MONITORING AND DECONTAMINATION OF PESTICIDE RESIDUES IN AGRICULTURAL COMMODITIES

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(2011-11-115)

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DECLARATION

I hereby declare that this thesis entitled **"Monitoring and decontamination of pesticide residues in agricultural commodities"** is a bonafide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award of any degree, diploma, associate ship, fellowship or other similar title, of any other University or Society.

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Dedicated to my mother

CONTENTS

LIST OF TABLES

LIST OF TABLES CONTINUED

LIST OF TABLES CONTINUED

LIST OF TABLES CONTINUED

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

%	Per Cent
m^{-2}	Per square metre
@	At the rate of
a.i.	Active Ingredient
AINP (PR)	All India Network Project on Pesticide Residue
AR	Analytical Reagent
BDL	Below Detectable Limit
CRM	Certified Reference Material
C.D.	Critical Difference
cm	Centimeter(s)
${}^{0}C$	Degree Celsius
DAS	Days after spraying
EC	Emulsifiable Concentrate
et al	And others
Fig.	Figure
g^{-1}	Per gram
GC	Gas Chromatography
h	Hour
HPLC	High Performance Liquid Chromatography
ha^{-1}	Per hectare
HAS	Hours After Spraying
kg	Kilogram
l^{-1}	Per litre
LOD	Limit of Detection
LOQ	Limit of Quantification
m	Metre
ml	Milli litre
µl	Microlitre
m^{-2}	Per square metre

MRL	Maximum Residue Limit
OC	Organochlorines
OP	Organophosphates
ppm	Parts per million
RSD	Relative Standard Deviation
SC	Suspension Concentrate
SD	Standard Deviation
SL	Soluble Liquid
sp.	Species
viz.	Namely

Introduction

1. INTRODUCTION

Pesticides are used globally for the protection of food, fibre, feed and human health. If the credits of pesticides include enhanced economic potential in terms of increased production of food and fibre and amelioration of vector borne diseases, then their debits have resulted in serious health implications to man and his environment. The rampant use of these chemicals, under the adage, 'if little is good, a lot more will be better' has played havoc with human and other life forms.

In India, where meeting food demand is a big challenge, use of chemicals like pesticides, antibiotics and fertilizers are unavoidable inputs to ensure a sustained production of food grain to meet the increasing demand. Pesticide residues in or on plants may not be unavoidable even when pesticides are used in accordance with Good Agricultural Practice (GAP). Eventhough considerable progress has been made in the development of effective pesticides, only a very small fraction of all the applied pesticides is directly involved in the pest control mechanism. Out of the total pesticidal chemicals applied in the plant protection operations, less than 5 % are estimated to reach the actual initial target. This implies that most of the applied pesticides result in leaving residues in the environment both in the terrestrial and aquatic food chains where they undergo concentration and likely to exert potential long term adverse health effects. It has been postulated that the long term low dose exposure of these pesticides are increasingly linked to human health effects such as immunosuppresion, hormone disruption, reproductive abnormalities and cancer (Hazara *et al.*, 2012)

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 All India Network Project on Pesticide Residue AINP(PR), Kerala Agricultural University (KAU), Vellayani centre 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 this 9.69 per cent samples, 3.92 per cent samples had pesticide residues above Maximum Residue Limit (MRL) fixed by Food Safety and 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 %), okra (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.

Zhang *et al.* (2010) reported that organophosphate insecticides like malathion, chlorpyriphos, dichlorovos (DDVP), fenitrothion and synthetic pyrethroids like cypermethrin are misused widely as grain protectants during storage. Almost all types of foods are vulnerable to pesticide residues. Food contaminated with toxic pesticide is likely to be associated with severe effects on human health. So safe food is a basic requirement, implying acceptable and safe level of contaminants, adulterants, naturally occurring toxins or any other substances that make food injurious to health. Since daily diet of Keralites include cereals like rice and wheat spices like cardamom and cumin seed, monitoring of pesticide residues in these commodities is very essential. Based on the report of AINP(PR), Vellayani, agricultural commodities like rice, wheat, cardamom, capsicum, okra and curry leaf are found to be contaminated with pesticide residues.

Food processing at domestic level would offer a suitable means to tackle the current scenario of unsafe food (Kaushik *et al.*, 2009). Hence it is essential to explore strategies that address this situation affecting food safety especially for the developing countries where pesticide contamination is widespread due to indiscriminate usage. To ensure food safety for consumers, constant monitoring of pesticide residue levels in food commodities and standardization of simple, cost effective strategies adoptable by consumers is necessary. In the light of the above facts, a detailed study entitled "Monitoring and decontamination of pesticide residues in agricultural commodities" has been undertaken with the following objectives:

1. To monitor the pesticide residues in agricultural commodities like rice, wheat, rice flour, wheat flour, cardamom, cumin seed, capsicum, okra and curry leaf.
2. To study the effect of different decontamination techniques on removal of pesticide residues.

Review of literature

2. REVIEW OF LITERATURE

Agriculture has greatly benefitted from the discovery, development and use of a broad range of pesticides. However, their widespread use together with their unique physical, chemical and biological properties has raised serious concern among the public regarding their adverse effects on human health and environment. Several studies conducted in Kerala had led to a conclusion that the direct health effects of pesticide residues entering the human system through contaminated food are much more serious than the indirect effects through food chain and environment (Mathew *et al.*, 2012). Hence, great significance has to be given to monitor pesticide residues in agricultural commodities and to standardize the simple cost effective methods practiced by home makers to eliminate pesticide residues.

A study was conducted to monitor the pesticide residues in agricultural commodities and to standardize decontamination techniques to remove the residues. The earlier work done in connection with the above topic is reviewed here.

2.1 PESTICIDE RESIDUES IN AGRICULTURAL COMMODITIES

2.1.1 Cereals

Cereals constitute the main food and also the basic ingredient of the regional diets in the world. They are grown in over 73 per cent of total harvested area of the world and contribute over 60 per cent of the world food production (Das *et al.*, 2011). Among the cereals, rice and wheat are the major ingredients in the diet of a vast number of the world's population (Saikia and Deka, 2011).

In order to maintain its constant supply all the year round and to preserve its quality until use, grains are frequently stored for long terms (3 - 36 months). During storage, pesticides will be applied in godowns to reduce loss due to storage pests (Holland *et al.*, 1994).

2.1.1.1 *Rice*

Tayaputch (1998) revealed that traces of banned organochlorine insecticide was found in milled and husked rice grain samples collected from different parts of Thailand. Residues of organophosphate and carbamate insecticides such as monocrotophos, malathion, carbofuran, isocarb and carbaryl were also detected in rice grain samples at low levels.

In India, monitoring studies conducted by All India Network Project on Pesticide Residue revealed that during the period of 1985-1995, more than 80 per cent of the rice grain samples analyzed were found to be contaminated and the contaminants were predominantly Hexa Chloro Hexane (HCH) and Dichloro Diphenyl Trichloroethane (DDT). Residues of HCH varied from traces of 5.32 mg kg^{-1}and DDT from 0.005 to 1.32 mg kg^{-1} (AICRP (PR), 1996). However, in 2003 the contaminants reported from rice were carbofuran, phorate and endosulphan (AICRP (PR), 2003). Ciscato *et al.* (2003) reported that, out of 32 rice samples, pesticide residues were detected in 21.90 per cent of the analyzed samples. The pesticides detected were endosulphan, fenitrothion, monocrotophos, pirimiphos methyl and triadimefon.

A multicenter study was conducted by Indian Council of Medical Research to monitor pesticide residues in rice samples collected from the rural and urban areas of 13 states representing different geographical regions of India. In that study, 58 to 73 per cent of the samples analyzed showed the presence of DDT and HCH. Concentrations of alpha, beta, gamma and delta HCH exceeded the Maximum Residue Limit of 0.05 mg kg^{-1} for each isomer in rice fixed by the Ministry of Health and Family Welfare of the Indian Government in 4.3, 2.6, 1.7 and 1.2 per cent of the samples respectively (Toteja *et al.*, 2003). In Dehradun, a study was conducted by Babu and his co workers (2003) and reported the presence of DDT, HCH, their isomers and metabolites in the samples of basmathi rice grains collected from ten different villages where basmati is grown. The average concentration of DDT varied from 0.002 to 0.040 mg kg^{-1}and that of HCH ranged from 0.013 to 0.113 mg kg^{-1}. All the four isomers of HCH were present in the grains.

Deka *et al.* (2004) reported the presence of pesticide residues in unpolished,

polished and parboiled rice in Assam. Residues of carbendazim was detected from rice grains at a concentration of 0.001 mg kg^{-1} (Arora *et al.*, 2008), and residues of endosulphan, dichlorovos, omethoate, methamidophos, parathion, methyl parathion and triazophos with concentrations ranging from 0.011 to1.756 mg kg^{-1} were detected in 2520 samples of milled rice in China (Chen *et al.*, 2009).

The consignments of basmathi rice from India were rejected in the US port due to the presence of residues of pesticides such as bavistin, isoprothiolane and tricyclazole which were not registered with the U.S. Food and Drug Administration (USFDA) (Anonymous, 2012).

2.1.1.2 *Wheat*

Saeed *et al.* (2001) reported that chlorpyriphos methyl was present in wheat flour (both white and brown) in Kuwait with a concentration ranging from 37 to 720 mg kg^{-1}. In China, Bai *et al.* (2006) reported the presence of residues of organophosphate pesticide in the market food samples including cereals and the residue levels were below MRLs. However, study conducted by Balinova and co workers (2006) in Turkey revealed the presence of organophosphate pesticides like chlorpyriphos methyl and malathion residues in stored wheat grains. They concluded that these pesticides were applied post harvest to wheat, as grain protectants, because of their relatively low rates of degradation in the grain under practical storage conditions. Maver *et al.* (2007) detected organophosphorus pesticide residues from cereals in Slovenia. In Serbia, Skrbic (2007) reported 20 organochlorine and 15 organophosphate pesticides in wheat. The concentration of organochlorine pesticides were 32–47 mg kg^{-1} for beta HCH, 28– 41 mg kg^{-1} for gamma HCH, <1–61 mg kg^{-1} for aldrin, 5–132 mg kg^{-1} for dieldrin, 15–111 mg kg^{-1} endrin ketone and < 1–77 mg kg^{-1} for endrin aldehyde.

A monitoring study conducted by Dalvie and London (2008) in South Africa revealed the presence of pesticide residues in both produced and imported wheat. The most frequently detected pesticides were mercaptothion (99 %), permethrin (19 %) and chlorpyriphos (17 %). Multiple pesticides were detected in about 30 per cent of local samples and 39 per cent of imported samples. Nine (11

%) samples exceeded the EU wheat MRL for permethrin (0.05 mg kg^{-1}) which included seven (10 %) local samples and two (15 %) imported samples. Guler *et al.* (2010) reported the presence of cis-chlordane and methoxychlor residues in wheat from Kenya region and Turkey.

In India, Rekha and Prasad (2006) found out the residues of endosulphan in wheat from all market samples but pesticide residues were well below the MRLs. Data generated by AINP (PR), KAU Vellayani centre during 2011-2012 revealed that 15.71 per cent of the wheat grain sampled from different districts of Kerala found to be contaminated with different pesticide like malathion, methyl parathion, fenvalerate and cypermethrin.

2.1.1.3 *Rice flour and wheat flour*

During storage, pesticides may be applied in godowns to reduce losses from storage pests (Holland *et al.*, 1994). Hence grain based foods have the potential to be a major source of residues in the diet for these pesticides.

A monitoring study was conducted by Bakore *et al.* (2004) to evaluate the pesticide contamination in wheat flour from Jaipur City, Rajasthan during 2004. The study revealed the presence of organochlorine pesticide residues like DDT and its metabolites, HCH and its isomers, heptachlor and its expoxide and aldrin. The amount of pesticide detected in wheat flour was higher than the permissible limits prescribed by WHO/FAO.

2.1.2 Spices

India is the largest producer and consumer of spices in the world. Spices have been the backbone of agricultural industry in India and earn a major part of foreign exchange annually. Spices have been an integral part of the Indian diet and the household consumption demand for spices is high (Shinoj and Mathur, 2006). However, the major constraint in the production of spices is its proneness to infestation by diverse groups of insects, pests and diseases. At present, these pests are kept under check with the steady use of pesticides. The residues of pesticides deposited during plant protection operations are a major concern of today and it was reported that pesticide use in cardamom plantations in Idukki was one of the world's highest (Mishra, 2011). Considering the number of rounds of pesticide sprays and quantity of pesticides used in cardamom, one can rate cardamom as the highest pesticide consuming rain fed crop in the world and hence reckoned as a pesticide hot spot of the world (Murugan *et al.*, 2011)

2.1.2.1 *Cardamom*

Pesticide residues of DDT and BHC were detected in 28 spice samples from 25 producing countries (Sullivan, 1980). In a monitoring study carried out by Chozhan and Regupathy (1989), 130 cardamom samples were analyzed to find out the residues of organophosphate insecticides, the number of samples which contained residues of quinalphos, monocrotophos and fenthion above MRL were 12, 25 and one respectively. Residues of more than one insecticide were detected in some samples. The level of residues varied from 0.008 - 0.72 mg kg^{-1} in the case of quinalphos 0.001 - 0.54 mg kg^{-1} in the case of fenthion and 0.004 - 0.98 mg kg^{-1} in the case of monocrotophos.

Spice samples including cardamom monitored during 1980 - 89 in India revealed that 75 - 100 per cent of samples were contaminated with DDT and HCH (Kathpal and Kumari, 1993). Studies conducted under the All India Network Project on Pesticide Residues indicated the presence of residues of insecticides in varying levels. Endosulphan, quinalphos and monocrotophos were the common pesticides which exceeded the MRL value (Anonymous, 2001).

Shetty (2006) reported the presence of residues of seven pesticides in cardamom samples collected from the cardamom hill including triazophos, quinalphos and endosulphan at higher levels.

Monitoring of pesticide residues in cardamom under DAC funded project on monitoring of pesticides residues at national level revealed the presence of residues of dichlorovos in cardamom samples collected from Coimbatore region. Similarly samples collected from Idukki and Trivandrum district showed the residues of quinalphos to the tune of 0.06 - 0.395 mg kg^{-1} (www.fsssai.gov.in./portal/o/pdf).

A study conducted by Mathew and co workers (1998) showed that residues of quinalphos were present in fresh and dried cardamom capsules. The results of the monitoring studies conducted in spice samples collected from different district of Kerala showed that out of 597 spice samples (cardamom, cumin, pepper, fennel) 37.18 per cent samples were contaminated with pesticide residues and 15.91 per cent samples with multiple residues of pesticides. Number of samples containing pesticide residues above PFA/Codex MRL were 52 whereas 372 were without PFA/Codex MRL (AICRP(PR), 2012). Among the spices monitored for pesticide residues from Kerala, cardamom (79.20 %) had detectable level of pesticide residues (Mathew *et al.*, 2012).

In a monitoring study conducted at Idukki district of Kerala, out of the total 180 cardamom samples analyzed, residues were detected in 173 samples. The most common contaminant was quinalphos which was detected in 121 out of 180 samples analyzed. Other major contaminants include lambda cyhalothrin, cypermethrin, endosulphan and profenophos. The levels of residues of quinalphos in all the samples were above PFA - MRL. Other residues of pesticides detected above the PFA/Codex MRL were alpha endosulphan, cypermethrin and malathion (Seena, 2013).

2.1.2.1 *Cumin seed*

The residues of organochlorine pesticides, DDT (0.055 mg kg^{-1}) and HCH (0.0467 mg kg^{-1}) were detected in cumin seed collected from the local markets of Lucknow, India (Srivastava *et al.*, 2001). It was reported that residues of both malathion (4.1 mg kg^{-1}) and diazinon (7.6 mg kg^{-1}) were detected in cumin seed samples collected from Iran (Sarkail *et al.*, 2012).

2.1.3 Vegetables

Vegetables play an important role in human nutrition and health by providing minerals, micronutrients, vitamins, antioxidants, phytosterols and dietary fiber. In India, vegetables are a major constituent of daily diet as majority of Indians are vegetarians (Kumari, 2008). However, the average yield per hectare is relatively low. The major limiting factor threatening vegetable production includes the extensive crop devastation due to increased pest menace, which causes an average of 40 per cent loss in different crops (Srinivasan, 1993). Therefore, a large number of pesticides are applied to control these pests, increasing the potential risk for human exposure, when freshly consumed. It is expected that fruits and vegetables contain higher pesticide residue levels compared to other foods of plant origin, such as bread based on cereal processing, because they are mainly consumed raw or semi-processed (Chen *et al.*, 2011). The main exposure to pesticides in humans is via foods (especially by fruit and vegetables), contributing five times more than other routes, such as air and drinking water (Claeys *et al.*, 2011).

Charan and his co workers (2010) conducted a study to determine the pesticide contamination in farm gate vegetables of central Aravalli region of Rajasthan. They reported that the level of contamination was 40.11 per cent and maximum contamination was reported in cauliflower (51.85 %) followed by brinjal (50.00 %), tomato (46.43 %), okra (32.00 %), cabbage (28.20 %) and potato (23.53 %). The MRL values of pesticides *viz.,* methyl parathion, monocrotophos, cypermethrin and quinalphos slightly exceeded MRL values.

Another monitoring study conducted in vegetable samples collected from local markets of Lucknow during the year 2009 revealed the presence of twenty three pesticides ranging from 0.005–12.35 mg kg^{-1}. The detected pesticides were, HCH, dicofol, endosulphan, fenpropathrin, permethrin-II, β-cyfluthrin-II, fenvalerate-I, dichlorvos, dimethoate, diazinon, malathion, chlorofenvinfos, anilophos and dimethachlor. In some vegetables like radish, cucumber, cauliflower, cabbage and okra, the detected pesticides (HCH, permethrin-II, dichlorvos, and chlorofenvinfos) were above MRL. However, in other vegetables, the levels of pesticide residues were either below detection limit or MRL (Srivastava *et al.*, 2011).

Vegetable samples of brinjal, okra, green chilli, crucifers, and cucurbits collected from farmer's field of Andaman Nicobar Islands, were tested for the presence of organochlorine (OC), organophosphorus (OP) and synthetic pyrethroid (SP) compounds. From the samples tested, 34.00 per cent contained pesticide residues. Among the OC compounds, alpha endosulphan, beta endosulphan, and endosulphan sulfate were detected in 14.50 per cent (crucifer, okra, green chilli and cucurbit) of the samples. SP residues *viz.*, alpha cypermethrin, fenvalerate I, fluvalinate I, deltamethrin, and lambda cyhalothrin were detected in 32 per cent of the samples. The residues of OP compounds such as chlorpyriphos, profenophoss, monocrotophos, triazophos, ethion, dimethoate and acephate were found in 54 per cent of the samples (Swarnam and Velmurugan, 2012).

Another study conducted by Kumar and co workers (2012) have shown the presence of organochlorine pesticides like aldrin, dieldrin, heptachlor and lindane in leafy vegetables like sugarbeet, coriander and fenugreek collected from local markets in Kolkata. The concentration of total organochlorine pesticides in sugar beet, fenugreek and coriander ranged between <0.01 - 4.38 mg kg^{-1}, <0.01-4.16 mg kg^{-1}and <0.01-6.00 mg kg^{-1} respectively.

Pesticides like endosulphan (2.80 mg kg^{-1}), profenophoss (22.70 mg kg^{-1}), triazophos (13.40 mg kg^{-1}), phosalone (0.10 mg kg^{-1}), bifenthrin (2.80 mg kg^{-1}) diethion (3.00 mg kg^{-1}), acephate (0.048 mg kg^{-1}), propargite (1.90 mg kg^{-1}) and acetamiprid (10 mg kg^{-1}) were detected in curry leaf samples exported from India to France during 2012 (RASFF, 2012).

In a monitoring study conducted at the local fields and various markets in the twin cities of Hyderabad, Secunderabad and R.R. District during 2012, it was found that both green and red capsicum had contaminated with chlorpyriphos (3.50 mg kg^{-1}), imazilil (4.80 mg kg^{-1}), thiabendazole (11.40 mg kg^{-1}) and diphenylamine (8.70 mg kg^{-1}) residues and brinjal with chlorpyriphos (1.40 mg kg^{-1}), imazilil (4.20 mg kg^{-1}), thiabendazole (44.40 mg kg^{-1}) diphenylamine (9.80 mg kg^{-1}), acephate (5.20 mg kg^{-1}), endosulphan (2.20 mg kg^{-1}), chlorothalonil (0.20 mg kg^{-1}) and phosmet (9.00 mg kg^{-1}) residues (Dasika *et al.*, 2012).

According to the data generated by Pesticide Residue Research and Analytical Laboratory (PRRAL), Kerala Agricultural University, Vellayani centre during 2011-2012, 60.76 per cent of curry leaf, 44.44 per cent of cowpea, 43.75 per cent of green chilli, 33.33 per cent of bittergourd, 17.24 per cent of capsicum, 12.21 per cent of cauliflower, 10.33 per cent of bhindi, 5.16 per cent of cabbage, 4.22 per cent of brinjal and 2.34 per cent of tomato samples had detectable levels of pesticide residues (Mathew *et al.*, 2012).

Viju (2012) quoted the results of study conducted by All India Network project on pesticide Residue, Vellayani Centre that most contaminated vegetable samples were chilly (18 of 48 samples) and curry leaves (47 of 79 samples) collected from different markets of Kerala had traces of pesticides which should not have been used.

Results of the project "Production and Marketing of Safe To Eat Vegetables, Govt. of Kerala" revealed the presence of pesticide residues in cauliflower, cabbage, cowpea, red amaranthus, red onion, aonla, green chilli, coriander leaves, curry leaf, drum stick, tomato, capsicum, mint leaves, ivy gourd and okra samples collected from Thiruvananthapuram region (Mathew, 2013). Alarming levels of pesticide residues were found from a sample of China apple collected from Palakkad market (Anonymous, 2013a).

2.1.4 Risk assessment of pesticide residues in agricultural commodities

Food and health authorities around the world are continuously monitoring pesticide residues in different agricultural commodities. The results of monitoring studies focus on the proper use of pesticides in terms of authorization and registration and on compliance with MRLs. MRLs encourage food safety by restricting the concentration of a pesticide residue permitted on a commodity, and by limiting the commodities on which it is allowed (Claeys *et al.*, 2011).

