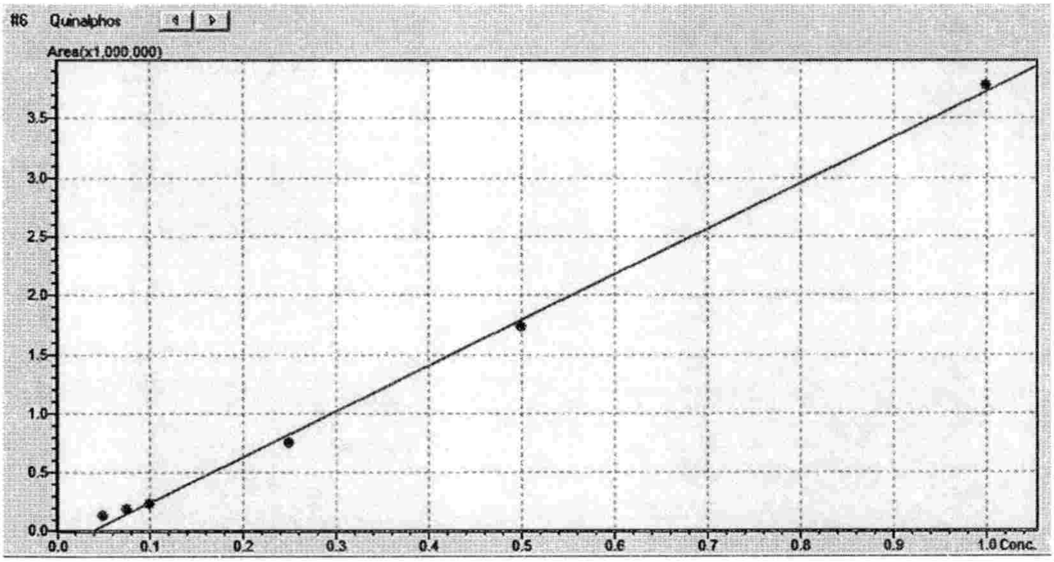


Calibration curve of thiamethoxam in LCMS/MS

APPENDIX VII

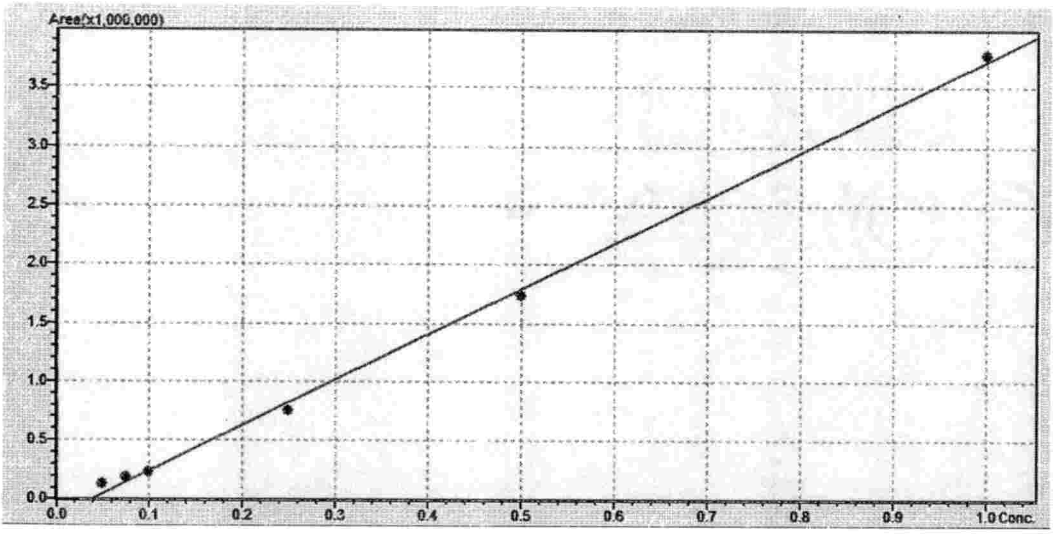


Calibration curve of dimethoate in GC-FPD



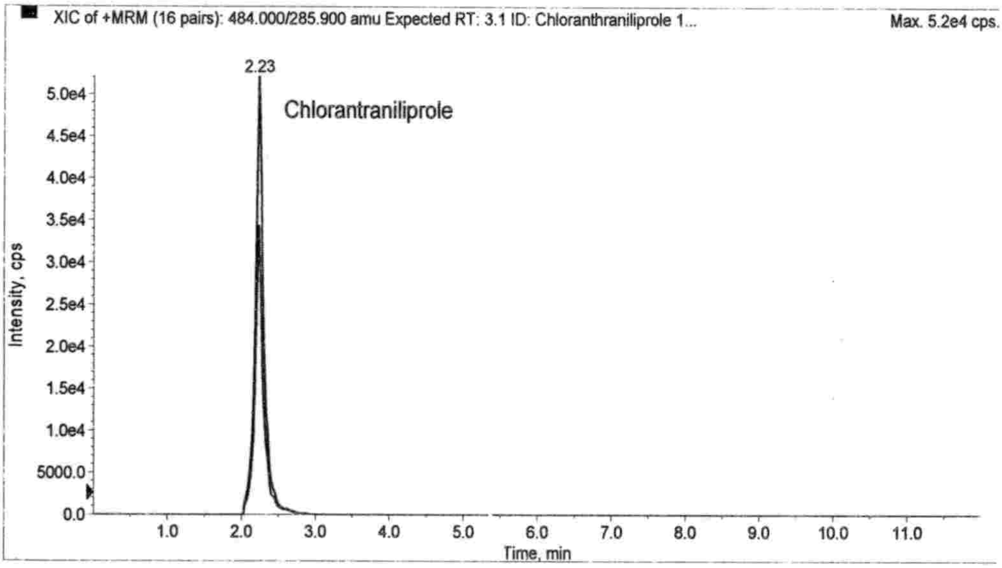
Calibration curve of quinalphos in GC-FPD