The potential health risks from acute and chronic dietary exposure to pesticides can be assessed by comparing the daily intake with the toxicological reference dose (WHO, 1997). The toxicological reference dose is an estimate of the amount of pesticide that can be ingested without appreciable health risk on the basis of all known facts at the time of the evaluation (JMPR, 2002). There are two types of reference dose: the Acute Reference Dose (ARfD) which is the amount

Table I. Long-term health effects associated with the pesticides detected in the present study as per Pesticide Property Data Base

Pesticide	Long-term health effects								
	Acetyl choline esterase inhibitor	Neurotoxicant	Skin irritant	Carcinogen	Mutagen	Endocrine disruptor	Reproduction/ developmental effect	Respiratory track irritant	Eye irritant
Profenophos	√	√	√	x	-	-	x	-	?
Malathion	√	√	x	?	?	?	?	?	x
Fenvalerate	-	x	√	x	-	√	-	√	√
Ethion	√	√	-	x	x	-	?	-	-
Cypermethrin	x	x	√	?	x	?	?	√	√
Methyl parathion	√	√	-	?	x	?	-	-	-
Chlorpyriphos	√	?	√	x	x	?	√	x	√
Quinalphos	√	√	√	?	-	-	-	√	√

PPDB: Pesticide http://sitem.herts.ac.uk/aeru/footprint/en/index.htm

√: Yes, known to cause a problem

X: No, known not to cause a problem

?: Possibly, status not identified

- : No data

that can be ingested over a short period of time, usually one meal or one day, and the Acceptable Daily Intake (ADI) which is the amount that can be ingested daily, over a life time. Long term health effects associated with the pesticides like its carcinogenity, mutagenity etc (Table 1) are accounted for in ADI setting (EFSA, 2008). Intake is often expressed simply as a percentage of a reference dose, a calculated intake above 4 per cent of the reference dose *ie* ADI and 50 per cent of ARfD is therefore considered an unacceptable risk contributing acute and chronic health risk (Tucker, 2008).

2.2 EFFECT OF HOUSEHOLD PRACTICES TO DECONTAMINATE PESTICIDE RESIDUES IN FOOD COMMODITIES

The food safety issue induced by food contamination concerning pesticide residues is becoming more and more important. Food processing at domestic and industrial level would offer a suitable means to tackle the current scenario of unsafe food. But the efficiency of food processing techniques depends on many factors like physicochemical properties of both the pesticide and the commodity, age of the residue etc. The major physiochemical properties of pesticides governing their removal during processing are given in Table 2.

2.2.1 Storage

Storage is the most important post harvest practice in crop production. Grains are frequently stored long term (3 - 36 months) at ambient temperature in bulk silos where insecticides may be applied post-harvest to reduce losses from storage pests. Grain based foods therefore have the potential to be a major source of residues in the diet for these insecticides. Studies on stored grain following post-harvest treatments with insecticides have generally shown that residues decline rather slowly due to their relative low rates of degradation under practical storage conditions (Holland *et al.*, 1994).

The studies on the degradation of ^{14}C-malathion on stored wheat under laboratory conditions in closed jars at 25°C and grain moisture content of 18.50 per cent, simulating closed storage barns in tropical conditions revealed that the degradation of malathion to be very rapid under these conditions and only 43 per

Table 2. Physio-chemical properties of pesticides detected in the present study as per Pesticide Property Data Base

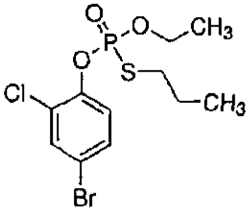
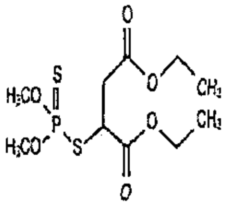
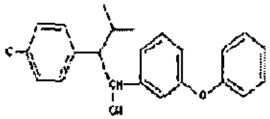
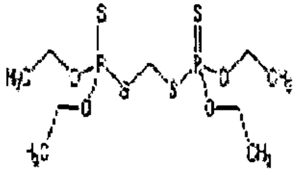
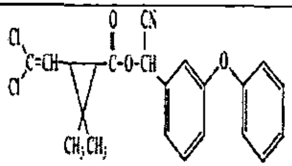
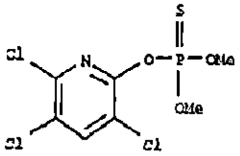
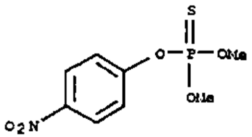
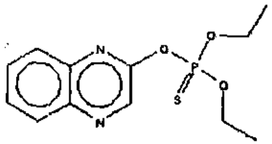
Pesticides	Chemical structure	Mode of action	pH sensitivity	Solubility in water at 20°C (mg l^{-1})	Boiling point (°C)	Octanol-water partition coefficient at pH 7, 20°C	Vapour pressure at 25°C (mPa)
Profenophos		Non-systemic with contact and stomach action.	-	28	-	1.7	2.53
Malathion		Non-systemic with contact, stomach and respiratory action.	No	143	Decomposes before boiling	2.75	3.1
Fenvalerate		Non-systemic with contact and stomach action.	-	0.001	Decomposes on *distillation*	5.01	0.0192
Ethion		Non-systemic with a predominate contact action.	-	2	165	5.07	0.2

Table 2 continued.

Pesticides	Chemical structure	Mode of action	pH sensitivity	Solubility in water at 20°C (mg l^{-1})	Boiling point (°C)	Octanol-water partition coefficient at pH 7, 20°C	Vapour pressure at 25°C (mPa)
Cypermethrin		Non-systemic with contact and stomach action.	-	0.009	Decomposes before boiling	5.30	0.00023
Chlorpyriphos		Non-systemic with contact and stomach action	No	1.05	Decomposes before boiling	4.70	1.43
Methyl parathion		Contact and stomach insecticide.	-	55	-	3	0.2
Quinalphos		Contact and stomach action	-	17.8	-	4.44	0.346

PPDB: Pesticide http://sitem.herts.ac.uk/aeru/footprint/en/index.htm cent of the applied parent pesticide remained in the grains after five weeks of storage and only 16 per cent after five months of storage (Matthews, 1990).

George and Dikshit (1995) reported that residues of deltamethrin on blackgram were reduced by 25.90 per cent within a period of six months of storage and that of cypermethrin on green gram were reduced by 41.10 per cent. Lal and Dikshit (2001) reported that the residues of deltamethrin on chickpea were reduced by 11.10 per cent, 60.50 per cent, and 78.40 per cent during the storage period of one, four and six months respectively. Dikshit (2001) reported that the residues of cypermethrin on black gram showed cumulative reduction of 38.40 per cent within a period of six months and respective reduction in case of chickpea was 40.10 per cent and cowpea 37.00 per cent. The cypermethrin residues on stored rice grains were reduced from 14.10 - 52.20 per cent within the period of two months to six months after treatment (Borah *et al.*, 2001). Organochlorine and synthetic pyrethroid residues are very stable under storage conditions when compared to organophosphate insecticides.

The mean concentration of chlorpropham in individual tubers stored at 5°C in dark was 3.80 mg kg^{-1} at 10 days post application which decreased to 2.90 mg kg^{-1} at 28 days post-application and became 2.20 mg kg^{-1} after 65 days of application (Lentza-Rizos and Balokas, 2001). Overall disappearances of 64 per cent and 47 per cent of initial dose of malathion from maize grains (initial 7.73 mg kg^{-1}) and beans (initial 7.52 mg kg^{-1}) respectively were obtained after 12 months of storage in an open basket. These high losses were explained by volatilization and possible settling of the pesticide dust formulation to the bottom and on the sides of basket during storage in the open and windy tropical laboratory (Lalah and Wandiga, 2002). Rani and co workers (2006) reported that the residues of deltamethrin in rice grains stored in jute bags showed reduction of 90.30 per cent and 96.70 per cent within 120 and 150 days after treatment respectively.

The initial DDVP residue level (1.74 mg kg^{-1}) in cucumber samples was decreased 48.10 per cent (0.901 mg kg^{-1}) by storage at 4°C for three days and 70.80 per cent (0.506 mg kg^{-1}) by the storage procedure at 4°C for six days

(Cengiz *et al.*, 2006). The effect of storage on the breakdown of malathion (initial concentration 10.20 mg kg^{-1}) was examined during five and a half months of storage. While the degradation of malathion and isomalathion in barley was observed to be about 65 - 72 per cent the malaoxon was degraded extensively (85 %) during the storage period (Uygun *et al.*, 2007).

The loss of endosulphan, fipronil, alpha endosulphan, beta endosulphan, lambda cyhalothrin and deltamethrin in wheat grains during 120 days of storage was 72.40 per cent, 50.70 per cent, 60.00 per cent, 67.00 per cent, 46.90 per cent and 62.40 per cent respectively (Pal and Shah, 2008).

The dynamics of incurred pesticide residues in apples variety Melrose, was monitored during their cold storage at 1 - 3°C for five months. Only six fungicides (captan, cyprodinyl, dodine, pyrimethanil, tebuconazole, tolyfluanid) and one insecticide (phosalone) were detected at the time of harvest. Successive decrease of residues occurred during storage period. Only one fungicide, dodin and one insecticide, phosalone were detected after five months (Ticha *et al.*, 2008). Kong *et al.* (2012) reported the residues of acephate and methamidophos in polished rice and they were dissipated quickly during the first two weeks of storage and then decreased at a slower rate until the end of storage.

2.2.2 Washing

Washing is a preliminary step done in food commodities both in household and commercial preparation. Household washing procedures are normally carried out with running or standing water at moderate temperature. Many studies are conducted to study the effect of washing on pesticide residues in raw agricultural commodity. Effectiveness of washing depends upon the physiochemical properties of the pesticides such as water solubility, hydrolytic rate constant, volatility and octanol water partitioning coefficient (P_{ow}) in conjunction with the actual physical location of the residues, age of residues, temperature and type of washing. (Cengiz *et al.*, 2007). The effect of washing on removal of pesticide residues in different agricultural commodities are reviewed in Table 3.

Table 3. Effect of washing on removal of pesticide residues in different agricultural commodities

Sl. No	Commodity	Type of treatment	Pesticides	Removal (%)	Reference
1	Rice grains	Washing with water	chlorpyriphos	60.00	Lee *et al.*, 1991
2	Rice grains	Washing with water	permethrin	100.00	Fukuhara *et al.*, 1994
3	Rice grains	Three aqueous washing in 30 min	acephate	35.30	Kong *et al.*, 2012
			methamidophos	45.20	
4	Green beans	Washing in cold water for two min	ethylene thiourea	45.00	Marshall, 1982
5	Soya bean	Two aqueous washing	dichlorovos	80-90	Miyahara and Saito, 1994
			malathion		
			chlorpyriphos		
			captan		
6	Chickpea	Washing in water	deltamethrin	15.69	Lal and Dikshit, 2001
7	Mango	Dipping in water for 10 minutes	dimethoate	66.00	Awasthi, 1993
			fenthion	68.00	
			fenvalerate	21.00	
			cypermethrin	27.00	
8	Peaches	Washing in water	iprodione	50.40	Lentza-Rizos, 1995
9	Apple	Washing in water	phosalone	30-50	Mergnat *et al.*, 1995

Table 3. continued

Sl. No	Commodity	Type of treatment	Pesticides	Removal (%)	Reference
10	Apple	Washing in water	azinphos - methyl	53.00	Ong *et al.*, 1996
11	Grapes	Washing in water	azoxystrobin	53.00	Lentza-Rizos *et al.*, 2006
12	Apple	Washing in water for 10-15 s with hand rubbing	captan	50.00	Rawn *et al.*, 2008
13	Apple	Washing in water	chlorpyriphos	17.00	Kong *et al.*, 2012
			cypermethrin	70.00	
			tebuconazole	32.00	
			acetamiprid	42.00	
			carbendazim	50.00	
14	Bittergourd	Washing with water for 30 s	endosulphan	59.05	Nath and Agnihotri, 1984
15	Egg plant	Washing in water	dithane M 45	47.50	Kumar and Agarwal, 1991
16	Tomato	Washing in water	ethylene thiourea	70.00	Knio *et al.*, 2000
17	Okra	Washing in water	beta cyfluthrin	42.20-35.70	Dikshit *et al.*, 2002
18	Cucumber	Washing in water for 15 s	diazinon	22.30	Cengiz *et al.*, 2006
19	Potato	Washing in water	chlorpropham	33-47	Lentza-Rizos and Balokas, 2001

Table 3 continued.

Sl. No	Commodity	Type of treatment	Pesticides	Removal (%)	Reference
20	Tomato	Washing in water	HCH	9.62	Abou-Arab, 1999
			lindane	15.30	
			p,p DDT	9.17	
			dimethoate	18.80	
			profenophos	22.17	
			pirimiphos-methyl	16.20	
21	Tomato	Washing in water	captan	60-80	Krol *et al.*, 2000
			chlorothalonil		
			endosulfan		
			permethrin		
22	Brinjal	Washing in water	cypermethrin	25.47	Walia *et al.*, 2010
23	Tomato	Washing in water	lambda cyhalothrin	39-30	Jayakrishnan *et al.*, 2005
24	Tomato	Washing in water for 15 s and rubbing under running water	procymidone	68.00	Cengiz *et al.*, 2007

Table 3. continued

Sl. No	Commodity	Type of treatment	Pesticides	Removal (%)	Reference
25	Asparagus	Washing in water	chlorpyriphos	24.00	Chavari *et al.*, 2005
			cypermethrin	32.00	
			ethylene bisdithiocarbamate	52.00	
26	Brinjal	Washing in water for 15 s	OP compounds	77.00	Kumari, 2008
27	Cauliflower	Washing in water for 15 s		74.00	
28	Okra	Washing in water for 15 s		50.00	
29	Tomato	Washing in water for one min	endosulphan	67.93	Kapoor, 2010
			carbaryl	65.10	
30	Okra	Washing in water	imidacloprid	27.69	Sheikh *et al.*, 2012
			emamectin benzoate	24.00	
31	Carrot	Washing in water for 5 min	boscalid	78.00	Bonnechere *et al.*, 2012
			difenoconazole	89.00	
			tebuconazole	68.00	
			chlorpyriphos	60.00	

Table 3 continued.

Sl. No	Commodity	Type of treatment	Pesticides	Removal (%)	Reference
32	Cardamom	Washing in water	mancozeb	62.00	Mathews *et al.*, 1999
33	Rice	Washing four times for 5 min	malathion	95.00	Nair *et al.*, 2012
			methyl parathion		
			chlorpyriphos		
			quinalphos		
			fenvalerate		
			cyperemthrin		
34	Wheat	Washing four times for 5 min	malathion	95.00	Nair *et al.*, 2013
			methyl parathion		
			chlorpyriphos		
			quinalphos		
			fenvalerate		
			cyperemthrin		

2.2.3 Sun drying

Drying is the oldest method done to preserve food. Food can be dried in several ways, for example, under sunlight or in an oven or a food dryer can also be used. Drying has been found to reduce pesticide residues considerably.

Drying under sunlight lead to 50 per cent reduction in bitertanol residues from apricot due to photodegradation (Cabras *et al.*, 1998a). Cabras *et al.* (1998b) reported that drying of raisins under sun decreased the dimethoate residues (1.02 mg kg^{-1}) by 81 per cent while oven drying, which was preceded by washing lead to 72 per cent reduction in residues. Drying of grapes led to 64.20 to 71.90 per cent loss of methamidophos due to evaporation of the pesticide during the process (Athanasopoulos *et al.,* 2005). Sun drying decreased the water soluble pesticides imidacloprid (18.90 %) and emamectin benzoate (4.21 %) in okra 24 hours after spraying (Sheikh *et al.*, 2012).

However all most all pesticides were susceptible to photodegradation to some degree, their reduction depends on intensity and spectrum of sunlight, length of exposure, and properties of the pesticide (Kaushik *et al.*, 2009).

2.2.4 Washing and drying

The residue of iprodione in prune fruits at harvest time was 0.68 mg kg^{-1} which became 0.30 mg kg^{-1} after washing with water for 5 min followed by oven drying and rehydration (Cabras *et al.,* 1998c).

2.2.5 Milling

Studies on the fate of pesticide residues on grain subjected to milling showed that the bulk of the insecticides deposited on the grain remained in the epidermis and were removed from the bran during milling. Most residues are present in the outer portions of the grains and consequently levels in bran are considerably higher than in wheat, usually by a factor of about 2 to 6. Even for the pesticides which can enter the grain by translocation, residues are higher in the bran than in the flour (Holland *et al.*, 1994).

Alnaji and Kadoum (1979) reported that when wheat fortified with phoxim-methyl was subjected to milling after a storage period of 365 days, 8-10 per cent reduction in concentration of phoxim-methyl was obtained. The highest residues of phoxim-methyl were found in the bran and shorts and very small amounts were in the flour. Residues of deltamethrin in whole grain was 1.84 mg kg^{-1} after three hours of treatment and the corresponding residue amount in the milled grain was 1.06 mg kg^{-1} contributing 42.39 per cent removal (Marei *et al.*, 1995). The pirimiphos methyl residues in processed products of wheat were low when compared to whole grain, however bran (richer in oil) had approximately 2.5 times more pirimiphos methyl residues, whole flour had about the same levels as grain and white flour had about 60 per cent of the residues (Sgarbiero *et al.*, 2002). Uygun *et al.* (2005) revealed that the reduction of malathion residues was about 95 per cent in wheat through milling (to flour) from an initial level of 8.89 mg kg^{-1}.

Stored grains are milled prior to their usage in various forms so that the combined effect of storage and milling assumes considerable significance. After treating wheat for 180 days with deltamethrin at an application rate of 0.50 mg kg^{-1}, the residues were between 0.03 and 0.20 mg kg^{-1} in various types of flour (Balinova *et al.*, 2006).

Rahula and Shah (2008) reported that milling of wheat grains resulted in 6.06 per cent loss of lambda cyhalothrin and 4.18 per cent loss of deltamethrin. The residues of endosulphan, fipronil, endosulphan, lambda cyhalothrin and deltamethrin were reduced by 17.30 per cent, 19.50 per cent, 30.60 per cent, 31.50 per cent and 20.20 per cent respectively in wheat through milling (Pal and Shah, 2008).

2.2.6 Cooking

Literature is replete with work on effect of cooking on removal of pesticide residues. It was reported that malathion and its polar metabolites, malathion a and malathion b monocarboxylic acids were completely eliminated by boiling (Lalah and Wandiga, 2002). The per centage removal of trifluralin, chlorpyriphos, decamethrin, cypermethrin and dichlorvos in rice and beans after cooking in a commercial microwave oven for 15 - 45 min was 92 per cent to 99 per cent (Castro *et al.*, 2002).

Kontou *et al.* (2004) investigated the effect of thermal processing by cooking at 100°C and sterilization at 121°C for 15 min on maneb residues in tomato homogenates. After cooking, only 26 per cent of initial maneb residues remained in the samples and 28 per cent was converted to ethylenethiourea (ETU). Sterilization eliminated the residues of the parent compound giving rise to conversion to ETU up to 32 per cent.

Radwan *et al.* (2005) reported that blanching and frying of egg plant for 5 min completely removed the profenophos residues which were initially present at level of 0.27 mg kg^{-1}. A study conducted by Zhang *et al.* (2007) revealed that 86.00 per cent of endosulphan residue was eliminated from dry polluted cabbage with stir-frying in a pan at 100°C for 5 min. Boiling reduced the residues of organophosphates by 100 per cent, 92 per cent and 75 per cent respectively in brinjal, cauliflower and okra (Kumari, 2008).

Cooking of rice in the pressure cooker, microwave oven and open vessel showed 10.60 per cent, 27.35 per cent and 49.20 per cent loss in case of lambda cyhalothrin and 11.30 per cent, 54.40 per cent and 71.50 per cent loss in case of deltamethrin respectively (Rahula and Shah, 2008). Cooking under closed conditions resulted in hydrolysis with 50 per cent of the chlorothalonil residues. Sengupta and co workers (2010) revealed that cooking is the best option in reducing pesticide residues of DDT, HCH, dimethoate, endosulphan and malathion in raw meat samples. Satpathy (2011) reported the average percentage removal of parathion, methyl parathion and formothion residues by cooking is higher than that of washing. The author also concluded that the average removal of endosulphan and malathion from tomato, okra and cauliflower was more difficult when compared to brinjal, beans and capsicum. Based on the type of vegetable and the pesticide treatment, the effects of cooking on removal of residues from vegetables were different (Ling *et al.*, 2011).

Soliman (2001) conducted a study to estimate the stability of pesticides in cooking. He observed that cooking removed organophosphate than organochlorine insecticides, as the percentage reduction of organophosphorous ranged from 49 per cent to 53 per cent at 100°C and the level of reduction ranged from 30.10 and 35.30 per cent for the organochlorines.

The disappearance of pesticide residues during cooking could be due to decomposition by the effect of heat (Abou-Arab and Abou-Donia, 2001). Balinova and co-workers (2006) explained the processes that normally occur during cooking as volatilization, hydrolysis and thermal breakdown at elevated temperature, which depends on different parameters, such as vapour pressure, boiling point, and susceptibility of pesticide to hydrolysis.

Generally vegetables are consumed after peeling followed by cooking. The blanching operation (after peeling) of the contaminated potatoes (at level of 1 mg kg^{-1}), resulted in the reduction of the residues by 28.30 per cent, 22.90 per cent, 26.00 per cent, 47.30 per cent, 46.30 per cent and 45.90 per cent for hexa chloro benzene, lindane, p p DDT, dimethoate, pirimiphos methyl and malathion respectively (Soliman, 2001).

2.2.7 Washing and cooking

Washing the apples followed by cooking (including processing apple to sauce) reduced the amount of residue by 98 per cent (Ong *et al.*, 1996). Lal and Dikshit (2001) reported that washing and steaming of chickpea grains completely removed the deltamethrin residues from an initial level of residue of 0.051 mg kg^{-1}. Complete removal of pesticides like iprobenfos, fenobucarb and propiconazole was observed in colored rice, glutinous rice (white rice and unpolished rice) by washing followed by cooking. However, the reduction of residues was more due to cooking (open system) than simple washing (Yang *et al.*, 2012).

2.2.8 Effect of chemical solutions on removal of pesticide residues

Traditional method of washing vegetables to remove debris and dirt prior to consumption has been assumed to reduce pesticide residues. Several washing solutions such as chlorine solution, ozonated water and strong acid have been proven successful in removal of pesticide residues during commercial crop process (Ong *et al.*, 1996; Zohair, 2001; Pugliese *et al.*, 2004).

Washing as a process is prevalent in most households since it can be done with easily available plain water and also with solutions formulated from chemicals readily available in a household kitchen (Krol *et al.,* 2000). The chemicals recommended for the purpose of removing residues are salt, baking soda, distilled vinegar and potassium permanganate (Extension Toxicology Network, 1996).

In a trial to study the influence of age of residues and different types of wash on residue removal, it was revealed that the residues get reduced from 0th day to 5th day and 2 per cent tamarind solution proved best in reducing residues at 0th and 5th day (Gopichand *et al.,* 1999). Adachi and Okano (2006) reported that chlorothalonil and tetradifon were successfully removed from commercial eggplant and cucumber with an average removal efficiency of 95 per cent just after five minutes of pickling the vegetables in rice bran paste. The treatment of fruits with lemon juice, a dip in 2 per cent tamarind solution for 5 min followed by a wash with tap water and steam cooking for 10 min were found to remove the residues of monocrotophos, fenitrothion and fenvalerate to an extent of 41.81, 100 and 100 per cent respectively (Gardenmo.net, 2011). Dipping in 2 per cent tamarind solution for 15 min followed by washing in tap water resulted in 68 to 75 per cent (Nair *et al.,* 2013) and 70-88 per cent (Nair *et al.,* 2012) of methyl parathion, malathion, chlorpyriphos, quinalphos, profenophos, ethion, cypermethrin and fenvalerate in okra and curry leaves respectively

Soaking in acidic solution like citric acid, ascorbic acid, acetic acid and hydrogen peroxide at a concentration of 5 and 10 per cent for 10 min indicates proficient reduction of pesticide residues. Similarly 18 to 65 per cent loss in pesticide residues was reported by Soliman (2001) by using 2, 4, 6, 8 and 10 per cent acetic acid solution in potato. Study conducted by Wheeler (2002) revealed that acidic solutions of 5 and 10 per cent citric and ascorbic acid give more pesticide dissipation (80 %) than neutral and alkaline solutions.

Kumar (1997) reported that dipping in 2 per cent salt water for one hour removed more than 90 per cent residues of monocrotophos and phosphamidon from bitter gourd. 28 to 93 per cent reduction in organochlorines and 100 per cent reduction in organophoshates was achieved by using 5 and 10 per cent NaCl solution (Wheeler, 2002). The percentage reduction in pesticide residues increases with the gradual increase in concentration of solutions. NaCl with 2, 4, 6, 8 and 10 per cent solution caused 20 to 90 per cent reduction in pesticide residues (Ismail *et al.*, 1993). Dipping grape berries in 2 per cent salt solution for 10 min followed by washing with water proved to be an effective decontamination procedure, facilitating removal of 67.52 and 62.50 per cent residues of endosulphan and 51.77 and 50 per cent quinalphos residues at one and 5 days respectively after spraying (Reddy and Rao, 2002).

Awasthi and Lalitha (1983) reported that dipping of fruits in NaOH solution removed 50 to 60 per cent surface residues of pyrethroids compared to 40 to 50 per cent removal by hydrolytic degradation.

A study was conducted by Hwang *et al.* (2001) to assess the effectiveness of chlorine, chlorine dioxide, ozone, and hydrogen peroxyacetic acid (HPA) treatments on the degradation of mancozeb and ethylenethiourea in apples. Residues of mancozeb decreased by 56 to 99 per cent with chlorine, 44 to 99 per cent with HPA, 56 to 97 per cent with ozone treatment and 36 to 87 per cent with chlorine dioxide treatments. ETU was completely degraded by 500 mg kg^{-1} of calcium hypochlorite and 10 mg $kg^{-1}$of chlorine dioxide. These treatments indicated good potential for the removal of pesticide residues on fruit and in processed products.

A study was conducted by Abou-Arab (1999) to assess the effectiveness of acidic and neutral solutions in removing pesticide residues in tomato. The study revealed that tomatoes contaminated at level of 1 mg kg^{-1} upon washing with different levels of acetic acid solution gave 51.30 per cent, 47.00 per cent, 33.70 per cent, 91.50 per cent, 86.00 per cent and 93.70 per cent loss in HCB, lindane, p p DDT, dimethoate, profenophoss and pirimiphos-methyl respectively followed by sodium chloride washing giving 42.90 per cent, 46.10 per cent, 27.20 per cent, 90.80 per cent, 82.40 per cent and 91.40 per cent loss in the same pesticides respectively (at 10 % NaCl). The trends of the data indicated that the loss of different pesticides under investigation depends on the levels of acetic acid and NaCl solutions (2 %, 4 %, 6 %, 8 %, and 10 %).

Zohair (2001) studied the effect of washing procedures on pesticide residues in potatoes. Washing with 5 per cent and 10 per cent radish solution completely removed aldrin, lindane and heptachlor epoxide. Similar results were obtained by washing with 10 per cent ascorbic acid and 10 per cent citric acid solutions, but the reduction in aldrin was 85 to 90 per cent. Washing with 10 per cent hydrogen peroxide gave removal percentages of 89.10 per cent, 78.00 per cent and 96.00 per cent respectively. Alkaline solution of 10 per cent sodium carbonate lead to 92 per cent, 88 per cent and 95 per cent removal of the residues while neutral solution of 10 per cent sodium chloride removed only 42 per cent, 76 per cent and 86 per cent of the residues. The acidic detergent solutions were more effective in the elimination of organochlorines than alkaline and neutral solutions. Radish solution was the most effective acidic solution in the elimination of pesticides, followed by citric acid and ascorbic acid solutions.

Materials and Methods

3. MATERIALS AND METHODS

Laboratory and pot culture experiments were carried out for monitoring the pesticide residues in agricultural commodities and standardization of techniques to decontaminate them. The experiments were carried out at College of Agriculture, Vellayani during the period 2011 to 2013. Laboratory experiments were carried out at Pesticide Residue Research and Analytical Laboratory (PRRAL), which is under the All India Network Project on Pesticide Residues, College of Agriculture, Vellayani. The pot culture experiments were conducted at the Instructional Farm, College of Agriculture, Vellayani.

3.1 VALIDATION OF MULTI RESIDUE METHODS (MRM) FOR PESTICIDE RESIDUE ANALYSIS IN AGRICULTURAL COMMODITIES

Multi Residue Methods (MRM) for each substrate was validated using the standard protocol. Validation experiments were conducted by Modified Standard Method "AOAC 18th edition 2007:2007.01". Validation parameters *viz.*, Limit of Detection, Limit of Quantification, Linearity, Recovery and Repeatability (Zanella *et al.*, 2000) were evaluated for pesticides under laboratory conditions at AINP on Pesticide Residue, College of Agriculture, Vellayani.

3.1.1 Rice flour and wheat flour (Atta and Maida)

3.1.1.1 *Reagents, Chemicals and Glasswares*

Certified Reference Materials (CRM) of different pesticides used in the present study having purity ranging from 95.10 to 99.99 per cent were purchased from M/s Sigma Aldrich and stored in a freezer at low temperature, with light and moisture excluded. The following glassware, reagents and equipment were used for the study.

1. Beaker 100, 250 and 500 ml
2. Centrifuge tube 15 ml and 50 ml
3. Class A pipette 0.5 ml, 1 ml, 2 ml, 5 ml and 10 ml
4. Conical flask 250 ml
5. Graduated test tube 5 ml, 10 ml, 15 ml, 20 ml and 25 ml.

6. Micropipette 1ml and 5 ml
7. Micro syringe 10 μL and 500 μl
8. Turbovap tube 20 ml and 30 ml

Chemical reagents

1. Acetic acid glacial
2. Acetone AR grade
3. Acetonitrile HPLC grade
4. Florisil AR grade
5. Magnesium Sulphate (hydrated) AR grade
6. n-Hexane HPLC grade
7. Primary Secondary Amine (PSA)
8. Sodium Chloride AR grade
9. Sodium Sulphate AR grade (anhydrous)

Laboratory equipments

1. Blender
2. Homogenizer
3. Hot air oven
4. Laboratory centrifuge
5. Mechanical shaker
6. Vortex shaker
7. Turbovap evaporator LV
8. Weighing balance
9. Gas Chromatograph – (Shimadzu GC 2010 A)

All the glassware were first washed with clean tap water, then with 1 per cent laboline, again washed thoroughly with tap water, distilled water and then rinsed with distilled acetone. These were kept at room temperature for drying and then kept in a hot air oven at 50^0C for 3 h. Syringes were thoroughly rinsed with acetone followed by n-hexane. Solvents used in the study were all glass distilled before use. Sodium sulphate, sodium chloride and magnesium sulphate were pre-washed with acetone, dried at room temperature and then activated in hot air oven at 450 ^{0}C for 5 h.

3.1.1.2 *Determination of Limit of Detection (LOD)*

3.1.1.2.1 *Preparation of standard pesticide mixture*

A weighed amount of analytical grade material of each pesticide was dissolved in a minimum quantity of distilled acetone and diluted with n-hexane: toluene (1:1) to obtain a stock solution of 1000 mg kg^{-1}. Intermediate standards of 100 mg kg^{-1} of individual pesticide was prepared from this stock solution. Aliquots of intermediate standards of individual pesticide group (10 organochlorines, seven organophosphates and five synthetic pyrethroids) were drawn in a separate volumetric flask to get separate working standard mixtures of each group at a concentration level of 10 mg kg^{-1}. Final volume was made up with n- hexane. From this, a working standard mixture of one mg kg^{-1} containing 21 different pesticides belonging to three different pesticide groups (Table 41) was prepared and it was serially diluted to lower concentrations of 0.5, 0.1, 0.075, 0.05, 0.025 and 0.01 mg kg^{-1}.

3.1.1.2.2 *Standardization of condition of Gas Chromatograph (GC)*

Gas Chromatograph – (Shimadzu GC 2010 A) equipped with ^{63}Ni Electron Capture Detector (ECD), fitted with DB-5 capillary column (dimethyl polysiloxane, 30m x 0.25mm i.d. x 0.5μm film thickness) was used for the analysis. Ultra high Purity (99.999 %) nitrogen was used as carrier gas with a column flow rate of 0.79 ml min^{-1} and linear velocity 26.00 cm S^{-1}. A column temperature programme was developed to get proper separation of all pesticides used in the analysis. The operating parameters of the instrument were: oven temperature 170^0C (5 min) $\rightarrow 1.5^0$C min^{-1} $\rightarrow 220^0$C (10 min) $\rightarrow 4^0$C $min^{-1} \rightarrow 280^0$C

(7 min), injection port at 250^{0}C and detector at 300^{0}C and the total run time as 70 min and split ratio 1: 10.

Table 4. List of Certified Reference Material (CRM) used in the preparation of pesticide mixture.

Sl No	Pesticide group	Certified Reference Material	Purity (%)
1.	Organochlorines	Alpha endosulphan	99.6
		Alpha HCH	99.8
		Beta endosulphan	99.8
		Beta HCH	99.2
		Delta HCH	99.5
		Lindane	99.8
		p p DDD	99.2
		p p DDE	99.9
2.	Organophosphates	Chlorpyriphos	99.9
		Ethion	97.8
		Malathion	97.2
		Methyl parathion	99.8
		Phorate	96.0
		Profenophos	98.2
		Quinalphos	99.2
		Dimethoate	98.2
3.	Synthetic pyrethroids	Cyfluthrin	99.8
		Cypermethrin	95.1
		Fluchloralin	98.7
		Fenvalerate	98.7
		Lambda cyhalothrin	97.4

The retention time of each pesticide was recorded by injecting 0.5 mg kg^{-1} individual standard. Two micro litre of each working standard (0.5, 0.1, 0.075, 0.05, 0.025 and 0.01 mg kg^{-1}) was injected in the Gas Chromatograph under set standard GC conditions. The Limit of Detection (LOD) of the instrument for each pesticide was calculated based on the lowest concentration of pesticide that can be identified under standard GC conditions. The Limit of Detection (LOD) for the pesticides is considered to be the concentration that produced a signal to noise ratio of more than 3, and LOD was estimated from the chromatogram corresponding to the lowest point used in the matrix-matched calibration.

3.1.1.3 *Calibration and Linearity*

Linearity was tested for all the 21 pesticides studied. Six concentration levels (0.5, 0.1, 0.075, 0.05, 0.025 and 0.01 mg kg^{-1}) of analyte mixture in two replicates were analysed to establish the calibration curves. The linearity response line (calibration curve) was plotted with concentration of pesticide at X-axis and peak area count at Y-axis. Simple linear regression analysis was performed to calculate the slope and the intercept. The linearity of each analyte was tested using the least square regression method and the coefficient of determination (R^2) was calculated.

3.1.1.4 *Determination of Limit of Quantification (LOQ)*

Limit of Quantification (LOQ) of the analytical methodology for the extraction of pesticide residues was also calculated. It is the lowest level meeting the method performance acceptability criteria (mean recoveries for each representative commodity in the range 70 - 120 %, with a RSD <20 %). LOQs were obtained from the LODs values, applying the following formula: LOQ=3.3 x LOD. (Marchis *et al.*, 2012)

3.1.1.5 *Determination of Recovery and Repeatability*

3.1.1.5.1 *Sample processing*

One kilogram of control samples (pesticide residues below detectable level) of rice flour and wheat flour (atta and maida) were procured from a shop in Trivandrum district and stored for recovery studies. For determining recovery and repeatability, five gram of rice flour, atta and maida samples were taken in 50 ml centrifuge tubes in four replicates each and soaked in 10 ml of water for 10 min.

These were spiked with organochlorine, organophosphate and synthetic pyrethroid pesticides (Table 41) at the required fortification levels (0.01, 0.05, 0.25, 0.5 and 1.0 mg kg^{-1}), by adding an appropriate volume of working standard of 10 mg kg^{-1}. This mixture was then shaken in order to attain a proper homogeneity of pesticides in the samples. The tubes containing fortified samples were left open for a while, for the evaporation of excess solvent. Then, the samples were extracted using 15 ml acetonitrile in a 50 ml centrifuge tube with 150 µL of acetic acid. Subsequently, 6.0 g anhydrous magnesium sulphate and 1.5 g sodium acetate were added, immediately shaken for one min and then the extract was centrifuged at 1500 rpm for 5 min. Ten ml of the upper layer was transferred to a 15 ml centrifuge tube containing 500 mg of Primary Secondary Amine (PSA) and 1.5 g of anhydrous magnesium sulphate. The centrifuge tube was shaken for 30 seconds followed by centrifugation for one min at 1500 rpm. Six ml from the upper layer was taken and concentrated to dryness using Turbovap (50^{0}C) and final volume was made up to one ml using n-hexane and analyzed by GC.

3.1.1.5.2 *Estimation*

The cleaned extracts were analyzed in a Gas Liquid Chromatograph (Shimadzu GC-2010) equipped with ^{63}Ni Electron Capture Detector (ECD) fitted with capillary column (DB-5) of 30m×0.25mm i.d. × 0.25µm dimension. The sample was injected in a split mode with split ratio 1:10. The injector and detector temperature were maintained at 250°C and 300^{0}C respectively and the column temperature was programmed at 160°C to 270°C as described under 3.1.1.2.2. The volume of sample injected was one µl. Ultra high purity (UHP) nitrogen (99.999 %) was used as carrier gas with flow rate of 0.79 ml min^{-1} and linear gas velocity of 26.0 cm s^{-1}.

3.1.1.5.3 *Residue quantification and recovery calculation*

Pesticide residue in substrate (mg kg^{-1}) =

$$\frac{\text{Peak area of sample} \times \text{Concentration of standard injected} \times \text{Volume of sample injected} \times \text{DF}}{\text{Peak area of standard} \times \text{Volume of standard injected}}$$

Dilution Factor (DF) =

$$\frac{\text{Volume of solvent added x Final volume of the extract}}{\text{Weight of sample (g) x Volume of extract taken for concentration}}$$

Percentage recovery (%) =

$$\frac{\text{Concentration of pesticide residue obtained x 100}}{\text{Concentration of pesticide residue added}}$$

3.1.2 Rice and Wheat grains

Validation of multi residue methods for the analysis of pesticide residues in rice and wheat grains were carried out following the protocol as described in 3.1.1 except the sample processing step.

3.1.2.1 *Sample processing*

Twenty five gram of coarsely ground control samples (pesticide residues below detectable level) of rice and wheat grain were taken in 200 ml centrifuge tubes in three replicates each and were spiked with organochlorine, organophosphate and synthetic pyrethroid pesticides (Table 41) at the required fortification levels that is, LOQ, 5 x LOQ and 10 x LOQ, adding an appropriate volume of working standard of 10 mg kg^{-1}. This mixture was then shaken in order to attain a proper homogeneity of pesticides in the samples. The tubes containing fortified samples were left open for a while, just to allow the evaporation of the excess solvent. To this, 25 ml distilled water and 50 ml acetonitrile was added and the mixture was placed on a mechanical shaker for 30 min at 1200 strokes min^{-1}. A total of 12-15 g of activated sodium chloride was added. After centrifuging at 2500 rpm for 4 min, 16 ml supernatant was transferred into a 50 ml centrifuge tube containing 2.0 g sodium sulphate and 2.0 g magnesium sulphate and vortexed at full speed for 30 s and then centrifuged for 5 min at 2500 rpm. Twelve ml of upper organic phase was transferred to another 15 ml centrifuge tube containing 0.75 g and 0.10 g each of anhydrous magnesium sulphate and Primary Secondary Amine (PSA) respectively. After centrifuging at 2500 rpm for 5 min, an aliquot of 4.0 ml supernatant was concentrated using Turbovap (50^0C) and final volume was made up to one ml using n-hexane and analyzed by Gas Chromatograph.

3.1.3 Cardamom and Cumin seed

Validation of multi residue methods for the analysis of pesticide residues in cardamom and cumin seed were carried out following the protocol described in 3.1.1 except the sample processing step.

3.1.3.1 *Sample processing*

Eight gram of coarsely ground cardamom and cumin seed samples taken in 50 ml centrifuge tubes in three replicates each were spiked with organochlorine, organophosphate and synthetic pyrethroid pesticides (Table 41) at the required fortification levels *ie.* LOQ, 5 x LOQ and 10 x LOQ, adding an appropriate volume of working standard of 10 mg L^{-1}. This mixture was then shaken, in order to attain a proper homogeneity of pesticides in the samples. The tubes containing fortified samples were left open for a while, just to allow the evaporation of the excess solvent. To this, 4.0 g activated magnesium sulphate and 1.0 g sodium chloride were added. Then 10 ml of chilled distilled water (4^0C) and 15 ml of acetonitrile were added and the samples were shaken for one min in a vortex and centrifuged at 3500 rpm for 2 min. A dispersive solid phase extraction cleanup process was carried out by transferring the supernatant (6.0 ml) to a centrifuge tube (15 ml) containing 1.0 g magnesium sulphate (hydrated) and 0.30 g PSA (Primary Secondary Amine) and 0.50 g florisil. These tubes containing the supernatant and the reagents were shaken for a few seconds followed by centrifugation at 3500 rpm for 2 min. The cleaned supernatant extract was evaporated to dryness using Turbovap (50°C). The dry residue was reconstituted to one ml with a mixture of n-hexane: acetone (7:3, v/v basis) and analyzed in a Gas Chromatograph

3.1.4 Capsicum, Curry leaf and Okra

Validation of multi residue methods for the analysis of pesticide residues in capsicum, curry leaf and okra were carried out following the protocol described in 3.1.1 except the sample processing step.

3.1.4.1 *Sample processing*

Twenty five gram each of control samples (pesticide residues below detectable level) of blended curry leaf, capsicum and okra were taken in 200 ml centrifuge tubes in three replicates each were spiked with organochlorine, organophosphate and synthetic pyrethroid pesticides (Table 41) at the required fortification levels *ie.* LOQ, 5 x LOQ and 10 x LOQ, adding an appropriate volume of working standard of 10 mg L^{-1}. This mixture was then shaken, in order to attain a proper homogeneity of pesticides in the samples. The tubes containing fortified samples were left open for a while, just to allow the evaporation of excess solvent. A volume of 50 ml acetonitrile was added to the mixture and then homogenized at 14000 rpm for one min. Ten gram of sodium chloride was added to the mixture and centrifuged at 2000-2500 rpm for 4 min. From this, 16 ml supernatant was transferred to a 50 ml centrifuge tube containing 6.0 g sodium sulphate and vortexed. A total of 12 ml supernatant was then transferred to a 15 ml centrifuge tube containing 1.2 g magnesium sulphate and 0.2 g Primary Secondary Amine (PSA) and vortexed again at full speed for 30 s and centrifuged at 2500 rpm for 3 min. After that, 4.0 ml of upper layer was evaporated to dryness using Turbovap at 50^0C. The dry residue was reconstituted to one ml using n-hexane and analyzed in a Gas Chromatograph.

3.2 MONITORING OF PESTICIDE RESIDUES IN AGRICULTURAL COMMODITIES

Agricultural commodities like rice (parboiled, raw and basmathi), branded rice flour, wheat, wheat flour (atta and maida), cardamom, cumin seed, capsicum, okra and curry leaf were tested for the presence of pesticide residues. One sample each of above mentioned commodities were collected from Thiruvanathapuram district at monthly intervals for a period of six months (January 2012 - June 2012). Samples were collected randomly from the lots brought for sale in the markets in such a way that they were representative samples. One kilogram of rice (parboiled, raw and basmathi), branded rice powder, wheat (whole wheat grains and wheat products like atta and maida), 500 g each of cardamom and cumin seed, 2 kg of capsicum, okra and curry leaf were collected and carried in a cloth/polythene cover to the laboratory with labelling. When the samples were taken to the lab, they were prepared for the analysis. The whole quantity of each commodity is blended and a representative sample of 25 g (parboiled rice, raw rice, basmathi rice, wheat, leaflets removed from curry leaf, capsicum and okra), 5 g (rice flour, atta and maida) and 8 g (cardamom and cumin) were analyzed for the presence of pesticide residues.

Samples of parboiled rice, raw rice, basmathi rice and wheat were analyzed following the method described in 3.1.2.1. Samples of rice flour, atta and maida were analysed following the method described in 3.1.1.1. Samples of cardamom and cumin seed were analyzed following the method as described in 3.1.3.1. Samples of capsicum, okra and curry leaf were analyzed following the method as described in 3.1.4.1.

3.3 ASSESSMENT OF THE EFFECT OF WASHING, SOAKING AND COOKING ON REMOVAL OF INSECTICIDE RESIDUES IN RICE

Based on the monitoring data (experiment 3.2), six insecticides viz. malathion, methyl parathion, chlorpyriphos, quinalphos, cypermethrin and fenvalerate were selected for assessing the effect of washing, soaking and cooking on the removal of insecticide residues in rice.