APPENDIX VIII

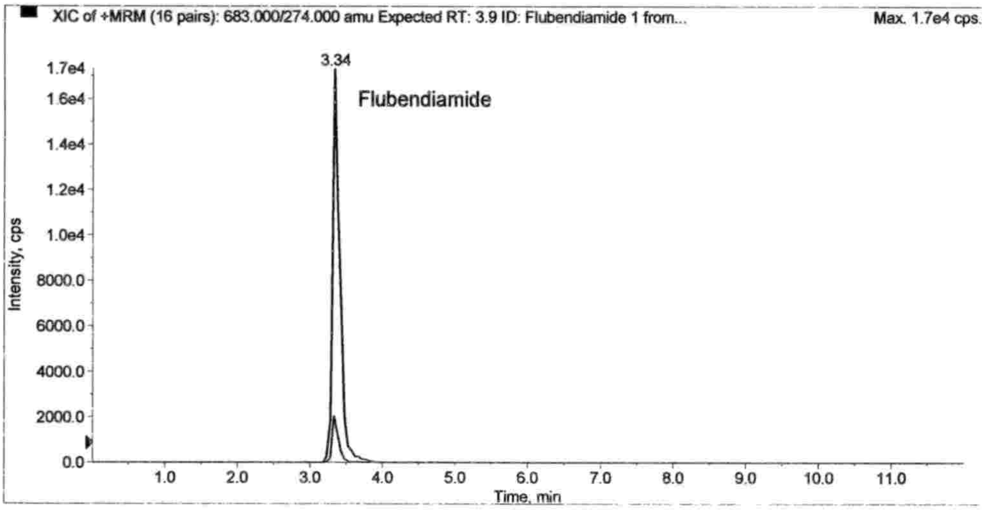


Calibration curve of cypermethrin in GC-ECD

APPENDIX - IX

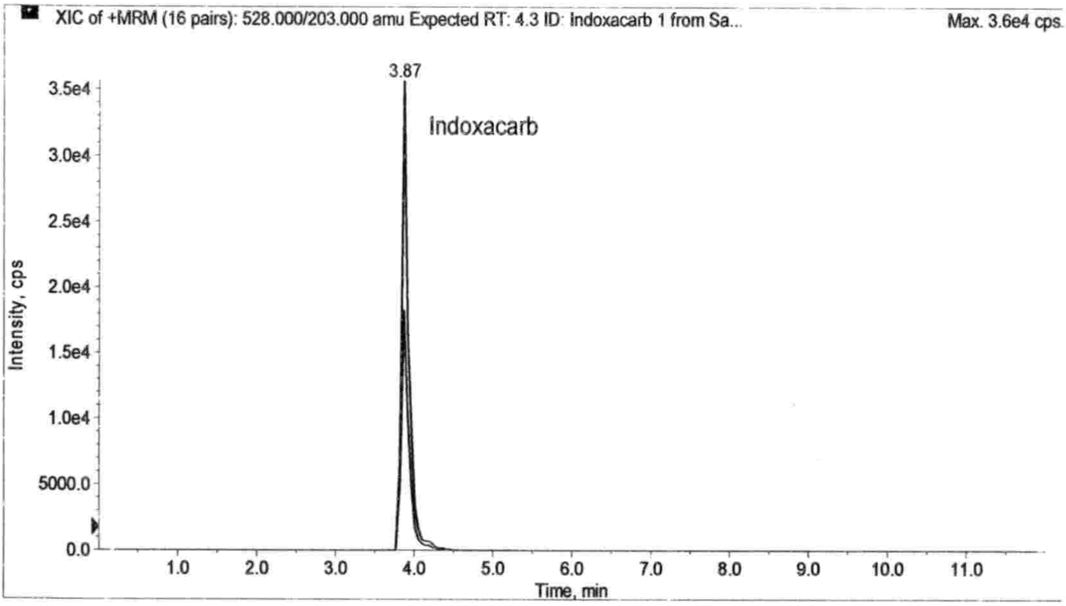