3.3.1 Method validation in cooked rice

Validation of multi residue methods for analysis of pesticide residues in cooked rice was carried out following the protocol described in 3.1.2

3.3.2 Treatment of sample with pesticides

Rice grains with no infestation/contamination were procured, washed four times and sundried. A pesticide emulsion mixture was prepared which contained recommended concentrations of detected insecticides namely malathion (Hilmala 50 EC 2.30 ml L^{-1}), methyl parathion (Folidon 50 EC 3.0 ml L^{-1}), chlorpyriphos (Radar 20 EC 2.50 ml L^{-1}), quinalphos (Ekalux 25 EC 2.0 ml L^{-1}), cypermethrin (Cyperkill 10 EC 1.10 ml L^{-1}) and fenvalerate (Fenval 20 EC 0.60 ml L^{-1}) in one litre. This formulation was evenly sprayed over rice grains (6 kg) spread on a PVC sheet, grains were mixed thoroughly and allowed to dry at room temperature. Dried grains were collected in polythene bags and stored under ambient condition (25°C).

3.3.3 Processing treatments

The rice grains were subjected to normal household processing techniques at five hours and 2 weeks after pesticide application. The different processing techniques used in this experiment are mentioned below.

- Two washings in tap water for two minutes along with rubbing of grains.
- Four washings in tap water for two minutes along with rubbing of grains.
- Soaking (six hours)
- Soaking (six hours) + two washings in tap water for two minutes along with rubbing. of grains.
- Soaking (six hours) + four washings in tap water for two minutes along with rubbing of grains.
- Cooking in water, followed by decanting rice gruel.
- Two washings in tap water for two minutes along with rubbing of grains + cooking.
- Four washings in tap water for two minutes along with rubbing of grains + cooking.

3.3.4 Sample preparation

To study the effect of washing, 250 g of fortified rice grains were subjected to washing (two times and four times) in three replicates for two minutes using 500 ml portion of tap water along with rubbing of grains by hand and then allowed to dry at room temperature overnight. To study the effect of soaking, 250 g of fortified rice grains were soaked in 500 ml of tap water for six hours in three replicates. After treatment, grains were allowed to dry at room temperature. Combined effect of soaking and washing (two times and four times) was also studied following the procedure described above.

To study the effect of cooking, 250 g of fortified rice in three replicates was cooked with 500 ml of tap water in a 5 L steel vessel for 20 min using an induction cooker. After 20 min, the rice gruel was decanted and the cooked rice was allowed to cool at room temperature. Combined effect of washing (two times and four times) and cooking was also studied following the procedure described above.

A representative sample of 25 g was used for residue analysis along with control. The analytical procedure for residue estimation for the six different insecticides in rice grains and cooked rice was followed which is described in detail under section 3.1.2.1.

3.3.5 Processing factor

Levels of pesticides present in processed and unprocessed commodity was estimated using the formula given in 3.1.1.5.3. Based on the disposition of residues in the various processed products, processing factors (PFs) were calculated.

$$PF = \frac{\text{residue concentration in the processed commodity (mg kg}^{-1}\text{)}}{\text{residue concentration in the raw commodity (mg kg}^{-1}\text{)}}$$

PF value of <1 (= reduction factor) indicate a reduction of the residue in the processed commodity, whereas a value >1 (=concentration factor) indicate a concentration effect of the processing procedures.

3.4 ASSESSMENT OF THE EFFECT OF WASHING, DRYING AND MILLING ON REMOVAL OF INSECTICIDE RESIDUES IN WHEAT

Based on the monitoring data (experiment 3.2), six insecticides *viz.*, malathion, methyl parathion, chlorpyriphos, quinalphos, cypermethrin and fenvalerate were selected for assessing the effect of washing, drying and milling on the removal of insecticide residues in wheat.

3.4.1 Treatment of sample with pesticides

Wheat grains with no infestation/contamination were procured, washed four times and sundried for sterilization. A pesticide emulsion mixture was prepared which contained recommended concentrations of detected insecticides *viz.*, malathion (Hilmala 50 EC 2.30 ml L^{-1}), methyl parathion (Folidon 50 EC 3.0 ml L^{-1}), chlorpyriphos (Radar 20 EC 2.50 ml L^{-1}), quinalphos (Ekalux 25 EC 2.0 ml L^{-1}), cypermethrin (Cyperkill 10 EC 1.10 ml L^{-1}) and fenvalerate (Fenval 20 EC 0.60 ml L^{-1}) in one litre. This formulation was evenly sprayed over wheat grains (6 kg) spread on a PVC sheet, grains were mixed thoroughly and allowed to dry at room temperature. Dried grains were collected in polythene bags and stored under ambient condition (25°C).

3.4.2 Processing treatments

The wheat grains were subjected to normal household processing techniques at 5 h and 2 weeks after insecticide application. The different processing techniques used in this experiment are given below.

- Two washings in tap water for two minutes along with rubbing of grains.
- Four washings in tap water for two minutes along with rubbing of grains.
- Sun drying (five hours)
- Milling
- Two washings in tap water for two minutes along with rubbing of grains + sun drying (five hours) + milling.
- Four washings in tap water for two minutes along with rubbing of grains + sun drying (five hours) + milling.

3.4.3 Sample preparation

To study the effect of washing, 250 g of fortified wheat grains were subjected to washing (two times and four times) in three replicates for 2 min using 500 ml portion of tap water along with the rubbing of grains by hand and then allowed to dry at room temperature overnight.

To study the effect of sun drying, 250 g of fortified wheat grains were sun dried for five hours in three replicates. After treatment, grains were allowed to cool at room temperature.

To study the effect of milling, 250 g of fortified wheat grains in three replicates were coarsely ground in a mixer grinder and sieved through sieve filter of 257µm pore size to separate the flour from bran germ. Combined effect of washing (two times and four times), sun drying (five hours) and milling was also studied following the procedure described above.

A representative sample of 25 g was used for residue analysis along with control. The analytical procedure for residue estimation of six different insecticides was followed as per the section 3.1.2.1 (wheat grains) and 3.1.1.5.1 (wheat flour).

3.4.4 Processing factor

Levels of pesticides present in processed and unprocessed commodity was estimated using the formula given in 3.1.1.5.3 and processing factor was estimated following the formula described in 3.3.6.

3.5 ASSESSMENT OF THE EFFECT OF DECORTICATION ON REMOVAL OF INSECTICIDE RESIDUES IN CARDAMOM

Cardamom samples with presence of more than one insecticide during the monitoring period (January - June 2012) were subjected to decortication. Samples (10 g) from each cardamom lot was taken and divided into two portions and one portion was analysed as such (5 g). Second portion was decorticated into two subsamples viz., capsule cover alone (1 g) and seed alone (4 g). The samples were analyzed separately as per the protocol described in 3.1.3.1 and the levels of pesticide present in the processed and unprocessed commodity was estimated using the formula given in 3.1.1.5.3.

3.6 STANDARDISATION OF WASHING WITH SOLUTIONS OF HOUSE HOLD PRODUCTS TO REMOVE INSECTICIDE RESIDUES FROM SELECTED VEGETABLES

3.6.1 Field experiment

3.6.1.1 *Capsicum*

Two kg capsicum fruits of uniform size were procured from organic vegetable shop and brought to the laboratory. Fruits were washed with water and wiped with acetone to remove traces of pesticides remaining on the fruit surface if any. An insecticide emulsion mixture containing commonly detected insecticides *viz.*, malathion (Hilmala 50 EC 2.0 ml L^{-1}), methyl parathion (Folidon 50 EC 2.0 ml L^{-1}), chlorpyriphos (Radar 20 EC 2.0 ml L^{-1}), quinalphos (Ekalux 25 EC 1.60 ml L^{-1}), profenophos (Curacron 50 EC 3.0 ml L^{-1}), ethion (Fosmite 50 EC 3.0 ml L^{-1}), cypermethrin (Cyperkill 25 EC 1.10 ml L^{-1}) and fenvalerate (Fenval 20 EC 0.60 ml L^{-1}) in one litre was prepared and fruits were soaked in insecticide emulsion for 5 min to enable deposition of insecticide on them. The treated samples were then air dried in shade. Five hours after insecticide application, one part of treated fruits was subjected to dipping in different de-contaminating solutions and the other part was kept as control for comparison.

3.6.1.2 *Okra*

The okra variety Varsha Upahar was raised in pots under controlled conditions in the Instructional Farm, College of Agriculture, Vellayani. An insecticide emulsion mixture containing commonly detected insecticides *viz.*, malathion (Hilmala 50 EC 2.0 ml L^{-1}), methyl parathion (Folidon 50 EC 2.0 ml L^{-1}), chlorpyriphos (Radar 20 EC 2.0 ml L^{-1}), quinalphos (Ekalux 25 EC 1.60 ml L^{-1}), profenophos (Curacron 50 EC 3.0 ml L^{-1}), ethion (Fosmite 50 EC 3.0 ml L^{-1}), cypermethrin (Cyperkill 25 EC 1.10 ml L^{-1}) and fenvalerate (Fenval 20 EC 0.60 ml L^{-1}) in one litre was prepared and sprayed at fruiting stage using a hand sprayer. Okra fruits were collected after five hours, 1st day, 3rd day and 5th day after insecticide spraying and were subjected to dipping in different decontaminating solutions, followed by washing with water

3.6.1.3 *Curry leaf*

Curry leaf plants raised organically in the Instructional Farm, College of Agriculture, Vellayani was sprayed with an insecticide emulsion mixture containing malathion (Hilmala 50 EC 2.0 ml L^{-1}), methyl parathion (Folidon 50 EC 2.0 ml L^{-1}), chlorpyriphos (Radar 20 EC 2.0 ml L^{-1}), quinalphos (Ekalux 25 EC 1.60 ml L^{-1}), profenophos (Curacron 50 EC 3.0 ml L^{-1}), ethion (Fosmite 50 EC 3.0 ml L^{-1}), cypermethrin (Cyperkill 25 EC 1.10 ml L^{-1}) and fenvalerate (Fenval 20 EC 0.60 ml L^{-1}) in one litre using a hand sprayer. Curry leaves collected after five hours, 1st day, 3rd day and 5th day of insecticide spraying were subjected to dipping in different decontaminating solutions.

3.6.2 Decontamination treatments

The different decontaminating solutions used in this experiment are mentioned below:

- Tamarind 2 % (20g of tamarind pulp extracted in one litre water)
- Common salt 2 % (20g of common salt dissolved in one litre water)
- Turmeric powder 1 % (10g of turmeric powder dissolved in one litre water)
- Vinegar 2 % (20 ml of vinegar diluted in one litre water)
- Butter milk 2 % (20 ml of buttermilk diluted in one litre water)
- Luke warm water (36-40°C)

- Water (untreated control)

Samples (250 g capsicum fruit, 100 g curry leaves and 250 g okra fruit) were dipped individually in these treatment solutions for fifteen minutes followed by washing in tap water. Samples were then homogenised after chopping into small pieces and the representative sample (25 g) in three replicates was used for residue estimation. The analytical procedure for residue estimation of the different insecticides in different substrates was followed as mentioned in the section 3.1.4.1

3.6.3 Processing factor

Levels of pesticides present in processed and unprocessed commodity was estimated using the formula given in 3.1.1.5.3 and the processing factor was estimated using the formula described in 3.3.6.

Results

4. RESULTS

The salient findings of the study "Monitoring and decontamination of pesticide residues in agricultural commodities" is presented below under the following heads.

4.1 VALIDATION OF MULTI RESIDUE METHODS (MRM) FOR PESTICIDE RESIDUE ANALYSIS IN AGRICULTURAL COMMODITIES

Development of a Multi Residue Method (MRM) satisfying the requirements of Limit of Detection, Limit of Quantification, Linearity, Recovery and Repeatability for the estimation of multiple residues in agricultural commodities is essentially required for monitoring pesticide residues. Results of the preliminary method validation studies for pesticide residue analysis in different agricultural commodities are presented in Table 7 to16.

4.1.1 Rice flour

4.1.1.2 *Determination of Limit of Detection (LOD)*

The Limit of Detection (LOD) of GC for 21 pesticides were considered to be the concentration that produced a signal to noise ratio of more than 3, and LOD was estimated from the chromatogram corresponding to the lowest point used in the matrix-matched calibration. In this work, the LOD of GC for 21 pesticides under study were 0.01mg kg^{-1} and at LOD, the S/N ratio for all the 21 pesticides were >3. The retention time of test pesticides under specified operating conditions of GC are given in Table 5.

4.1.1.3 *Calibration and Linearity*

A calibration curve was prepared by plotting concentrations (0.5, 0.1, 0.075, 0.05, 0.025 and 0.01 mg kg^{-1}) vs. peak area (Appendix I). Good linearity was found within the range of 0.01-0.5 mg kg^{-1} which is evident

Table 5. The retention time of test pesticides under specified operating conditions of Gas Chromatograph

Sl No	Pesticide	Retention Time (min)
1	Phorate	10.503
2	Alpha HCH	10.937
3	Dimethoate	11.133
4	Beta HCH	12.656
5	Lindane	12.894
6	Fluchloralin	13.356
7	Delta HCH	14.621
8	Methyl parathion	17.447
9	Malathion	20.775
10	Chlorpyriphos	21.678
11	Quinalphos	25.824
12	Alpha endosulphan	27.941
13	Profenophos	30.412
14	p,p-DDE	30.762
15	Beta endosulphan	33.778
16	p,p-DDD	35.162
17	Ethion	35.862
18	Lambda cyhalothrin	54.819
19 a	Cyfluthrin -1	61.247
19 b	Cyfluthrin -2	61.428
20 a	Cypermethrin -1	61.694
20 b	Cypermethrin -2	62.092
20 c	Cypermethrin- 3	62.332
20 d	Cypermethrin- 4	62.494
21 a	Fenvalerate - 1	64.883
21 b	Fenvalerate - 2	65.704

Table 6. The LOD of Gas Chromatograph and LOQ of the analytical method for each group of pesticide in different substrate.

Commodity	Organochlorines		Organophosphates		Synthetic pyrethroids	
	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	LOD (mg kg^{-1})	LOQ (mg kg^{-1})	LOD (mg kg^{-1})	LOQ (mg kg^{-1})
Rice grain	0.01	0.05	0.01	0.05	0.01	0.05
Cooked rice	0.01	0.05	0.01	0.05	0.01	0.05
Wheat grain	0.01	0.05	0.01	0.05	0.01	0.05
Rice flour	0.01	0.05	0.01	0.05	0.01	0.05
Atta	0.01	0.05	0.01	0.05	0.01	0.05
Maida	0.01	0.05	0.01	0.05	0.01	0.05
Cardamom	0.01	0.05	0.01	0.05	0.01	0.05
Cumin seed	0.01	0.05	0.01	0.05	0.01	0.05
Capsicum	0.01	0.05	0.01	0.05	0.01	0.05
Okra	0.01	0.05	0.01	0.05	0.01	0.05
Curry leaf	0.01	0.05	0.01	0.05	0.01	0.05

Coefficient of Determination (R^2) for each pesticide. The chromatograms of the standard mixture fortified at 0.5, 0.1, 0.075, 0.05, 0.025 and 0.01 mg kg^{-1} were kept as Appendix II.

4.1.1.4 *Determination of Limit of Quantification (LOQ)*

The Limit of Quantification (LOQ) of the proposed method were calculated by considering a value of 10 times more than that of background noise. The LOQs of all the 21 pesticides in this method were calculated as 0.05 mg kg^{-1}.The LOD of Gas Chromatograph and LOQ of the analytical method for each group of pesticide in different substrates are given in Table 6.

4.1.1.5 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides *ie.* repeatability in rice flour essential to assess the method are presented in Table 7. The pesticides in the table are given in the order of their retention time in GC which ranged from 10.50 to 66.70 min. The repeatability in terms of recovery percentage of the method was determined at five levels 0.01mg kg^{-1}, 0.05mg kg^{-1}, 0.25mg kg^{-1}, 0.5mg kg^{-1} and 1.0 mg kg^{-1}.

At 1.0 mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (90.20 %), beta HCH (104.25 %), lindane (95.25 %), delta HCH (110.02 %), alpha endosulphan (103.90 %), p p DDE (70.80 %), beta endosulphan (91.00 %) and p p DDD (75.60 %). At 0.5 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (107.87 %), beta HCH (88.45 %), lindane (88.15 %), delta HCH (104.60 %), alpha endosulphan (82.82 %), p p DDE (103.10 %), beta endosulphan (74.20 %) and p p DDD (76.87 %). At 0.25 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (102.10 %), beta HCH (73.54 %), lindane (79.82 %), delta HCH (104.62 %), alpha endosulphan (76.50 %), p p DDE (75.71 %), beta endosulphan (75.98 %) and p p DDD (78.36 %). At 0.05 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (97.27 %), beta HCH (87.41 %), lindane (90.69 %), delta HCH (95.31 %), alpha endosulphan (85.42 %), p p DDE (94.26 %), beta endosulphan (103.73 %) and p p DDD (97.44 %). At 0.01 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (104.87 %), beta HCH (78.17 %), lindane (99.87 %), delta HCH (108.73 %), alpha endosulphan (111.13 %), p p DDE (100.40 %), beta endosulphan (109.40 %) and p p DDD (108.07 %).

At the fortification level of 1.0 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (74.62 %), dimethoate

Table 7. Recovery and repeatability of insecticides in rice flour at different fortification levels

Insecticides	Level of fortification									
	0.01 mg kg^{-1}		0.05 mg kg^{-1}		0.25 mg kg^{-1}		0.50 mg kg^{-1}		1.00 mg kg^{-1}	
	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD
Phorate	71.87 ± 5.63	5.63	91.84 ± 10.80	11.76	84.65 ± 13.10	15.47	89.60 ± 2.51	4.82	74.62 ± 4.48	4.74
Alpha HCH	104.87 ± 2.75	2.75	97.27 ± 10.59	10.89	102.10 ± 14.12	17.20	107.87 ± 4.72	3.94	90.20 ± 3.27	3.62
Dimethoate	70.23 ± 6.21	6.21	100.52 ± 7.45	7.42	82.37 ± 16.07	19.51	100.52 ± 3.96	8.05	76.27 ± 2.57	2.67
Beta HCH	78.17 ± 2.55	2.55	87.41 ± 7.75	8.86	73.54 ± 13.44	16.09	88.45 ± 7.12	7.19	104.25 ± 2.87	2.76
Lindane	99.87 ± 4.83	4.83	90.69 ± 8.77	9.68	79.82 ± 13.90	17.42	88.15 ± 6.33	3.93	95.25 ± 2.96	3.11
Fluchloralin	70.67 ± 6.15	6.15	97.45 ± 11.57	11.87	72.56 ± 14.23	17.24	104.50 ± 4.11	3.03	75.12 ± 1.62	1.70
Delta HCH	108.73 ± 0.45	0.45	95.31 ± 10.87	11.41	104.62 ± 16.04	18.96	104.60 ± 3.17	3.83	110.02 ± 3.47	3.85
Methyl parathion	90.67 ± 6.15	6.15	101.72 ± 5.37	5.28	104.32 ± 16.73	19.84	96.97 ± 3.71	1.67	93.10 ± 6.96	7.48
Malathion	108.73 ± 0.45	0.45	73.12 ± 14.95	16.05	85.36 ± 13.26	15.53	102.87 ± 1.72	9.94	75.40 ± 3.34	3.91
Chlorpyriphos	84.40 ± 1.34	1.34	95.66 ± 2.95	3.08	101.55 ± 15.73	19.29	102.05 ± 10.14	7.97	99.40 ± 3.43	3.45
Quinalphos	99.30 ± 1.80	1.80	77.41 ± 6.66	6.84	79.68 ± 14.24	17.87	105.77 ± 7.63	3.46	106.92 ± 3.30	3.09
Alpha endosulphan	111.13 ± 2.13	2.13	85.42 ± 3.63	4.25	76.50 ± 13.92	18.19	82.82 ± 2.87	4.27	103.90 ± 2,68	2.85
Profenophos	102.20 ± 2.69	2.69	75.66 ± 16.77	17.53	87.42 ± 14.64	16.74	75.12 ± 3.63	2.68	93.50 ± 6.93	7.41

Table 7 continued.

Insecticides	Level of fortification									
	0.01 mg kg^{-1}				0.01 mg kg^{-1}				0.01 mg kg^{-1}	
	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD
Beta endosulphan	109.40 ± 0.88	0.88	103.73 ±12.29	13.11	75.98 ± 12.05	15.86	74.20 ± 2.52	7.25	91.00 ± 6.11	6.71
p p DDE	100.40 ± 7.17	7.17	94.26 ± 7.47	7.93	75.71 ± 12.55	16.58	103.10 ± 2.77	3.00	70.80 ± 5.46	6.01
p p DDD	108.07 ± 2.82	2.82	97.44 ± 5.21	5.35	78.36 ± 16.06	20.49	76.87 ± 7.02	2.22	75.60 ± 3.68	3.85
Ethion	92.97 ± 3.31	3.31	103.35 ± 5.22	6.26	78.65 ± 14.70	18.68	101.24 ± 2.25	6.36	89.90 ± 2.36	2.63
Lambda cyhalothrin	110.57 ± 3.80	3.80	105.53 ± 3.74	3.92	78.28 ± 14.80	18.91	96.05 ± 6.11	4.78	106.20 ± 4.74	4.93
Cyfluthrin	107.03 ± 4.14	4.14	96.14 ± 8.81	9.16	81.78 ± 14.58	17.82	106.42 ± 4.61	7.32	77.70 ± 3.60	3.68
Cypermethrin	96.63 ± 7.74	7.74	106.62 ± 5.40	5.59	73.74 ± 15.59	18.62	99.42 ± 7.28	3.04	92.75 ± 4.84	5.22
Fenvalerate	93.53 ± 1.43	1.43	93.40 ± 11.43	12.23	86.31 ± 15.52	17.99	105.17 ± 3.20	4.82	78.15 ± 5.22	5.93

Number of replicates at each level (n) = 4

RSD - Relative Standard Deviation

(76.27 %), methyl parathion (93.10 %), malathion (75.40 %), chlorpyriphos (99.40 %), quinalphos (106.92 %), profenophos (93.50 %) and ethion (89.90 %). The mean per cent recovery values were phorate (89.60 %), dimethoate (100.52 %), methyl parathion (96.97 %), malathion (102.87 %), chlorpyriphos (102.05 %), quinalphos (105.77 %), profenophos (75.12 %) and ethion (101.24 %) at the fortification level of 0.5 mg kg^{-1}. At the fortification level of 0.25 mg kg^{-1}, the mean per cent recovery were phorate (84.65 %), dimethoate (82.37 %), methyl parathion (104.32 %), malathion (85.36 %), chlorpyriphos (101.55 %), quinalphos (79.68 %), profenophos (87.42 %) and ethion (78.65 %). The mean per cent recovery values were phorate (91.84 %), dimethoate (100.52 %), methyl parathion (101.72 %), malathion (73.12 %), chlorpyriphos (95.66 %), quinalphos (77.41 %), profenophos (75.66 %) and ethion (103.35 %) at the fortification level of 0.05 mg kg^{-1}. At the fortification level of 0.01 mg kg^{-1}, the mean per cent recovery were phorate (71.87 %), dimethoate (70.23 %), methyl parathion (90.67 %), malathion (108.73 %), chlorpyriphos (84.40 %), quinalphos (99.30 %), profenophos (102.20 %) and ethion (92.97 %).

The mean per cent recovery values were 106.20, 92.75 and 78.15 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 75.12 and 77.70 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 1.0 mg kg^{-1}. At 0.5 mg kg^{-1} fortification level, the mean per cent recovery values were 96.05, 99.42 and 105.17 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 104.50 and 106.42 per cent for fluchloralin and cyfluthrin respectively. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 78.28, 73.74 and 86.31 for lambda cyhalothrin, cypermethrin and fenvalerate and 72.56 and 81.78 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 105.53, 106.62 and 93.40 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 97.45 and 96.14 per cent for fluchloralin and cyfluthrin respectively. At 0.01 mg kg^{-1} fortification level, the mean per cent recovery values were 110.57, 96.63 and 93.53 for lambda cyhalothrin, cypermethrin and fenvalerate and 70.67 and 107.03 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were within the range 70-110 per cent at five levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=4 at each spiking level, confirmed that the method is sufficiently reliable for pesticide analysis in rice flour.

4.1.1a Wheat flour (atta)

4.1.1a.5 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides ie repeatability in wheat flour (atta) essential to assess the method are presented in Table 8. The repeatability in terms of recovery percentage of the method was determined at five levels 0.01mg kg^{-1}, 0.05mg kg^{-1}, 0.25mg kg^{-1}, 0.5mg kg^{-1} and 1.0 mg kg^{-1}.

At 1.0 mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (84.72 %), beta HCH (77.65 %), lindane (93.05 %), delta HCH (93.13 %), alpha endosulphan (94.18 %), p p DDE (73.09 %), beta endosulphan (95.73 %) and p p DDD (83.15 %). At 0.5 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (84.72 %), beta HCH (80.99 %), lindane (86.75 %), delta HCH (90.00 %), alpha endosulphan (80.43 %), p p DDE (95.73 %), beta endosulphan (83.15 %) and p p DDD (95.87 %). At 0.25 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (106.27 %), beta HCH (87.72 %), lindane (104.66 %), delta HCH (103.87 %), alpha endosulphan (108.69 %), p p DDE

Table 8. Recovery and repeatability of insecticides in atta at different fortification levels

Insecticides	Level of fortification									
	0.01 mg kg^{-1}		0.05 mg kg^{-1}		0.25 mg kg^{-1}		0.50 mg kg^{-1}		1.00 mg kg^{-1}	
	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD
Phorate	89.07 ± 4.37	4.90	90.56 ± 5.03	5.56	105.96 ± 4.48	4.23	90.20 ± 9.45	9.45	90.20 ± 9.45	10.47
Alpha HCH	88.00 ± 5.84	6.63	100.10 ± 3.92	3.92	106.27 ± 1.32	1.24	84.72 ± 2.70	2.70	84.72 ± 2.70	3.19
Dimethoate	93.23 ± 4.93	5.29	105.90 ± 1.89	1.79	90.86 ± 5.23	5.76	95.89 ± 5.95	5.95	95.89 ± 5.95	6.21
Beta HCH	90.48 ± 5.08	5.61	101.86 ± 4.37	4.29	87.72 ± 5.38	6.14	80.99 ± 0.49	0.49	77.65 ± 4.56	5.87
Lindane	101.54 ± 5.76	5.68	105.00 ± 2.26	2.16	104.66 ± 1.74	1.66	86.75 ± 3.89	3.89	93.05 ± 5.34	5.63
Fluchloralin	98.80 ± 4.75	4.81	107.34 ± 1.76	1.64	108.28 ± 2.42	2.24	93.13 ± 2.03	2.03	83.62 ± 3.73	4.46
Delta HCH	85.75 ± 2.34	2.73	83.65 ± 0.31	0.37	103.87 ± 1.76	1.69	90.00 ± 7.04	7.04	93.13 ± 2.03	2.18
Methyl parathion	104.21 ± 4.87	4.67	104.05 ± 2.18	2.10	99.07 ± 12.58	12.70	97.56 ± 2.09	2.09	90.00 ± 7.04	7.82
Malathion	83.46 ± 2.37	2.84	85.41 ± 1.65	1.94	103.69 ± 1.56	1.50	87.35 ± 2.80	2.80	97.56 ± 2.09	2.15
Chlorpyriphos	100.87 ± 3.96	3.93	98.31 ± 0.88	0.89	105.69 ± 1.07	1.02	88.41 ± 4.48	4.48	87.35 ± 2.80	3.20
Quinalphos	88.69 ± 5.44	6.14	98.28 ± 1.12	1.14	86.75 ± 5.60	6.46	94.18 ± 3.10	3.10	88.41 ± 4.48	5.07
Alpha endosulphan	91.98 ± 3.71	4.03	93.55 ± 4.19	4.48	108.69 ± 0.15	0.14	80.43 ± 0.10	0.10	94.18 ± 3.10	3.29
Profenophos	98.43 ± 4.38	4.45	106.92 ± 2.62	2.45	95.93 ± 5.83	6.08	73.08 ± 1.45	1.45	80.43 ± 0.10	0.13
p p DDE	93.90 ± 5.19	5.52	99.63 ± 1.81	1.82	106.71 ± 2.66	2.50	95.73 ± 3.77	3.77	73.09 ± 1.43	1.96

Table 8 continued.

Insecticides	Level of fortification									
	0.01 mg kg^{-1}		0.05 mg kg^{-1}		0.25 mg kg^{-1}		0.50 mg kg^{-1}		1.00 mg kg^{-1}	
	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD
Beta endosulphan	92.44 ± 2.50	2.71	97.33 ± 2.30	2.37	101.48 ± 7.08	6.98	83.15 ± 0.93	0.93	95.73 ± 3.77	3.94
p p DDD	105.89 ± 4.21	3.98	93.35 ± 7.83	8.38	81.50 ± 0.75	0.92	95.87 ± 8.47	8.47	83.15 ± 0.93	1.12
Ethion	106.85± 11.36	10.63	88.66 ± 12.53	14.14	91.68 ± 2.87	3.13	82.50 ± 2.64	2.64	95.87 ± 8.47	8.83
Lambda cyhalothrin	92.95 ± 5.09	5.48	95.92 ± 4.65	4.85	99.18 ± 7.86	7.92	94.95 ± 4.17	4.17	82.50 ± 2.64	3.20
Cyfluthrin	103.82 ± 5.95	5.73	96.86 ± 3.31	3.41	91.12 ± 7.61	8.35	86.67 ± 3.58	3.58	94.95 ± 4.17	4.39
Cypermethrin	102.30 ± 6.49	6.35	101.85 ± 1.11	1.09	102.01 ± 5.75	5.64	95.94 ± 3.20	3.20	86.67 ± 3.58	4.13
Fenvalerate	104.60 ± 4.23	4.05	98.44 ± 1.23	1.25	105.96 ± 4.48	4.23	82.82 ± 0.85	0.85	95.94 ± 3.20	3.34

Number of replicates at each level (n) = 4

RSD - Relative Standard Deviation

(106.71 %), beta endosulphan (101.48 %) and p p DDD (81.50 %). At 0.05 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (100.10 %), beta HCH (101.86 %), lindane (105.00 %), delta HCH (83.65 %), alpha endosulphan (93.55 %), p p DDE (99.63 %), beta endosulphan (97.33 %) and p p DDD (93.35 %). At 0.01 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (88.00 %), beta HCH (90.48 %), lindane (101.54 %), delta HCH (85.75 %), alpha endosulphan (91.98 %), p p DDE (93.90 %), beta endosulphan (92.44 %) and p p DDD (105.89 %).

At the fortification level of 1.0 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (90.20 %), dimethoate (95.89 %), methyl parathion (90.00 %), malathion (97.56 %), chlorpyriphos (87.35 %), quinalphos (88.41 %), profenophos (80.43 %) and ethion (95.87 %). The mean per cent recovery values were phorate (90.20 %), dimethoate (95.89 %), methyl parathion (97.56 %), malathion (87.35 %), chlorpyriphos (88.41 %), quinalphos (94.18 %), profenophos (73.08 %) and ethion (82.50 %) at the fortification level of 0.5 mg kg^{-1}. At the fortification level of 0.25 mg kg^{-1}, the mean per cent recovery were phorate (105.96 %), dimethoate (90.86 %), methyl parathion (99.07 %), malathion (103.69 %), chlorpyriphos (105.69 %), quinalphos (86.75 %), profenophos (95.93 %) and ethion (91.68 %). The mean per cent recovery values were phorate (90.56 %), dimethoate (105.90 %), methyl parathion (104.05 %), malathion (85.41 %), chlorpyriphos (98.31 %), quinalphos (98.28 %), profenophos (106.92 %) and ethion (88.66 %) at the fortification level of 0.05 mg kg^{-1}. At the fortification level of 0.01 mg kg^{-1}, the mean per cent recovery were phorate (89.07 %), dimethoate (93.23 %), methyl parathion (104.21 %), malathion (83.46 %), chlorpyriphos (100.87 %), quinalphos (88.69 %), profenophos (98.43 %) and ethion (106.85 %).

The mean per cent recovery values were 82.50, 86.67 and 95.94 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 83.62 and 94.95 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 1.0 mg kg^{-1}. At 0.5 mg kg^{-1} fortification level, the mean per cent recovery values were 94.95 %, 95.94 % and 82.82 % for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 93.13 and 86.67 per cent for fluchloralin and cyfluthrin respectively. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 99.18, 102.01 and 105.96 for lambda cyhalothrin, cypermethrin and fenvalerate and 108.28 and 91.12 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 95.92, 101.85 and 98.44 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 107.34 and 96.86 per cent for fluchloralin and cyfluthrin respectively. At 0.01 mg kg^{-1} fortification level, the mean per cent recovery values were 92.95, 102.30 and 104.60 for lambda cyhalothrin, cypermethrin and fenvalerate and 98.80 and 103.82 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were within the range 70-110 per cent at five levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=4 at each spiking level, confirmed that the method is sufficiently reliable for pesticide residue analysis in wheat flour (atta).

4.1.1b Wheat flour (maida)

4.1.3.4 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides ie repeatability in wheat flour (maida) essential to assess the method are presented in Table 9. The repeatability in terms of recovery percentage of the method was determined at five levels, 0.01mg kg^{-1}, 0.05mg kg^{-1}, 0.25mg kg^{-1}, 0.5mg kg^{-1} and 1.0 mg kg^{-1}.

At 1.0 mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (93.11 %), beta HCH (74.01 %), lindane (92.67 %), delta HCH (95.57 %), alpha endosulphan (74.93 %), p p DDE (81.97 %), beta endosulphan (82.78 %) and p p DDD (70.82 %). At 0.5 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (79.43 %), beta HCH (85.81 %), lindane (86.49 %), delta HCH (94.61 %), alpha endosulphan (87.79 %), p p DDE (74.97 %), beta endosulphan (87.90 %) and p p DDD (88.90 %). At 0.25 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (87.07 %), beta HCH (74.11 %), lindane (86.81 %), delta HCH (88.29 %), alpha endosulphan (85.69 %), p p DDE (82.58 %), beta endosulphan (83.22 %) and p p DDD (114.44 %). At 0.05 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (75.15 %), beta HCH (91.79 %), lindane (89.83 %), delta HCH (75.05 %), alpha endosulphan (82.05 %), p p DDE (113.27 %), beta endosulphan (82.55 %) and p p DDD (81.82 %). At 0.01 mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (90.51 %), beta HCH (106.43 %), lindane (88.80 %), delta HCH (91.24 %), alpha endosulphan (81.06 %), p p DDE (81.33 %), beta endosulphan (72.46 %) and p p DDD (82.55 %)

At the fortification level of 1.0 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (79.52 %), dimethoate (106.34 %), methyl parathion (103.14 %), malathion (75.54 ± 2.91 %), chlorpyriphos (93.91 %), quinalphos (91.11 %), profenophos (99.14 %) and ethion (91.46 %). The mean per cent recovery values were phorate (81.34 %), dimethoate (99.24 %), methyl parathion (92.44 %), malathion (97.32 %), chlorpyriphos (92.37 %), quinalphos (70.29 %), profenophos (94.11 %) and ethion (76.65 %) at the fortification level of 0.5 mg kg^{-1}. At the fortification level of 0.25 mg kg^{-1}, the mean per cent recovery were phorate (70.57 %),

Table 9. Recovery and repeatability of insecticides in maida at different fortification levels

Insecticides	Level of fortification									
	0.01 mg kg^{-1}		0.05 mg kg^{-1}		0.25 mg kg^{-1}		0.50 mg kg^{-1}		1.00 mg kg^{-1}	
	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD
Phorate	103.74 ± 3.30	3.52	85.20 ± 3.46	4.06	70.57 ± 8.33	9.20	81.34 ± 0.88	1.08	79.52 ± 1.37	1.54
Alpha HCH	90.51 ± 4.14	4.58	75.15 ± 2.13	2.50	87.07± 2.08	2.39	79.43 ± 1.44	1.61	93.11 ± 1.85	1.99
Dimethoate	77.14 ± 4.81	5.52	89.02 ±0.97	1.09	102.75 ± 5.85	5.70	99.24 ± 1.07	1.08	106.34 ± 1.90	1.97
Beta HCH	106.43 ± 3.71	3.85	91.79 ± 1.43	1.56	74.11 ± 2.59	3.08	85.81 ± 1.24	1.45	74.01 ± 3.24	3.86
Lindane	88.80 ± 7.23	8.14	89.83 ± 4.87	5.43	86.81 ± 2.06	2.37	86.49 ± 2.21	2.56	92.67 ± 1.55	1.67
Fluchloralin	74.51 ± 8.07	8.54	81.93 ± 1.10	1.35	100.93 ± 1.36	1.35	87.89 ± 1.70	1.93	74.11 ± 1.80	2.14
Delta HCH	91.24 ± 5.90	6.47	75.05 ± 3.77	4.44	88.29 ± 3.64	4.12	94.61 ±2.36	2.49	95.57 ± 2.86	2.99
Methyl parathion	105.59 ± 3.39	3.96	84.91 ± 3.12	3.67	85.35 ± 3.17	3.71	92.44 ± 0.65	0.71	103.14 ± 2.25	2.18
Malathion	99.64 ± 1.77	1.78	112.51 ± 1.96	2.12	106.08 ± 4.75	4.48	97.32 ± 1.06	1.09	75.54 ± 2.91	3.40
Chlorpyriphos	92.32 ± 1.36	1.48	84.36 ±3.04	3.60	74.17 ± 2.12	2.52	92.37 ± 0.88	0.95	93.91 ± 0.57	0.61
Quinalphos	75.98 ± 2.66	3.09	104.48 ± 3.61	4.27	85.19 ± 2.34	2.75	70.29 ± 1.73	1.92	91.11 ± 1.10	1.21
Alpha endosulphan	81.06 ± 0.76	0.94	82.05 ± 0.53	0.65	85.69 ± 1.85	2.16	87.79 ± 3.05	3.47	74.93 ± 1.46	1.71
Profenophos	103.44 ± 3.06	3.27	84.91 ± 3.12	3.67	76.08 ± 0.42	0.44	94.11 ± 1.29	1.37	99.14 ± 1.37	1.39
p p DDE	81.33 ± 0.47	0.57	113.27 ± 1.63	1.96	82.58 ± 2.71	3.28	74.97 ± 0.65	0.76	81.97 ± 1.03	1.26

Table 9 continued.

Insecticides	Level of fortification									
	0.01 mg kg^{-1}		0.05 mg kg^{-1}		0.25 mg kg^{-1}		0.50 mg kg^{-1}		1.00 mg kg^{-1}	
	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD	Mean recovery (%) ± SD	RSD
Beta endosulphan	72.46 ± 3.26	3.95	82.55 ± 1.99	2.41	83.22 ± 1.80	2.16	87.90 ± 0.91	1.03	82.78 ± 1.32	1.59
p p DDD	82.55 ± 1.65	2.00	81.82 ± 1.87	2.29	114.44 ± 3.57	4.22	88.90 ± 1.12	1.26	70.82 ± 2.71	2.99
Ethion	75.24 ± 1.78	2.09	73.92 ± 3.00	3.58	94.46 ± 4.02	4.26	76.65 ± 0.92	0.95	91.46 ± 0.44	0.48
Lambda cyhalothrin	85.58 ± 3.46	4.05	83.10 ± 1.15	1.39	90.79 ± 1.47	1.62	86.50 ± 2.20	2.54	91.21 ± 1.21	1.33
Cyfluthrin	91.58 ± 4.63	5.05	82.35 ± 1.19	1.45	78.65 ± 1.10	1.11	91.61 ± 1.18	1.29	89.91 ± 0.64	0.71
Cypermethrin	73.10 ± 2.05	2.21	74.52 ± 0.54	0.64	85.42 ± 2.97	3.48	95.14 ± 0.96	1.01	74.50 ± 0.35	0.37
Fenvalerate	102.04 ± 2.82	2.77	86.08 ± 5.61	6.51	91.65 ± 1.36	1.49	73.14 ± 1.20	1.44	86.54 ± 0.56	0.65

Number of replicates at each level (n) = 4

RSD - Relative Standard Deviation

dimethoate (102.75 %), methyl parathion (85.35 %), malathion (106.08 %), chlorpyriphos (74.17 %), quinalphos (85.19 %), profenophos (76.08 %) and ethion (94.46 %). The mean per cent recovery values were phorate (85.20 %), dimethoate (89.02 %), methyl parathion (84.91 %), malathion (112.51 %), chlorpyriphos (84.36 %), quinalphos (104.48 %), profenophos (84.91 %) and ethion (73.92 %) at the fortification level of 0.05 mg kg^{-1}. At the fortification level of 0.01 mg kg^{-1}, the mean per cent recovery were phorate (103.74 %), dimethoate (77.14 %), methyl parathion (105.59 %), malathion (99.64 %), chlorpyriphos (92.32 %), quinalphos (75.98 %), profenophos (103.44 %) and ethion (75.24 %).

The mean per cent recovery values were 91.21, 79.50 and 86.54 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 74.51 and 89.91 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 1.0 mg kg^{-1}. At 0.5 mg kg^{-1} fortification level, the mean per cent recovery values were 86.50, 95.14 and 73.14 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 81.93 and 91.61 per cent for fluchloralin and cyfluthrin respectively. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 90.79, 85.42 and 91.65 for lambda cyhalothrin, cypermethrin and fenvalerate and 100.93 and 78.65 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 83.10, 74.52 and 86.08 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 81.93 and 82.35 per cent for fluchloralin and cyfluthrin respectively. At 0.01 mg kg^{-1} fortification level, the mean per cent recovery values were 85.58, 73.10 and 102.04 for lambda cyhalothrin, cypermethrin and fenvalerate and 74.51 and 91.58 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were with in the range 70-110 per cent at five levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=4 at each spiking level, confirmed that the method is sufficiently reliable for pesticide analysis in wheat flour (maida)

4.1.2 Rice grains

4.1.4.4 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides ie repeatability in rice grains essential to assess the method are presented in Table 10. The repeatability in terms of recovery percentage of the method was determined at three levels, 0.05mg kg^{-1} (LOQ), 0.25mg kg^{-1} (5 x LOQ) and 0.5mg kg^{-1} (10 X LOQ).

At 0.5mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (83.89 %), beta HCH (97.63 %), lindane (101.88 %), delta HCH (84.99 %), alpha endosulphan (93.26 %), p p DDE (89.46 %), beta endosulphan (91.52 %) and p p DDD (95.34 %). At 0.25mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (86.18 %), beta HCH (95.05 %), lindane (99.41 %), delta HCH (102.15 %), alpha endosulphan (95.90 %), p p DDE (83.76 %), beta endosulphan (89.99 %) and p p DDD (89.60 %). At 0.05mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (88.37 %), beta HCH (92.38 %), lindane (97.83 %), delta HCH (94.85 %), alpha endosulphan (97.29 %), p p DDE (88.12 %), beta endosulphan (95.16 %) and p p DDD (86.67 %)

At the fortification level of 0.5 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (84.42 %), dimethoate (85.45 %), methyl parathion (84.50 %), malathion (84.50 %), chlorpyriphos (84.00 %), quinalphos (85.57 %), profenophos (89.07 %) and ethion (82.57 %). The mean per cent recovery values were phorate (84.59 %), dimethoate (87.04 %), methyl parathion (86.46 %), malathion (98.45 %), chlorpyriphos

Table 10. Recovery and repeatability of insecticides in rice grains at different fortification levels

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Phorate	77.17 ± 4.39	5.68	84.59 ± 1.82	2.15	84.42 ± 3.13	3.70
Alpha HCH	88.37 ± 6.74	7.62	86.18 ± 2.90	3.36	83.89 ± 1.91	2.27
Dimethoate	83.27 ± 0.48	0.58	87.04 ± 3.08	3.54	85.45 ± 4.64	5.43
Beta HCH	92.38 ± 6.95	7.52	95.05 ± 5.22	5.49	97.63 ± 6.40	6.55
Lindane	97.83 ± 12.35	12.62	99.41 ± 6.89	6.93	101.88 ± 5.15	5.06
Fluchloralin	101.10 ± 5.48	5.42	101.13 ± 2.29	2.26	87.44 ± 2.33	2.67
Delta HCH	94.85 ± 6.27	6.61	102.15 ± 0.74	0.73	84.99 ± 4.15	4.88
Methyl parathion	105.10 ± 2.76	3.21	86.46 ± 3.17	3.66	84.50 ± 1.16	1.37
Malathion	107.75 ± 0.28	0.31	98.45 ± 0.87	0.88	84.50 ± 1.15	1.37
Chlorpyriphos	105.24 ± 7.85	8.08	100.28 ± 6.31	6.29	84.00 ± 4.57	5.44
Quinalphos	86.60 ± 2.67	2.89	99.98 ± 6.25	6.25	85.57 ± 3.81	4.45
Alpha endosulphan	97.29 ± 2.17	2.23	95.90 ± 2.31	2.40	93.26 ± 4.24	4.55
Profenophos	105.63 ± 1.39	1.48	99.16 ± 5.37	5.42	89.07 ± 1.05	1.17
p p DDE	88.12 ± 0.80	0.91	83.76 ± 4.71	5.62	89.46 ± 0.33	0.37

Table 10 continued.