LCMS/MS chromatogram of chlorantraniliprole

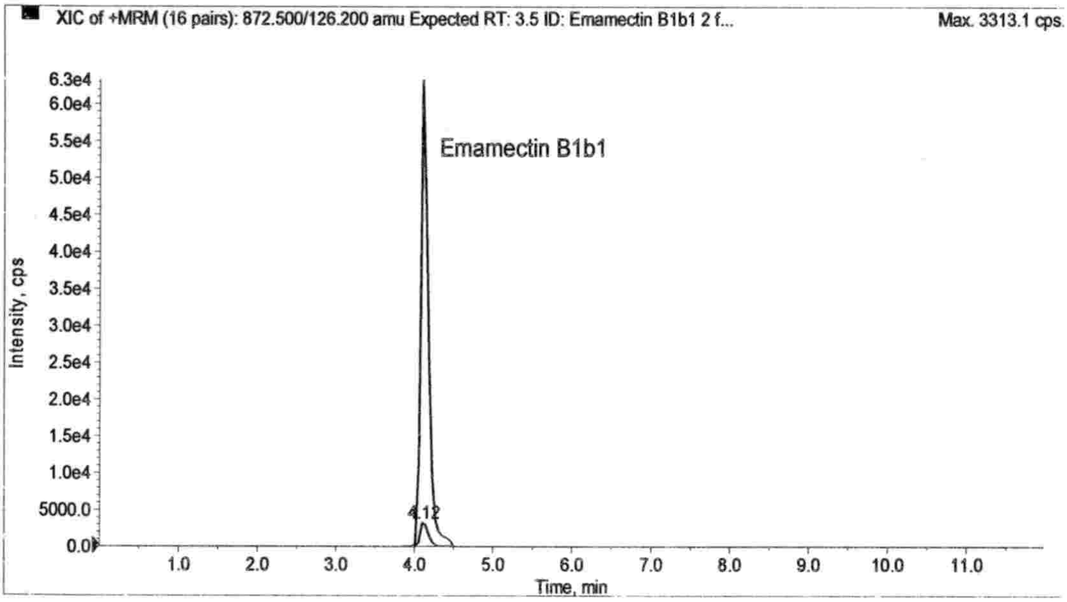


LCMS/MS chromatogram of flubendiamide

APPENDIX – X

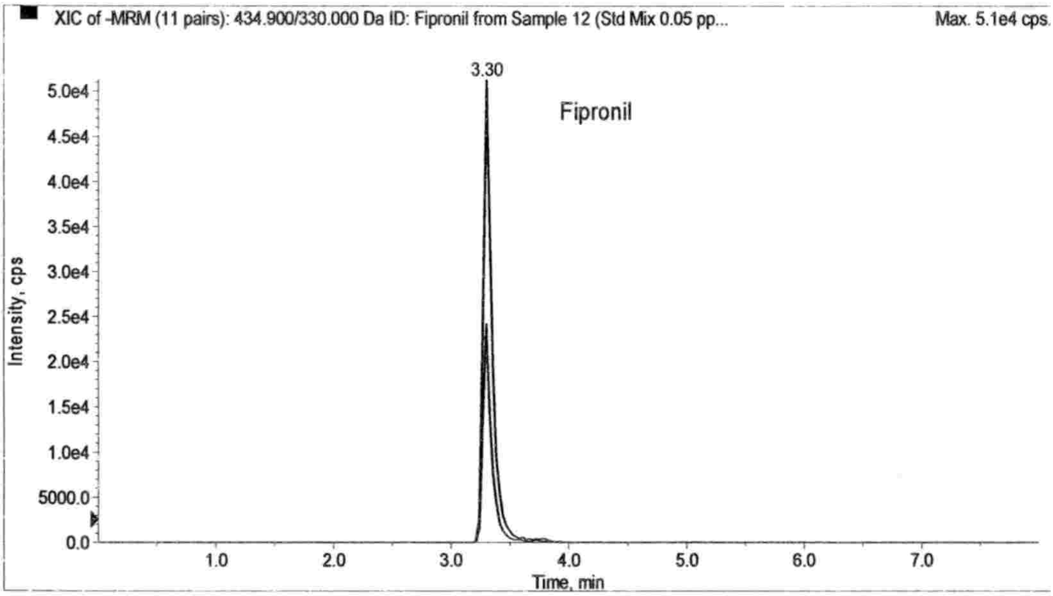


LCMS/MS chromatogram of indoxacarb