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
p p DDD	86.67 ± 2.57	2.97	89.60 ± 6.87	7.67	95.34 ± 3.43	3.60
Beta endosulphan	95.16 ± 2.50	2.63	89.99 ± 4.32	4.80	91.52 ± 6.97	7.61
Ethion	104.47 ± 2.23	2.50	84.93 ± 5.04	5.93	82.57 ± 2.99	3.62
Lambda cyhalothrin	96.97 ± 3.52	3.63	100.48 ± 1.23	1.23	100.63 ± 4.15	4.12
Cyfluthrin	100.13 ± 7.47	7.46	104.55 ± 2.10	2.00	100.72 ± 2.12	2.10
Cypermethrin	93.40 ± 5.54	5.94	97.61 ± 7.62	7.81	100.79 ± 1.41	1.40
Fenvalerate	89.97 ± 3.96	4.40	90.96 ± 6.44	7.08	82.63 ± 2.20	2.66

Number of replicates at each level (n) = 3

RSD - Relative Standard Deviation

(100.28 %), quinalphos (99.98 %), profenophos (99.16 %) and ethion (84.93 %) at the fortification level of 0.25 mg kg^{-1}. At the fortification level of 0.05 mg kg^{-1}, the mean per cent recoverywere phorate (77.17 %), dimethoate (83.27 %), methyl parathion (105.10 %), malathion (107.75 %), chlorpyriphos (105.24 %), quinalphos (86.60 %), profenophos (105.63 %) and ethion (104.47 %).

The mean per cent recovery values were 100.63, 100.79 and 82.63 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 87.44 and 100.72 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 0.5 mg kg^{-1}. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 100.48, 97.61 and 90.96 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 101.13 and 104.55 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 96.97, 93.40 and 89.97 for lambda cyhalothrin, cypermethrin and fenvalerate and 101.10 and 100.13 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were within the range 70-110 per cent at three levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=3 at each spiking level, confirmed that the method is sufficiently reliable for pesticide analysis in rice grains.

4.1.2a Wheat grains

4.1.5.4 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides ie repeatability in wheat grains essential to assess the method are presented in Table 11. The repeatability in terms of recovery percentage of the method was determined at three levels, 0.05mg kg^{-1} (LOQ), 0.25mg kg^{-1} (5 x LOQ) and 0.5mg kg^{-1} (10 X LOQ).

At 0.5mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (109.43 %), beta HCH (85.81 %), lindane (106.49 %), delta HCH (94.61 %), alpha endosulphan (107.79 %), p p DDE (74.97 %), beta endosulphan (87.90 %) and p p DDD (108.90 %). At 0.25mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (93.11 %), beta HCH (74.01 %), lindane (92.67 %), delta HCH (105.57 %), alpha endosulphan (84.93 %), p p DDE (81.97 %), beta endosulphan (72.78 %) and p p DDD (70.82 %). At 0.05mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (87.07 %), beta HCH (84.11 %), lindane (76.81 %), delta HCH (88.29 %), alpha endosulphan (105.69 %), p p DDE (72.58 %), beta endosulphan (83.22 %) and p p DDD (104.44 %).

At the fortification level of 0.5 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (71.34 %), dimethoate (99.24 %), methyl parathion (72.44 %), malathion (97.32 %), chlorpyriphos(102.37 %), quinalphos (90.29 %), profenophos (94.11 %) and ethion (76.65 %). The mean per cent recovery values were phorate (109.52 %), dimethoate (76.34 %), methyl parathion (103.14 %), malathion (75.54 %), chlorpyriphos (73.91 %), quinalphos (101.11 %), profenophos (79.14 %) and ethion (91.46 %) at the fortification level of 0.25 mg kg^{-1}. At the fortification level of 0.05 mg kg^{-1}, the mean per cent recovery were phorate (70.57 %), dimethoate (102.75 %), methyl parathion (85.35 %), malathion (106.08 %), chlorpyriphos (84.17 %), quinalphos (75.19 %), profenophos (96.08 %) and ethion (94.46 %).

The mean per cent recovery values were 86.50, 105.14 and 110.14 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 87.89 and 91.61 per cent for herbicides like

Table 11. Recovery and repeatability of insecticides in wheat grains at different fortification levels

Insecticides	Level of fortification (mg kg^{-1})					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Phorate	70.57 ± 10.21	11.27	109.52 ± 1.68	1.88	71.34 ± 1.08	1.32
Alpha HCH	87.07 ± 2.55	2.93	93.11 ± 2.27	2.44	109.43 ± 1.76	1.97
Dimethoate	102.75 ± 7.17	6.98	76.34 ± 2.33	2.42	99.24 ± 1.31	1.32
Beta HCH	84.11 ± 3.17	3.77	74.01 ± 3.97	4.73	85.81 ± 1.52	1.78
Lindane	76.81 ± 2.52	2.90	92.67 ± 1.89	2.04	106.49 ± 2.71	3.13
Fluchloralin	100.93 ± 1.67	1.65	74.11 ± 2.21	2.62	87.89 ± 2.08	2.36
Delta HCH	88.29 ± 4.46	5.05	105.57 ± 3.50	3.66	94.61 ± 2.89	3.05
Methyl parathion	85.35 ± 3.88	4.54	103.14 ± 2.76	2.67	72.44 ± 0.80	0.86
Malathion	106.08 ± 5.82	5.49	75.54 ± 3.57	4.17	97.32 ± 1.30	1.33
Chlorpyriphos	84.17 ± 2.60	3.09	73.91 ± 0.70	0.74	102.37 ± 1.08	1.16
Quinalphos	75.19 ± 2.87	3.37	101.11 ± 1.35	1.48	90.29 ± 2.12	2.35
Alpha endosulphan	105.69 ± 2.27	2.64	84.93 ± 1.78	2.10	107.79 ± 3.73	4.25
Profenophos	96.08 ± 0.51	0.53	79.14 ± 1.68	1.70	94.11 ± 1.58	1.68
p p DDE	72.58 ± 3.32	4.02	81.97 ± 1.26	1.54	74.97 ± 0.80	0.94

Table 11 continued

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Beta endosulphan	83.22 ± 2.21	2.65	72.78 ± 1.61	1.95	87.90 ± 1.11	1.26
p p DDD	104.44 ± 4.37	5.17	70.82 ± 3.32	3.66	108.90 ± 1.37	1.54
Ethion	94.46 ± 4.93	5.22	91.46 ± 0.53	0.58	76.65 ± 1.13	1.17
Lambda cyhalothrin	100.79 ± 1.80	1.98	110.21 ± 1.48	1.62	86.50 ± 2.69	3.11
Cyfluthrin	98.65 ± 1.35	1.36	79.91 ± 0.78	0.87	91.61 ± 1.45	1.58
Cypermethrin	75.42 ± 3.64	4.26	94.50 ± 0.43	0.46	105.14 ± 1.17	1.23
Fenvalerate	91.65 ± 1.67	1.82	86.54 ± 0.68	0.79	110.14 ± 1.46	1.76

Number of replicates at each level (n) = 3

RSD - Relative Standard Deviation

fluchloralin and cyfluthrin respectively at fortification level of 0.5 mg kg^{-1}. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 110.21, 94.50 and 86.54 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 74.11 and 79.91 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 100.79, 75.42 and 91.65 for lambda cyhalothrin, cypermethrin and fenvalerate and 100.93 and 98.65 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were within the range 70-110 per cent at three levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=3 at each spiking level, confirmed that the method is sufficiently reliable for pesticide analysis in wheat grains.

4.1.3 Cardamom

4.1.5.4 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides ie repeatability in cardamom essential to assess the method are presented in Table 12. The repeatability in terms of recovery percentage of the method was determined at three levels, 0.05mg kg^{-1} (LOQ), 0.25mg kg^{-1} (5 x LOQ) and 0.5mg kg^{-1} (10 X LOQ).

At 0.5mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (97.56 %), beta HCH (96.59 %), lindane (97.23 %), delta HCH (97.76 %), alpha endosulphan (95.13 %), p p DDE (85.53 %), beta endosulphan (97.30 %) and p p DDD (100.75 %). At 0.25mg kg^{-1} level of fortification, the mean per cent recovery were Alpha HCH (90.94 %), beta HCH (92.34 %), lindane (93.89 %), delta HCH (95.16 %), alpha endosulphan (89.19 %), p p DDE (85.24 %), beta endosulphan

Table 12. Recovery and repeatability of insecticides in cardamom at different fortification levels

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Phorate	91.77 ± 5.15	5.61	89.93 ± 8.77	9.75	92.53 ± 3.49	3.77
Alpha HCH	92.65± 4.93	5.32	90.94 ± 7.37	8.10	97.56 ± 1.82	1.86
Dimethoate	96.87 ± 4.73	4.89	93.38 ± 4.34	4.65	92.30 ± 5.91	6.41
Beta HCH	96.26 ± 1.40	1.45	92.34 ± 5.14	5.57	96.59 ± 2.69	2.79
Lindane	85.19 ± 4.23	4.97	93.89 ± 7.35	7.83	97.23 ± 2.77	2.85
Fluchloralin	88.81 ± 7.93	8.93	91.32 ± 5.71	6.25	94.62 ± 3.93	4.16
Delta HCH	99.96 ± 4.11	4.11	95.16 ± 7.22	7.59	97.76 ± 1.75	1.79
Methyl parathion	103.55 ± 3.62	3.50	91.95 ± 8.09	8.80	97.56 ± 4.52	4.63
Malathion	92.08 ± 2.07	2.25	91.66 ± 2.83	3.08	95.97 ± 2.15	2.24
Chlorpyriphos	89.66 ± 8.07	9.00	87.01 ± 5.78	6.65	96.36 ± 3.19	3.31
Quinalphos	93.19 ± 6.71	7.20	84.61 ± 3.42	4.05	96.44 ± 0.69	0.71
Alpha endosulphan	99.53 ± 6.47	6.50	89.19 ± 7.78	8.72	95.13 ± 2.35	2.47
Profenophos	100.75 ± 5.62	5.58	87.79 ± 6.82	7.76	94.33 ± 0.91	0.97
p p DDE	80.15 ± 2,53	3.14	85.24 ± 1.12	1.31	85.53 ± 1.42	1.66

Table 12 continued

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Beta endosulphan	96.01 ± 4.88	5.08	90.04 ± 6.98	7.75	97.30 ± 1.69	1.74
p p DDD	86.33 ± 7.14	8.27	92.72 ± 2.61	2.82	100.75 ± 1.50	1.48
Ethion	92.22 ± 1.98	2.15	97.35± 9.29	9.54	92.45 ± 3.07	3.32
Lambda cyhalothrin	93.31 ± 3.79	4.06	85.18 ± 1.12	1.32	87.54 ± 4.15	4.74
Cyfluthrin	100.63 ± 3.85	3.83	96.38 ± 11.28	11.70	97.09 ± 2.52	2.60
Cypermethrin	92.10 ± 5.21	5.65	96.18 ± 1.61	1.67	96.77 ± 5.72	5.92
Fenvalerate	95.93 ± 2.50	2.61	97.93 ± 9.97	10.18	98.27 ± 0.72	0.73
p p DDD	86.33 ± 7.14	8.27	92.72 ± 2.61	2.82	100.75 ± 1.50	1.48

Number of replicates at each level (n) = 3

RSD - Relative Standard Deviation

(90.04 %) and p p DDD (92.72 %). At 0.05mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (92.65 %), beta HCH (96.26 %), lindane (85.19 %), delta HCH (99.96 %), alpha endosulphan (99.53 %), p p DDE (80.15 %), beta endosulphan (96.01 %) and p p DDD (86.33 %)

At the fortification level of 0.5 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (92.53 %), dimethoate (92.30 %), methyl parathion (97.56 %), malathion (95.97 %), chlorpyriphos (96.36 %), quinalphos (96.44 %), profenophos (94.33 %) and ethion (92.45 %). The mean per cent recovery values were phorate (89.93 %), dimethoate (93.38 %), methyl parathion (91.95 %), malathion (91.66 %), chlorpyriphos (87.01 %), quinalphos (84.61 %), profenophos (87.79 %) and ethion (97.35 %) at the fortification level of 0.25 mg kg^{-1}. At the fortification level of 0.05 mg kg^{-1}, the mean per cent recovery were phorate (91.77 %), dimethoate (96.87 %), methyl parathion (103.55 %), malathion (92.08 %), chlorpyriphos (89.66 %), quinalphos (93.19 %), profenophos (100.75 %) and ethion (92.22 %).

The mean per cent recovery values were 87.54, 96.77 and 98.27 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 94.62 and 97.09 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 0.5 mg kg^{-1}. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 85.18, 96.18 and 97.93 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 91.32 and 96.38 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 93.31, 92.10 and 95.93 for lambda cyhalothrin, cypermethrin and fenvalerate and 88.81 and 100.63 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds satisfactory recoveries. The mean recovery of all the 21 pesticides under study were above 70 per cent at three levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=3 at each spiking level, confirmed that the method is sufficiently reliable for pesticide residue analysis in cardamom.

4.1.3a Cumin seed

4.1.6.4 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides ie repeatability in cumin seed essential to assess the method are presented in Table 13. The repeatability in terms of recovery percentage of the method was determined at three levels, 0.05mg kg^{-1} (LOQ), 0.25mg kg^{-1} (5 x LOQ) and 0.5mg kg^{-1} (10 X LOQ).

At 0.5mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (92.86 %), beta HCH (91.96 %), lindane (93.64 %), delta HCH (99.43 %), alpha endosulphan (74.84 %), p p DDE (83.01 %), beta endosulphan (73.05 %) and p p DDD (94.27 %). at 0.25mg kg^{-1} level of fortification, The mean per cent recovery were alpha HCH (90.90 %), beta HCH (75.38 %), lindane (93.09 %), delta HCH (108.92 %), alpha endosulphan (90.28 %), p p DDE (81.53 %), beta endosulphan (110.58 %) and p p DDD (89.07 %). at 0.05mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (95.56 %), beta HCH (96.33 %), lindane (92.15 %), delta HCH (100.26 %), alpha endosulphan (98.35 %), p p DDE (82.70 %), beta endosulphan (96.76 %) and p p DDD (91.85 %)

At the fortification level of 0.5 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (78.74 %), dimethoate (90.65 %), methyl parathion (95.25 %), malathion (97.27 %), chlorpyriphos (97.68 %), quinalphos (100.36 %), profenophos (108.99 %) and ethion (109.50 %). The mean per cent recovery values were phorate (87.44 %), dimethoate (88.57 %), methyl parathion (96.08 %), malathion (92.10 %), chlorpyriphos (98.29 %), quinalphos (108.50 %), profenophos (98.11 %) and

Table 13: Recovery and repeatability of insecticides in cumin at different fortification levels

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Phorate	91.02 ± 6.21	6.82	87.44 ± 3.90	4.46	78.74 ± 6.20	6.91
Alpha HCH	95.56 ± 4.08	4.27	90.90 ± 4.35	4.79	92.86 ± 6.31	6.79
Dimethoate	71.22 ± 3.08	3.20	88.57 ± 5.07	5.73	90.65 ± 7.14	7.88
Beta HCH	96.33 ± 2.39	2.48	75.38 ± 4.85	5.69	91.96 ± 1.72	1.87
Lindane	92.15 ± 9.04	9.81	93.09 ± 1.60	1.72	93.64 ± 2.15	2.30
Fluchloralin	89.64 ± 4.75	5.30	71.15 ± 7.68	8.43	98.96 ± 0.13	0.13
Delta HCH	100.26 ± 1.78	1.78	108.92 ± 4.08	4.12	99.43 ± 3.57	3.59
Methyl parathion	107.45 ± 5.13	5.26	96.08 ± 8.30	8.63	95.25 ± 7.46	7.83
Malathion	92.94 ± 1.94	2.09	92.10 ± 5.72	6.21	97.27 ± 0.56	0.57
Chlorpyriphos	74.98 ± 7.63	8.04	98.29 ± 3.59	3.65	97.68 ± 4.21	4.31
Quinalphos	89.90 ± 6.34	7.05	108.50 ± 5,85	5.93	100.36 ± 4.00	3.98
Alpha endosulphan	98.35 ± 7.45	7.58	90.28 ± 5.15	5.70	74.84 ± 0.59	0.63
Profenophos	113.58 ± 5.23	5.59	98.11 ± 2.37	2.42	108.99 ± 0.75	0.79

Table 13 continued

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
p p DDE	82.70 ± 2.52	3.05	81.53 ± 0.73	0.90	83.01 ± 2.21	2.66
Beta endosulphan	96.76 ± 1.57	1.62	110.58 ± 4.12	4.76	73.05 ± 2.33	2.51
p p DDD	91.85 ± 9.41	10.24	89.07 ± 1.25	1.40	94.27 ± 6.45	6.84
Ethion	91.64 ± 3.15	3.44	87.87 ± 3.51	3.99	109.50 ± 5.13	5.73
Lambda cyhalothrin	78.32 ± 5.81	6.58	96.10 ± 3.19	3.31	95.81 ± 3.48	3.64
Cyfluthrin	97.78 ± 3.94	4.03	95.66 ± 6.61	6.91	99.12 ± 3.15	3.18
Cypermethrin	98.27 ± 0.43	0.44	94.76 ± 0.76	0.80	98.38 ± 2.8	2.91
Fenvalerate	93.57 ± 3.66	3.91	87.69 ± 1.71	1.71	94.04 ± 4.64	4.93

Number of replicates at each level (n) = 3

RSD - Relative Standard Deviation

ethion (87.87 %) at the fortification level of 0.25 mg kg^{-1}. At the fortification level of 0.05 mg kg^{-1}, the mean per cent recovery were phorate (91.02 %), dimethoate (71.22 %), methyl parathion (107.45 %), malathion (92.94 %), chlorpyriphos (74.98 %), quinalphos (89.90 %), profenophos (113.58 %) and ethion (91.64 %).

The mean per cent recovery values were 95.81, 98.38 and 94.04 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 98.96 and 99.12 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 0.5 mg kg^{-1}. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 96.10, 94.76 and 87.69 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 71.15 and 95.66 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 78.32, 98.27 and 93.57 for lambda cyhalothrin, cypermethrin and fenvalerate and 89.64 and 97.78 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were within range 70-110 per cent at three levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=3 at each spiking level, confirmed that the method is sufficiently reliable for pesticide residue analysis in cumin seed.

4.1.4 Capsicum

4.1.7.4 ***Determination of Recovery and Repeatability***

The quality parameter for method validation of 21 pesticides ie repeatability in capsicum essential to assess the method are presented in Table 14. The repeatability in terms of recovery percentage of the method

Table 14. Recovery and repeatability of insecticides in capsicum fruits at different fortification levels

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Phorate	82.60 ± 1.68	2.04	87.80 ± 4.20	4.79	74.00 ± 0.50	0.60
Alpha HCH	78.13 ± 2.28	2.32	98.23 ± 6.94	7.07	99.35 ± 3.85	3.88
Dimethoate	106.13 ± 1.50	1.41	106.00 ± 3.90	3.68	107.50 ± 1.80	1.67
Beta HCH	102.90 ± 2.17	2.11	105.50 ± 0.46	0.43	103.70 ± 2.20	2.12
Lindane	87.23 ± 4.14	4.75	90.70 ± 6.49	7.15	87.30 ± 1.70	1.95
Fluchloralin	103.57 ± 2.73	2.64	105.47 ± 2.53	2.40	103.00 ± 0.20	0.19
Delta HCH	103.63 ± 1.79	1.73	108.23 ± 1.44	1.33	105.70 ± 3.60	3.41
Methyl parathion	105.10 ± 3.64	3.46	91.00 ± 6.14	6.75	77.75 ± 11.25	11.51
Malathion	107.47 ± 0.83	0.77	108.80 ± 2.11	2.40	105.20 ± 2.00	1.90
Chlorpyriphos	105.33 ± 2.47	2.35	108.23 ± 1.44	1.33	108.45 ± 0.85	0.78
Quinalphos	76.60 ± 0.30	0.35	107.70 ± 4.06	3.77	95.75 ± 8.85	9.24
Alpha endosulphan	78.17 ± 6.93	7.86	106.70 ± 1.76	1.65	96.00 ± 12.70	13.23
Profenophos	105.63 ± 3.71	3.51	108.76 ± 2.10	1.93	109.10 ± 0.40	0.37
p p DDE	85.81 ± 2.56	2.98	103.84 ± 2.97	2.86	74.72 ± 6.40	6.75

Table 14 continued.

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
p p *DDD*	103.50 ± 2.14	2.07	86.77 ± 1.50	1.73	75.50 ± 9.70	10.16
Beta endosulphan	86.63 ± 2.19	2.53	83.90 ± 2.00	2.38	73.40 ± 2.50	3.00
Ethion	104.47 ± 1.53	1.47	87.17 ± 2.99	3.43	77.85 ± 8.35	8.53
Lambda cyhalothrin	85.40 ± 1.26	1.47	84.70 ± 4.33	5.11	106.90 ± 2.80	3.22
Cyfluthrin	76.16 ± 3.82	4.43	83.50 ± 1.35	1.61	79.65 ± 0.45	0.55
Cypermethrin	83.80 ± 4.39	5.23	85.27 ± 4.66	5.47	89.50 ± 0.90	1.01
Fenvalerate	94.80 ± 3.32	4.20	76.20 ± 0.61	0.71	89.05 ± 3.55	3.99

Number of replicates at each level (n) = 3

RSD - Relative Standard Deviation

was determined at three levels, 0.05mg kg^{-1} (LOQ), 0.25mg kg^{-1} (5 x LOQ) and 0.5mg kg^{-1} (10 X LOQ).

At 0.5mg kg^{-1}level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (99.35 %), beta HCH (103.70 %), lindane (87.30 %), delta HCH (105.70 %), alpha endosulphan (96.00 %), p p DDE (74.72 %), beta endosulphan (73.40 %) and p p DDD (75.50 %). At 0.25mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (98.23 %), beta HCH (105.50 %), lindane (90.70 %), delta HCH (108.23 %), alpha endosulphan (106.70 %), p p DDE (103.84 %), beta endosulphan (83.90 %) and p p DDD (86.77 %). At 0.05mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (78.13 %), beta HCH (102.90 %), lindane (87.23 %), delta HCH (103.63 %), alpha endosulphan (78.17 %), p p DDE (85.81 %), beta endosulphan (86.63 %) and p p DDD (103.50 %)

At the fortification level of 0.5 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (74.00 %), dimethoate (107.50 %), methyl parathion (77.75 %), malathion (105.20 %), chlorpyriphos (108.45 %), quinalphos (95.75 %), profenophos (109.10 %) and ethion (77.85 %). The mean per cent recovery values were phorate (87.80 %), dimethoate (106.00 %), methyl parathion (91.00 %), malathion (108.80 %), chlorpyriphos (108.23 %), quinalphos (107.70 %), profenophos (108.76 %) and ethion (87.17 %) at the fortification level of 0.25 mg kg^{-1}. At the fortification level of 0.05 mg kg^{-1}, the mean per cent recovery were phorate (82.60 %), dimethoate (106.13 %), methyl parathion (105.10 %), malathion (107.47 %), chlorpyriphos (105.33 %), quinalphos (76.60 %), profenophos (105.63 %) and ethion (104.47 %).