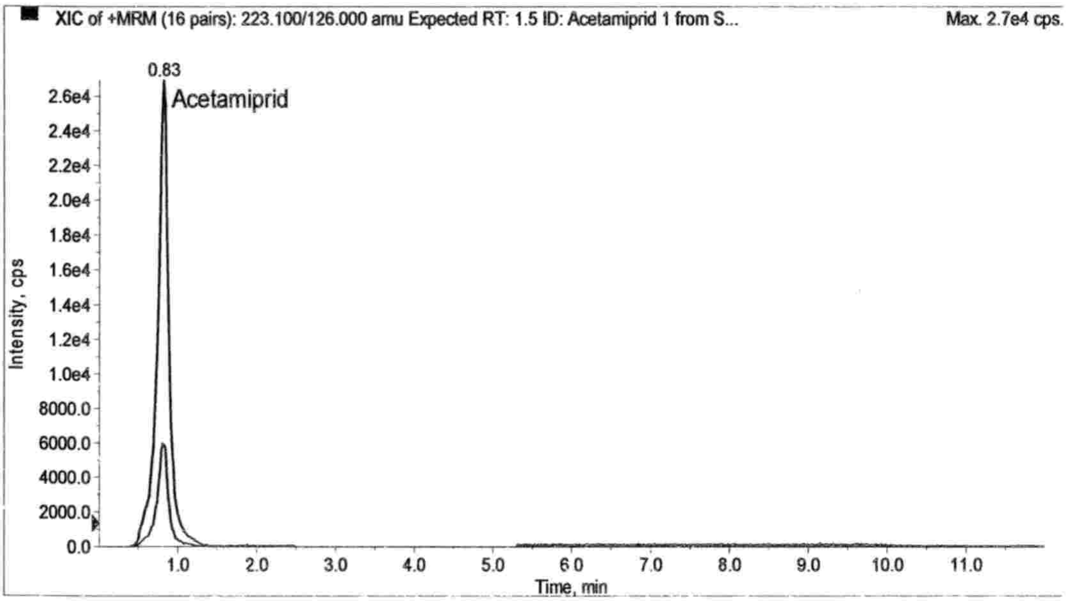


LCMS/MS chromatogram of emamectin benzoate

APPENDIX – XI

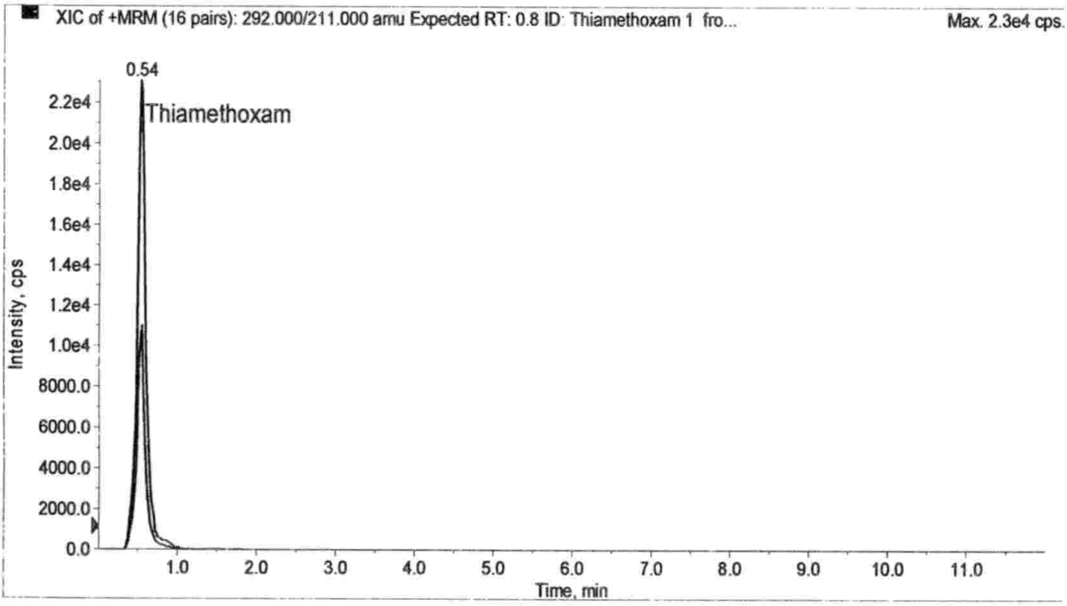


LCMS/MS chromatogram of fipronil