The mean per cent recovery values were 106.90, 89.50 and 89.05 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 103.00 and 79.65 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 0.5 mg kg^{-1}. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 84.70, 85.27 and 76.20 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 105.47 and 83.50 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 85.40, 83.80 and 94.80 for lambda cyhalothrin, cypermethrin and fenvalerate 103.57 and 76.16 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were within the range 70-110 per cent at three levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=3 at each spiking level, confirmed that the method is sufficiently reliable for pesticide residue analysis in capsicum.

4.1.4a Okra

4.1.8.4 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides ie repeatability in rice grains essential to assess the method are presented in Table 15. The repeatability in terms of recovery percentage of the method was determined at three levels, 0.05mg kg^{-1} (LOQ), 0.25mg kg^{-1} (5 x LOQ) and 0.5mg kg^{-1} (10 X LOQ).

At 0.5mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (85.59 %), beta HCH (82.66 %), lindane (106.42 %), delta HCH (102.67 %), alpha endosulphan (95.09 %), p p DDE (101.04 %), beta endosulphan (105.96 %) and p p DDD (109.54 %). At 0.25mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (75.03 %), beta HCH (73.18 %), lindane (85.21 %), delta HCH (104.99 %), alpha endosulphan (108.45 %), p p DDE (100.50 %), beta endosulphan

Table 15. Recovery and repeatability of insecticides in okra fruits at different fortification levels

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Phorate	74.83 ± 4.26	5.02	84.37 ± 1.69	2.01	79.52 ± 1.49	1.67
Alpha HCH	82.61 ± 2.59	3.13	75.03 ± 1.96	2.31	85.59 ±3.24	3.78
Dimethoate	101.81 ± 0.56	0.68	101.80 ± 0.26	0.25	104.34 ± 3.71	3.56
Beta HCH	85.71 ± 1.16	1.36	73.18 ± 2.11	2.54	82.66 ± 1.80	2.18
Lindane	72.54 ± 2.17	2.63	85.21 ± 5.05	5.93	106.42 ± 3.10	3.59
Fluchloralin	88.84 ± 7.62	8.58	76.39 ± 4.10	4.64	76.84 ± 0.76	0.87
Delta HCH	71.54 ± 4.37	4.78	104.99 ± 2.44	2.33	102.67 ± 2.71	2.64
Methyl parathion	91.13 ± 5.53	6.07	105.11 ± 2.98	2.84	104.60 ± 3.84	3.67
Malathion	105.60 ± 6.75	7.89	85.94 ± 5.41	6.29	106.99 ± 2.18	2.51
Chlorpyriphos	84.71 ± 0.58	0.68	76.71 ± 7.30	8.41	82.38 ± 1.35	1.63
Quinalphos	73.05 ± 0.47	0.56	85.94 ± 4.42	5.14	78.85 ± 0.71	0.72
Alpha endosulphan	87.31 ± 3.10	3.55	108.45 ± 1.40	1.59	95.09 ± 4.08	4.29
Profenophos	85.84 ± 3.22	3.75	85.65 ± 3.34	3.90	105.64 ± 1.21	1.26
p p DDE	93.63 ± 7.97	8.51	100.50 ± 14.10	14.02	101.04 ± 0.79	0.79

Table 15 continued.

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Beta endosulphan	78.54 ± 6.22	7.03	76.47 ± 1.77	2.05	105.96 ± 5.04	5.86
p p DDD	87.35 ± 8.35	9.56	87.27 ± 1.95	2.24	109.54 ± 1.27	1.16
Ethion	85.91 ± 4.36	5.08	106.33 ± 3.47	4.02	88.39 ± 1,71	1.94
Lambda cyhalothrin	72.58 ± 6.54	7.06	86.99 ± 5.60	6.44	107.00 ± 0.67	0.77
Cyfluthrin	103.78 ± 4.62	4.46	102.72 ± 1.48	1.45	84.24 ± 1.13	1.35
Cypermethrin	96.16 ± 10.03	10.43	87.24 ± 3.48	3.99	84.86 ± 1.83	2.16
Fenvalerate	72.62 ± 4.01	4.31	82.02 ± 1.16	1.41	105.33 ± 3.60	3.78

Number of replicates at each level (n) = 3

RSD - Relative Standard Deviation

(76.47 %) and p p DDD (87.27 %). At 0.05mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (82.61 %), beta HCH (85.71 %), lindane (72.54 %), delta HCH (71.54 %), alpha endosulphan (87.31 %), p p DDE (93.63 %), beta endosulphan (78.54 %) and p p DDD (87.35 %)

At the fortification level of 0.5 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (79.52 %), dimethoate (104.34 %), methyl parathion (104.60 %), malathion (106.99 %), chlorpyriphos (82.38 %), quinalphos (78.85 %), profenophos (105.64 %) and ethion (88.39 %). The mean per cent recovery values were phorate (84.37 %), dimethoate (101.80 %), methyl parathion (105.11 %), malathion (85.94 %), chlorpyriphos (76.71 %), quinalphos (85.94 %), profenophos (85.65 %) and ethion (106.33 %) at the fortification level of 0.25 mg kg^{-1}. At the fortification level of 0.05 mg kg^{-1}, the mean per cent recovery were phorate (74.83 %), dimethoate (101.81 %), methyl parathion (91.13 %), malathion (105.60 %), chlorpyriphos (84.71 %), quinalphos (73.05 %), profenophos (85.84 %) and ethion (85.91 %).

The mean per cent recovery values were 107.00, 84.86 and 105.30 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 76.84 and 84.24 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 0.5 mg kg^{-1}. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 86.99, 87.24 and 82.02 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 87.39 and 102.72 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 72.58, 96.16 and 72.62 for Lambda cyhalothrin, Cypermethrin and Fenvalerate and 88.84 and 103.78 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were within the range 70-110 per cent at three levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=3 at each spiking level, confirmed that the method is sufficiently reliable for pesticide residue analysis in okra.

4.1.4b Curry leaf

4.1.6.4 *Determination of Recovery and Repeatability*

The quality parameter for method validation of 21 pesticides ie repeatability in curry leaf essential to assess the method are presented in Table 16. The repeatability in terms of recovery percentage of the method was determined at three levels, 0.05mg kg^{-1} (LOQ), 0.25mg kg^{-1} (5 x LOQ) and 0.5mg kg^{-1} (10 X LOQ).

At 0.5mg kg^{-1} level of fortification, the mean per cent recovery among organochlorine pesticides were alpha HCH (84.66 %), beta HCH (94.00 %), lindane (101.46 %), delta HCH (84.96 %), alpha endosulphan (71.43 %), p p DDE (109.40 %), beta endosulphan (90.95 %) and p p DDD (75.33 %). At 0.25mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (78.23 %), beta HCH (88.74 %), lindane (106.83 %), delta HCH (77.06 %), alpha endosulphan (90.24 %), p p DDE (82.19 %), beta endosulphan (84.94 %) and p p DDD (109.08 %). At 0.05mg kg^{-1} level of fortification, the mean per cent recovery were alpha HCH (92.49 %), beta HCH (75.46 %), lindane (81.61 %), delta HCH (96.05 %), alpha endosulphan (76.95 %), p p DDE (104.23 %), beta endosulphan (87.68 %) and p p DDD (74.24 %)

At the fortification level of 0.5 mg kg^{-1}, the mean per cent recovery among the organophosphate pesticides were phorate (74.17 %), dimethoate (73.53 %), methyl parathion (73.83 %), malathion (84.87 %), chlorpyriphos (75.93 %), quinalphos (87.67 %), profenophos (88.70 %) and ethion (83.81 %). The mean per cent recovery values were phorate (87.95 %), dimethoate (93.40 %), methyl parathion (94.36 %), malathion (90.54 %), chlorpyriphos

Table 16: Recovery and repeatability of insecticides in curry leaf at different fortification levels

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Phorate	83.31 ± 2.10	2.41	87.95 ± 1.26	1.43	74.17 ± 3.10	3.68
Alpha HCH	92.49 ± 6.91	7.47	78.23 ± 5.12	5.80	84.66 ± 1.38	1.62
Dimethoate	94.91 ± 12.89	13.58	93.40 ± 4.24	4.55	73.53 ± 3.22	3.86
Beta HCH	75.46 ± 9.94	10.41	88.74 ± 5.57	6.28	94.00 ± 1.13	1.20
Lindane	81.61 ± 0.89	1.09	106.83 ± 5.89	6.08	101.46 ± 5.10	5.03
Fluchloralin	104.11 ± 7.19	7.64	91.73 ± 9.43	10.28	86.45 ± 1.59	1.84
Delta HCH	96.05 ± 9.55	9.94	77.06 ± 4.56	4.70	84.96 ± 4.15	4.88
Methyl parathion	98.86 ± 5.64	5.71	94.36 ± 5.62	5.96	73.83 ± 0.07	0.08
Malathion	73.79 ± 13.01	13.87	90.54 ± 8.90	9.84	84.87 ± 0.96	1.13
Chlorpyriphos	94.89 ± 10.81	11.39	73.35 ± 0.02	0.02	75.93 ± 3.11	3.62
Quinalphos	84.93 ± 1.37	1.61	71.52 ± 1.30	1.42	87.67 ± 1.15	1.31
Alpha endosulphan	76.95 ± 1.85	2.13	90.24 ± 3.63	4.02	71.43 ± 2.80	3.07
Profenophos	95.73 ± 6.37	6.65	102.52 ± 2.83	2.76	88.70 ± 0.82	0.93

Table 16 continued.

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
p p DDE	104.23 ± 8.33	8.84	82.19 ± 0.88	1.08	109.40 ± 0.31	0.35
Beta endosulphan	87.68 ± 1.42	1.62	84.94 ± 0.41	0.48	90.95 ± 6.90	7.58
p p DDD	74.24 ± 9.96	10.57	109.08 ± 5.29	5.94	75.33 ± 3.43	3.60
Ethion	104.29 ± 9.61	10.19	85.59 ± 5.39	6.29	83.81 ± 2.08	2.48
Lambda cyhalothrin	108.49 ± 0.01	0.01	76.01 ± 5.75	5.98	103.01 ± 0.55	0.53
Cyfluthrin	95.46 ± 5.66	5.93	108.48 ± 7.92	8.04	101.60 ± 1.48	1.45
Cypermethrin	72.70 ± 2.70	3.26	93.00 ± 1.74	1.87	71.51 ± 0.68	0.66
Fenvalerate	75.83 ± 3.57	3.73	85.89 ± 0.45	0.52	71.91 ± 1.80	2.20

Number of replicates at each level (n) = 3

RSD - Relative Standard Deviation

(73.35 %), quinalphos (71.52 %), profenophos (102.52 %) and ethion (85.59 %) at the fortification level of 0.25 mg kg^{-1}. At the fortification level of 0.05 mg kg^{-1}, the mean per cent recovery were phorate (83.31 %), dimethoate (94.91 %), methyl parathion (98.96 %), malathion (73.79 %), chlorpyriphos (94.89 %), quinalphos (84.93 %), profenophos (95.73 %) and ethion (104.29 %).

The mean per cent recovery values were 103.01, 71.51 and 71.91 for synthetic pyrethroid pesticides like lambda cyhalothrin, cypermethrin and fenvalerate respectively and 86.45 and 101.60 per cent for herbicides like fluchloralin and cyfluthrin respectively at fortification level of 0.5 mg kg^{-1}. At 0.25 mg kg^{-1} fortification level, the mean per cent recovery values were 76.01, 93.00 and 85.89 for lambda cyhalothrin, cypermethrin and fenvalerate respectively and 91.73 and 108.48 per cent for fluchloralin and cyfluthrin respectively. At 0.05 mg kg^{-1} fortification level, the mean per cent recovery values were 108.49, 72.70 and 75.83 for lambda cyhalothrin, cypermethrin and fenvalerate and 104.11 and 95.46 per cent for fluchloralin and cyfluthrin respectively

A satisfactory recovery was obtained for almost all the compounds fortified. Method validation was accomplished with good linearity and satisfactory recoveries. The mean recovery of all the 21 pesticides under study were within the range 70-110 per cent at three levels of fortification. The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=3 at each spiking level, confirmed that the method is sufficiently reliable for pesticide residue analysis in curry leaf.

4.2 MONITORING OF PESTICIDE RESIDUES IN AGRICULTURAL COMMODITIES

The data on residues of pesticides in agricultural commodities during January to June 2012 from Thiruvananthapuram district are presented in

Table 17 and the extent of contamination in terms of Maximum Residue Limits (MRL) value is depicted in Fig. 1

4.2.1 Rice flour and wheat flour (atta and maida)

No samples of rice flour, atta and maida did show the presence of OC, OP and SP insecticide residues during the study period January-June 2012.

4.2.2 *Rice*

The data on pesticide residues (mg kg^{-1}) in rice (parboiled and raw) collected from Thiruvananthapuram during January to June 2012 indicated that none of the samples showed the presence of any of OC, OP and SP insecticide residues. Monitoring of pesticide residues in basmathi rice revealed that out of six samples analyzed, five of them contained residues with a range of 0.011 - 0.08 mg kg^{-1}. Malathion was seen in two samples with a range of 0.06 - 0.08 mg kg^{-1} and the values were below FSSAI MRL. Chlorpyriphos (0.025 mg kg^{-1}) was detected in one sample, but the level was below FSSAI MRL. Fenvalerate (0.052 mg kg^{-1}), methyl parathion (0.046 mg kg^{-1}) and cypermethrin (0.011 mg kg^{-1}) were also detected in one sample each. However, MRL has not been fixed by FSSAI, or any of these pesticides in basmathi rice. The highest level of pesticides in basmathi rice observed during the study period were malathion (0.08 mg kg^{-1}) followed by fenvalerate (0.052 mg kg^{-1}).

4.2.3 *Wheat*

In the case of wheat samples collected from Thiruvananthapuram district, a total of four different pesticides were detected from 5 samples at varying levels. Pesticides detected in these samples included chlorpyriphos, quinalphos, malathion and methyl parathion with a range of 0.024 – 0.31 mg kg^{-1} and the highest concentration observed was 0.31 mg kg^{-1} for chlorpyriphos. Malathion was seen in three samples with a range of 0.024-

Table 17. Pesticide residues in various agricultural commodities collected from market during January - June 2012.

	Monitoring period											
	January 2012		February 2012		March 2012		April 2012		May 2012		June 2012	
Commodity	Insecticide detected	Concentration (mg kg^{-1})	Insecticide detected	Concentration (mg kg^{-1})	Insecticide detected	Concentration (mg kg^{-1})	Insecticide detected	Concentration (mg kg^{-1})	Insecticide detected	Concentration (mg kg^{-1})	Insecticide detected	Concentration (mg kg^{-1})
Parboiled rice	ND		ND		ND		ND		ND		ND	
Raw rice	ND		ND		ND		ND		ND		ND	
Basmathi rice	Malathion	0.06	Malathion	0.08	Chlorpyriphos	0.025	ND		Fenvalerate	0.052	Methyl parathion	0.046
											Cypermethrin	0.011
Rice flour	ND		ND		ND		ND		ND		ND	
Wheat	Chlorpyriphos	0.047	Chlorpyriphos	0.31	Malathion	0.19	Malathion	0.024	ND		Malathion	0.025
			Quinalphos	0.039			Methyl parathion	0.065			Quinalphos	0.046
Atta	ND		ND		ND		ND		ND		ND	
Maida	ND		ND		ND		ND		ND		ND	
Cardamom	Chlorpyrifos	0.238	Chlorpyrifos	0.057	Chlorpyrifos	0.091	Chlorpyrifos	0.353	Profenophos	0.509	Quinalphos	1.625

	Quinalphos	0.137	Quinalphos	0.150	Quinalphos	2.044	Quinalphos	0.199	Lambda cyhalothrin	0.077	Profenophos	0.166
	Profenophos	0.268	Profenophos	0.139	Profenophos	0.540	Profenophos	0.954	Cypermethrin	0.150	Ethion	0.344
	Bifenthrin	0.106	Lambda cyhalothrin	0.132	Lambda cyhalothrin	0.225	Lambda cyhalothrin	0.364	Chlorpyrifos	0.087	Lambda cyhalothrin	0.133
	Lambda cyhalothrin	0.058	Cypermethrin	0.061	Cypermethrin	0.071	Cypermethrin	0.461	-		Cypermethrin	0.105
	Cypermethrin	0.266										
Cumin	Profenophos	0.520	Alpha endosulphan	0.135	Profenophos	0.66	Profenophos	0.59	Profenophos	0.488	Profenophos	1.45
	Chlorpyriphos	0.270	Quinalphos	0.139	Chlorpyriphos	0.04	Chlorpyriphos	0.053	Chlorpyriphos	0.205	Chlorpyriphos	0.27
									Alpha endosulphan	0.115		
Curry leaf	Quinalphos	0.259	Chlorpyriphos	0.014	Chlorpyriphos	0.12	Chlorpyriphos	0.049	Chlorpyriphos	1.34	Chlorpyriphos	1.34
	Profenophos	3.08	Profenophos	4.48	Profenophos	1.62	Profenophos	16.27	Profenophos	25.63	Profenophos	12.24
	Triazophos	0.369	Triazophos	1.58	Triazophos	1.58	Quinalphos	0.209	Cypermethrin	1.44	Cypermethrin	0.315
	Cypermethrin	0.134	Cypermethrin	0.224	Cypermethrin	0.12	Methyl parathion	0.113	Alpha endosulphan	0.015	Ethion	1.15
	Alpha endosulphan	0.023	Fenpropathrin	0.12	Fenpropathrin	0.143			Malathion	0.078	Malathion	0.439
					Cyfluthrin	0.08					Bifenthrin	0.104

Capsicum	Chlorpyriphos	0.047	ND		Profenophos	0.033	Chlorpyriphos	0.024	ND		ND	
Okra	ND		Malathion	0.038	Profenophos	0.121	ND		ND		ND	

0.19 mg kg^{-1}. However, the level of all insecticides were below the FSSAI MRL. Chlorpyriphos was detected in two samples with a range of 0.047-0.31 mg kg^{-1} of which one was below FSSAI MRL. Methyl parathion was detected in one sample (0.065 mg kg^{-1}) and quinalphos was detected in two samples (0.039-0.046 mg kg^{-1}) for which no FSSAI MRL exists.

4.2.4 *Cardamom*

The data on pesticide residues (mg kg^{-1}) in cardamom collected from Thiruvananthapuram during January to June 2012 indicated that all the samples showed the presence of multiple pesticide residues at varying levels. Pesticides detected were chlorpyriphos, quinalphos, profenophos, bifenthrin, lambda cyhalothrin, cypermethrin and ethion. Profenophos, lambda cyhalothrin and cypermethrin were present in all the samples with a range of 0.139 - 0.954 mg kg^{-1}, 0.058-0.364 mg kg^{-1} and 0.061 - 0.461 mg kg^{-1} respectively, however no MRL have been fixed by FSSAI for profenophos and lambda cyhalothrin in cardamom. Cypermethrin was detected in all the six samples, of which 4 samples were above Codex MRL. Five samples showed the presence of chlorpyriphos and quinalphos with a the range of 0.057-0.353 mg kg^{-1} and 0.137-2.044 mg kg^{-1} respectively out of which 4 samples having chlorpyriphos were below Codex MRL and all the samples containing quinalphos residues were above FSSAI MRL. Bifenthrin (0.106 mg kg^{-1}) and ethion (0.344 mg kg^{-1}) were detected in one sample each. No FSSAI MRL have been fixed for bifenthrin and ethion in cardamom. The highest level of pesticide residues in cardamom observed during the study period was quinalphos (2.044 mg kg^{-1}) followed by profenophos (0.954 mg kg^{-1}).

4.2.5 Cumin seed

Monitoring of pesticide residues in cumin seed collected from Thiruvananthapuram during January to June 2012 revealed that out of six samples analyzed, all of them contained multiple residues of pesticides with a

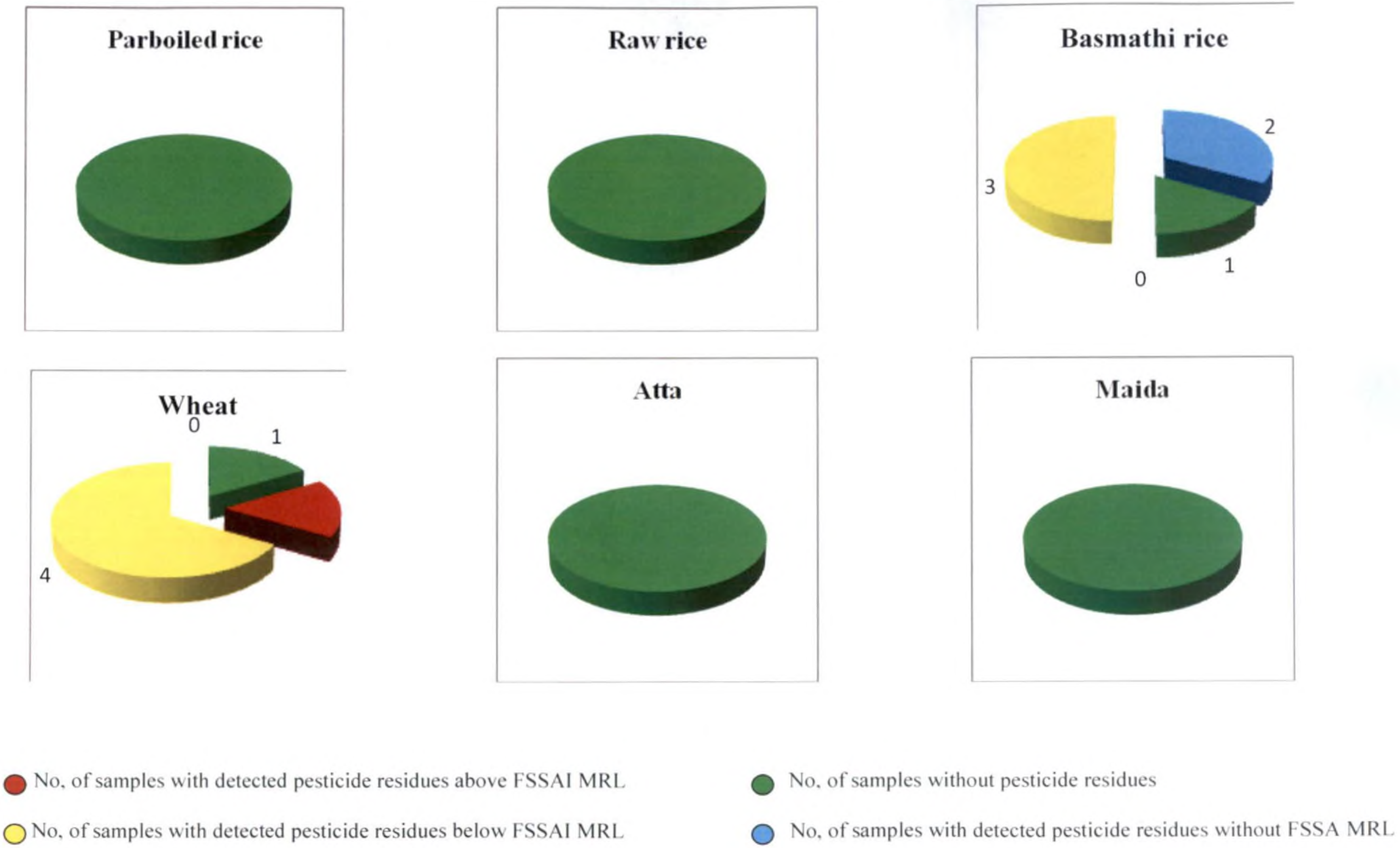


Fig. 1. Extent of contamination of pesticide residues in agricultural commodities collected from Thiruvananthapuram district during January-June 2012.