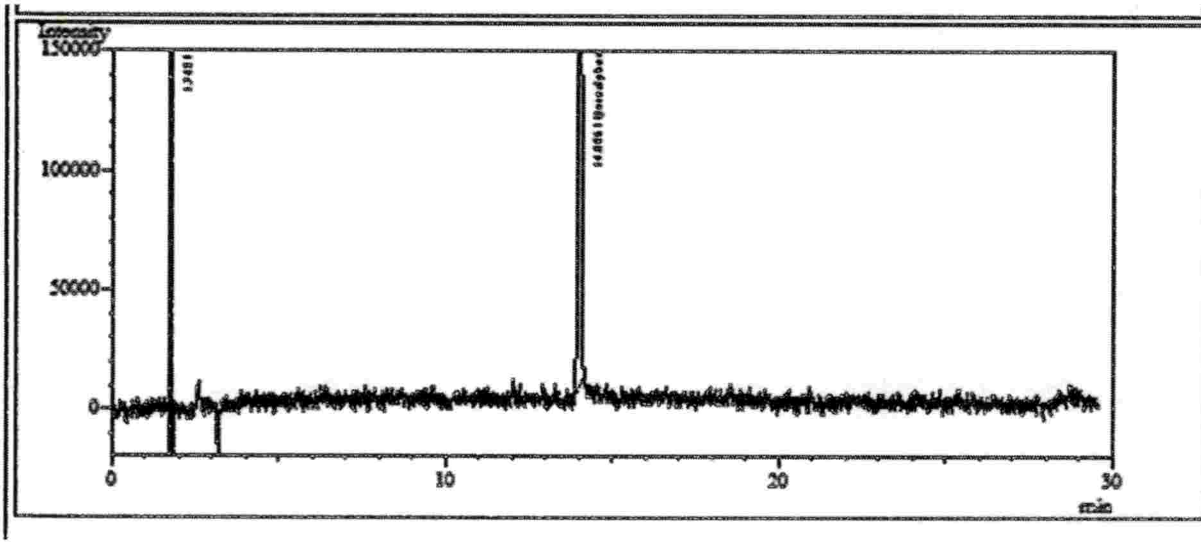


LCMS/MS chromatogram of acetamiprid

APPENDIX – XII

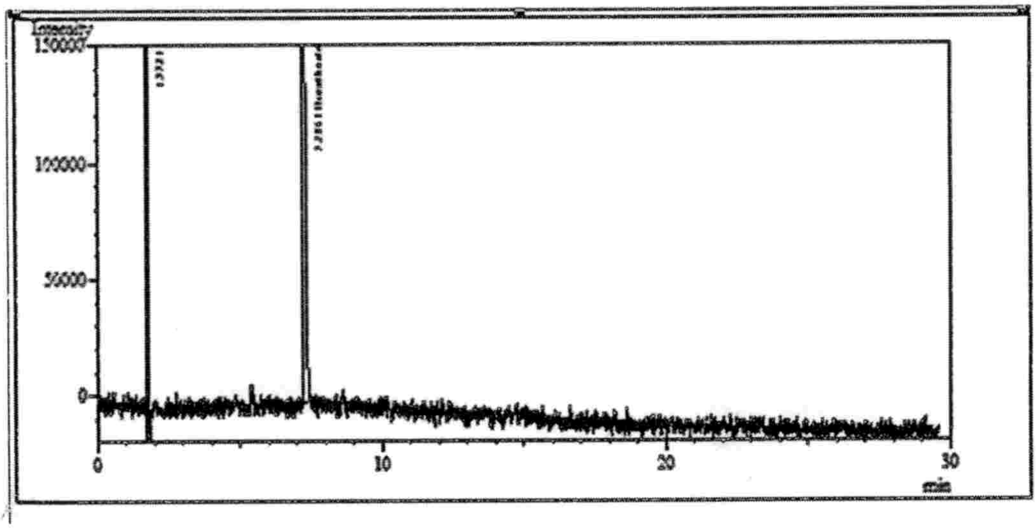


LCMS/MS chromatogram of thiamethoxam

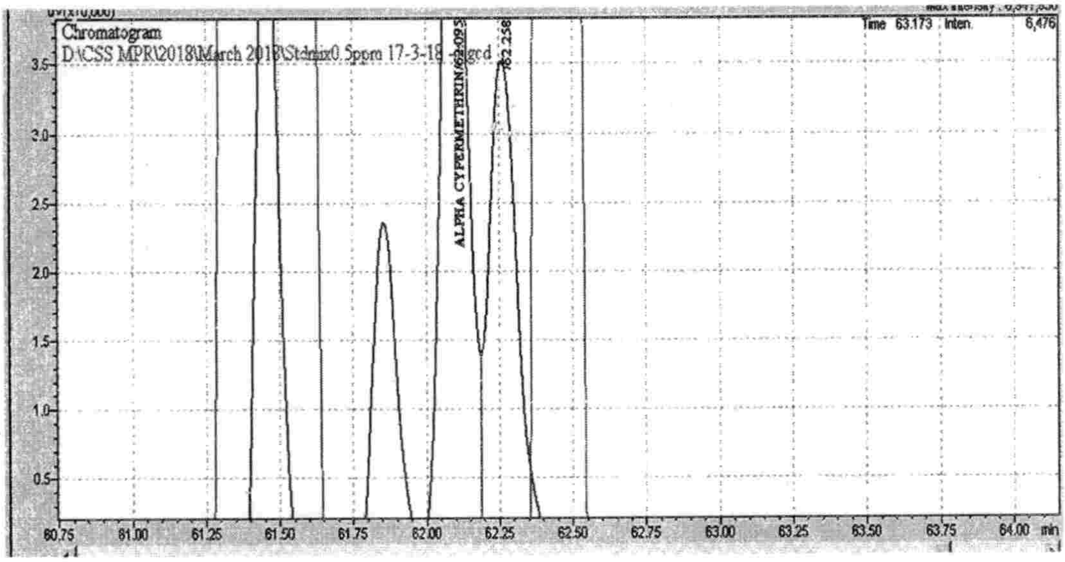


GC- FPD chromatogram of quinalphos

APPENDIX – XIII



GC- FPD chromatogram of dimethoate



GC- ECD chromatogram of cypermethrin