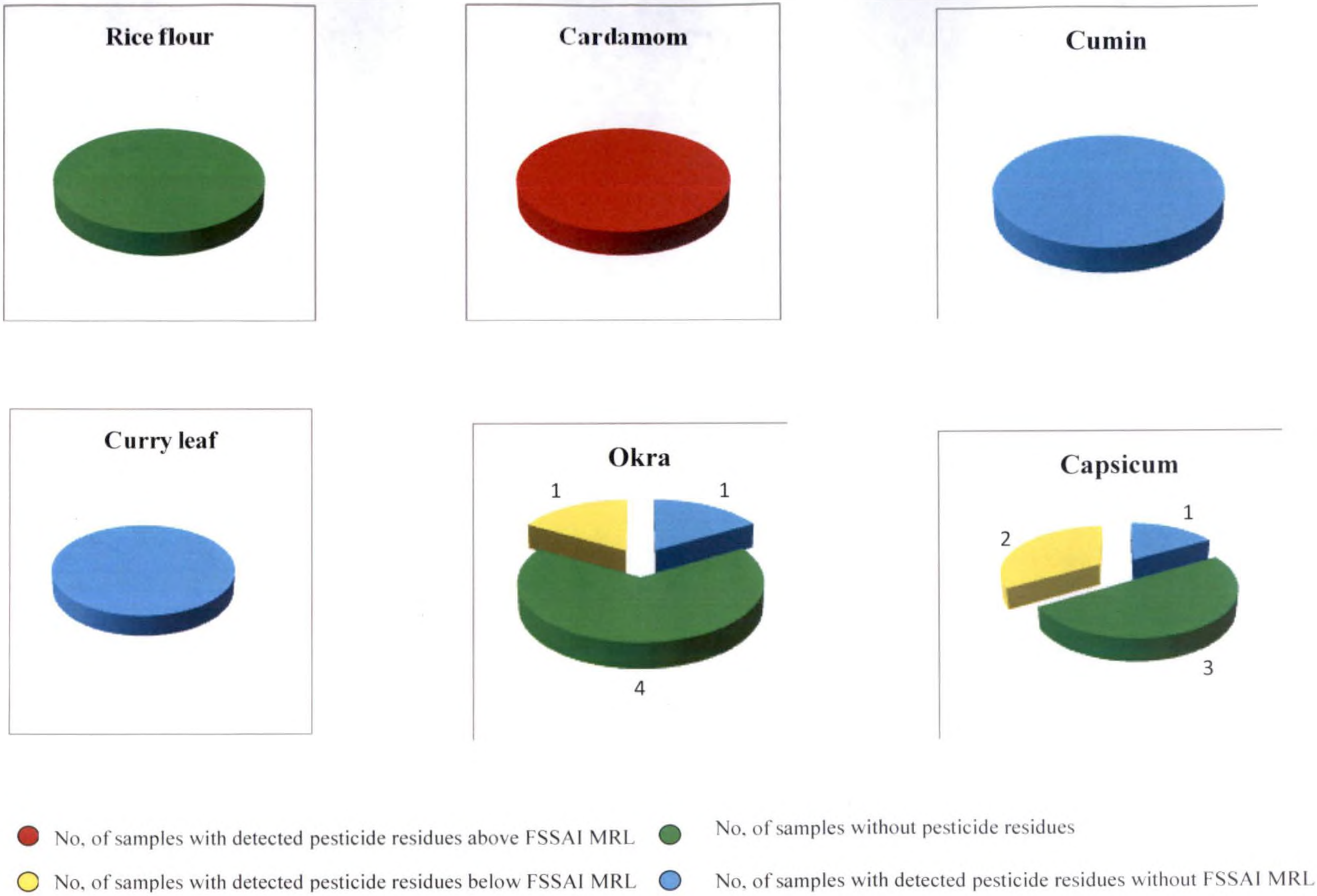


Fig. 1. Extent of contamination of pesticide residues in agricultural commodities collected from Thiruvananthapuram district during January-June 2012.

range of 0.04 - 1.45 mg kg^{-1}. Profenophos and chlorpyriphos were seen in five samples with a range of 0.488 - 1.45 mg kg^{-1} and 0.04 - 0.27 mg kg^{-1} respectively for which no FSSAI MRL exists in cumin seed for profenophos. Alpha endosulphan was detected in two samples with a range of 0.115 - 0.135 mg kg^{-1} which was below FSSAI MRL and quinalphos was detected in one sample, the level being 0.139 mg kg^{-1} having no FSSAI MRL for reference.

4.2.6 *Capsicum*

Out of the six samples analyzed during January to June 2012, three of them contained residues of pesticide with a range of 0.024 - 0.047 mg kg^{-1}. The highest value was for chlorpyriphos (0.047 mg kg^{-1}) which was detected in two samples falling below FSSAI MRL. One sample showed the presence of profenophos at 0.033 mg kg^{-1}, which has no FSSAI MRL in capsicum.

4.2.7 *Okra*

Monitoring of pesticide residues in okra revealed that out of six samples analyzed, two samples contained residues of pesticides. One sample showed the presence of profenophos (0.121 mg kg^{-1}) which has no FSSAI MRL and malathion (0.038 mg kg^{-1}) in another sample which is below FSSAI MRL.

4.2.8. *Curry leaf*

Pesticide residues (mg kg^{-1}) in curry leaf collected from Thiruvananthapuram during January to June 2012 indicated that all the samples contained multiple residues of pesticides with a range of 0.014 – 25.63 mg kg^{-1}. An array of OP and SP pesticides were detected *viz.,* chlorpyriphos, quinalphos, profenophos, triazophos, methyl parathion, cypermethrin, alpha endosulphan, malathion, fenpropathrin, cyfluthrin, bifenthrin and ethion. Highest level of residues observed in curry leaf was of profenophos (25.63 mg kg^{-1}) followed by triazophos (1.58 mg kg^{-1}) and cypermethrin (1.44 mg kg^{-1}). Levels of profenophos residues detected in all the samples ranged from 1.62 mg kg^{-1} to a level as high as 25.63 mg kg^{-1}.

Five samples showed the presence of chlorpyriphos and cypermethrin with the range of 0.014-1.34 mg kg^{-1} and 0.224-1.44 mg kg^{-1} respectively. Triazophos was detected in three samples (0.369-1.58 mg kg^{-1}), quinalphos in two samples (0.209-0.259 mg kg^{-1}), malathion in two samples (0.078-0.439 mg kg^{-1}), fenpropathrin in two samples (0.12-0.143 mg kg^{-1}) and alpha endosulphan in two samples (0.015-0.023 mg kg^{-1}). Methyl parathion, bifenthrin, cyfluthrin and ethion were detected in one sample each, the levels being 0.113, 0.104, 0.08 and 1.15 mg kg^{-1} respectively. No FSSAI MRL have been fixed for any of these pesticides detected in curry leaf.

4.3 ASSESSMENT OF THE EFFECT OF WASHING, SOAKING AND COOKING ON REMOVAL OF INSECTICIDE RESIDUES IN RICE

4.3.1 Method validation in cooked rice

The Limit of Detection (LOD) for the six pesticides was considered to be the concentration that produced a signal to noise ratio of more than three, and LOD was estimated from the chromatogram corresponding to the lowest point used in the matrix-matched calibration. In this work, the LODs of six pesticides were 0.01mg kg^{-1} and at LOD, the S/N ratio for all the 21 pesticides were >3.

A calibration curve was prepared by plotting concentrations (0.5, 0.25, 0.1, 0.075, 0.05, 0.025 and 0.01 mg kg^{-1}) vs. peak area. Good linearity was found within the range of 0.01-0.5 mg kg^{-1} which is evident from the coefficient of determination (R^2) for each pesticide. The Limit of Quantification (LOQ) of the proposed method was calculated by considering a value of 10 times more than that of background noise. The LOQs of all the six pesticides in this method were calculated as 0.05 mg kg^{-1}.

Table 18 presents the recovery and repeatability for the three concentration levels (LOQ 0.05 mg kg^{-1}, 5 x LOQ 0.25 mg kg^{-1}, 10 x LOQ

Table 18. Recovery and repeatability of insecticides on cooked rice at different fortification levels

Insecticides	Level of fortification					
	LOQ (0.05 mg kg^{-1})		5 X LOQ (0.25 mg kg^{-1})		10 X LOQ (0.5 mg kg^{-1})	
	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)	Mean recovery (%) ± SD	RSD (%)
Methyl parathion	92.23 ± 7.63	8.27	104.82 ± 4.02	3.84	106.33 ± 3.68	3.46
Malathion	94.67 ± 0.36	0.38	103.33 ± 6.06	5.87	97.31 ± 1.53	1.57
Chlorpyriphos	86.52 ± 1.89	2.18	85.71 ± 1.14	1.33	86.22 ± 2.06	2.38
Quinalphos	86.23 ± 1.98	2.30	90.72 ± 5.63	6.21	83.69 ± 2.98	3.56
Cypermethrin	93.76 ± 4.26	4.55	100.36 ± 1.99	1.99	103.47 ± 2.10	2.03
Fenvalerate	98.94 ± 4.69	4.74	103.50 ± 5.96	5.75	101.42 ± 3.64	3.59

Number of replicates at each level (n) = 3

RSD - Relative Standard Deviation

0.50 mg kg^{-1}). The mean recovery percentage of malathion, methyl parathion, chlorpyriphos, quinalphos, cypermethrin and fenvalerate in cooked rice when fortified at a level of 0.05 mg kg^{-1} were 94.67, 92.23, 86.52, 86.23, 93.76 and 98.94 per cent respectively. When fortified at 0.25 mg kg^{-1}, the mean per cent recovery came to around 103.33, 104.82, 85.71, 90.72, 100.36 and 103.50 for malathion, methyl parathion, chlorpyriphos, quinalphos, cypermethrin and fenvalerate respectively. At higher level of fortification, 0.5 mg kg^{-1}, 97.31, 106.33, 86.22, 83.69, 103.47 and 101.42 per cent of residues were recovered in the case of malathion, methyl parathion, chlorpyriphos, quinalphos, cypermethrin and fenvalerate respectively. The recovery percentage in this study was in the range of 83.69 - 106.33, which indicated a good and validated analytical procedure.

The repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % with n=3 at each spiking level, confirmed that the method is sufficiently reliable for pesticide residue analysis in cooked rice.

4.3.3 Processing treatments

Data pertaining to dissipation of insecticides in rice grains during storage is presented in Table 19 and depicted in Fig. 2.The extent of removal of insecticide residues from rice grains using different household processing techniques, 5 h and 2 weeks after insecticide application are presented in Table 20 to 21 and the processing factor for different technique in each insecticide is depicted in Fig. 3.

4.3.3.1 *Methyl parathion*

Concentration of methyl parathion in rice grains at 5 h after insecticide application was 8.35 mg kg^{-1} and the residues reached to 8.14 mg kg^{-1} after 2 weeks resulting in 2.51 per cent loss (Table 19). There was no significant reduction in the concentration of methyl parathion residues in rice grains when subjected to residue analysis done at two weeks after spraying.

Table19. Persistence of organophosphate and synthetic pyrethroid insecticides in rice grains

Insecticides	Residues (mg kg^{-1}) ± SD		Dissipation (%)
	5 h after spraying	2 weeks	
Methyl parathion	8.35 ± 0.22	8.14 ± 0.14	2.51
Malathion	0.52 ± 0.01	0.48 ± 0.03	7.69
Chlorpyriphos	3.04 ± 0.02	2.71 ± 0.01	10.85
Quinalphos	4.00 ± 0.02	3.46 ± 0.05	13.50
Cypermethrin	0.10 ± 0.10	0.10 ± 0.01	0.00
Fenvalerate	1.56 ± 0.07	1.45 ± 0.06	7.05

Percentage removal of methyl parathion residues in rice grains when subjected to processing techniques showed that all the processing techniques except two *viz.*, two washings followed by cooking and four washings followed by cooking significantly differed among each other in their efficiency in removing the residues. These two techniques were found to be significantly superior to all other techniques resulting in more than 85 per cent removal of methyl parathion residues.

The percentage removal of methyl parathion residues when subjected to different processing techniques 5 h after insecticide application (Table 20) were 67.56 (two washing), 73.32 (four washing), 25.98 (soaking), 70.20 (soaking + two washing), 78.95 (soaking + four washing), 90.57 (cooking), 97.18 (two washing + cooking) and 98.23 (four washing + cooking). The losses incurred due to different processing techniques 2 weeks after insecticide application were 38.01 (two washing), 44.94 (four washing), 22.23 (soaking), 57.30 (soaking + two washing), 62.46 (soaking + four washing), 79.98 (cooking), 87.48 (two washing + cooking) and 89.92 (four washing + cooking) per cent.

4.3.3.2 *Malathion*

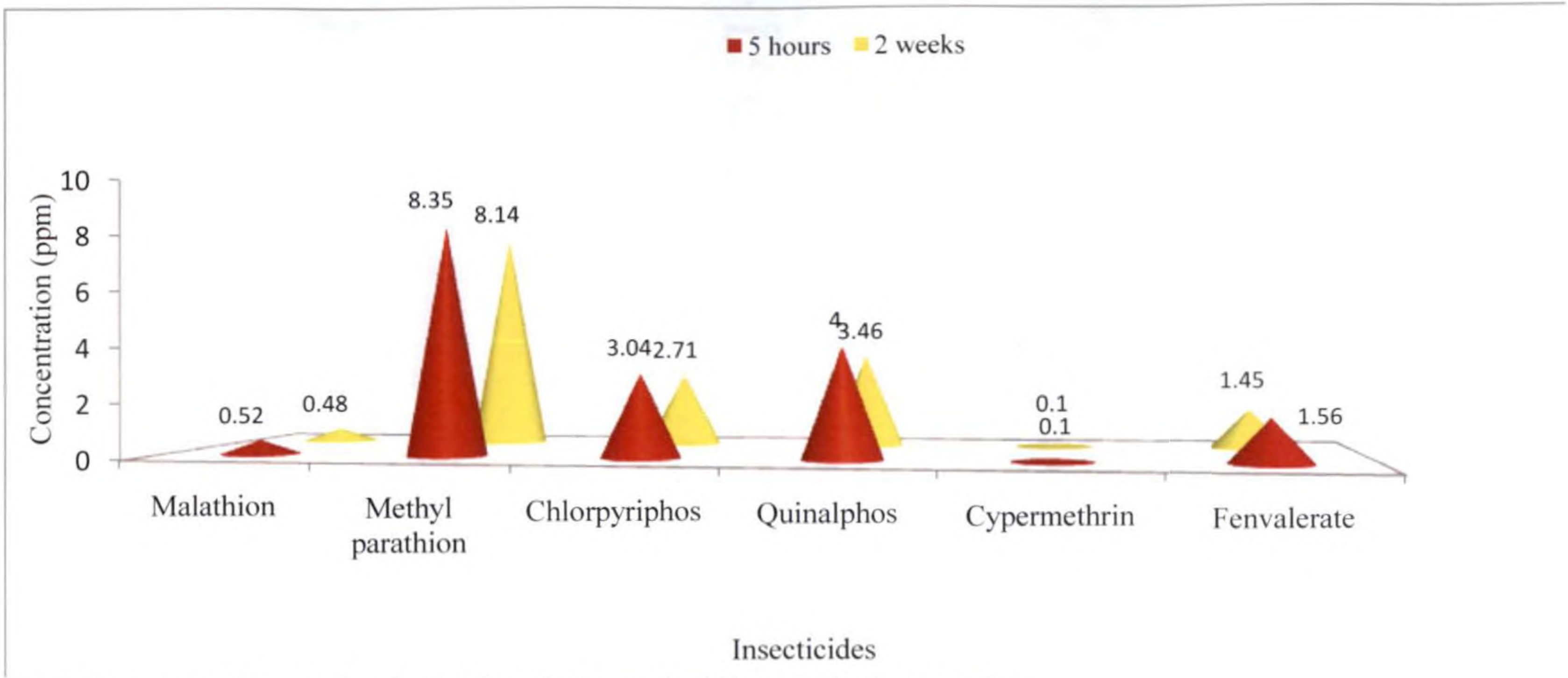


Fig. 2. Persistence of organophosphate and synthetic pyrethroid insecticides in rice grains

Treatment of insecticide emulsion on rice grains resulted in 0.52 mg kg^{-1} of malathion residues at 5 h after insecticide application which later dissipated to 0.48 mg kg^{-1} in 2 weeks (Table19). There was no significant reduction in malathion residues in 2 weeks. The two techniques *viz.*, two washing followed by cooking and four washing followed by cooking were found to be on par and significantly superior over all the other techniques.

Percentage removal of malathion residues when subjected to different processing techniques 5 h after insecticide application were 81.93 (two washing), 84.27 (two washing), 34.56 (soaking), 86.80 (soaking + two washing) and 89.26 (soaking + four washing). During cooking, the residue level decreased significantly accounting to 92.59 per cent of the initial deposit. Two washings followed by cooking and four washings followed by cooking resulted in 97.67 and 98.11 per cent loss. The losses incurred due to different processing techniques 2 weeks after insecticide application were 52.11 (two washing), 55.48 (four washing), 27.78 (soaking), 76.10 (soaking + two washing), 73.19 (soaking + four washing), 82.01 (cooking), 88.14 (two washing + cooking) and 89.94 (four washing + cooking) per cent.

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of each processing techniques in removing the residues of insecticides at two intervals (5 h and 2 weeks after insecticide application).

4.3.3.3 *Chlorpyriphos*

Concentration of chlorpyriphos in rice grains at 5 h after insecticide application was 3.04 mg kg^{-1} and the residues reached to 2.71 mg kg^{-1} after 2 weeks resulting in 10.85 per cent loss (Table19). There was no significant reduction in the concentration of chlorpyriphos residues in rice grains when subjected to residue analysis 2 weeks after spraying. Similar scenario with respect to best processing technique, which was observed in methyl parathion

Table 20. Extent of removal of insecticide residues from rice grains by the use of different household processing techniques 5 h after spraying

Processing techniques	Mean per cent removal of insecticides (%) ± SD					
	Methyl parathion	Malathion	Chlorpyriphos	Quinalphos	Cypermethrin	Fenvalerate
Two washings in tap water for two minutes along with rubbing of grains	67.56 ± 0.78 (2.70)	81.93 ± 0.35 (0.28)	70.93 ± 0.70 (0.88)	72.34 ± 0.98 (1.10)	79.98 ± 0.78 (0.02)	75.66 ± 0.95 (0.12)
Four washings in tap water for two minutes along with rubbing of grains	73.32 ±1.17 (2.22)	84.27 ± 0.80 (0.20)	73.97 ± 1.23 (0.88)	76.22 ± 1.06 (0.95)	83.84 ± 2.78 (0.02)	82.18 ± 0.91 (0.09)
Soaking of grains in water for six hours	25.98 ± 3.26 (6.18)	34.56 ± 3.15 (1.02)	23.99 ± 2.20 (2.31)	22.57 ± 0.55 (3.09)	34.08 ± 3.81 (0.06)	23.22 ± 0.59 (0.39)
Soaking (six hours) + two washings in tap water for two minutes along with rubbing of grains	70.20 ± 1.20 (2.48)	86.80 ± 0.79 (0.20)	76.04 ± 0.73 (0.72)	47.83 ± 0.98 (2.08)	85.61 ± 0.47 (0.01)	79.50 ± 0.80 (0.10)
Soaking (six hours) + four washings in tap water for two minutes along with rubbing of grains	78.95 ± 0.62 (1.75)	89.26 ± 0.48 (0.16)	79.71 ± 1.27 (0.61)	54.79 ± 1.06 (1.80)	88.63 ± 1.14 (0.01)	85.43 ± 3.10 (0.07)
Cooking followed by decanting rice gruel	90.57 ± 1.34 (0.78)	92.59 ± 1.00 (0.11)	90.92 ± 2.13 (0.27)	91.73 ± 1.18 (0.33)	90.48 ± 0.66 (0.01)	89.40 ± 1.32 (0.05)
Two washings in tap water for two minutes along with rubbing of grains + cooking	97.18 ± 0.89 (0.23)	97.67 ± 0.60 (0.03)	98.37 ± 0.27 (0.04)	84.74 ± 0.60 (0.61)	96.49 ± 0.23 (0.01)	97.83 ± 0.55 (0.01)
Four washings in tap water for two minutes along with rubbing of grains + cooking	98.23 ± 0.17 (0.14)	98.11 ± 0.19 (0.02)	98.48 ± 0.10 (0.04)	97.78 ± 0.06 (0.08)	96.59 ± 0.08 (0.01)	98.63 ± 0.12 (0.09)
CD (0.05%)	1.48					

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

and malathion was found in the case of chlorpyriphos also.

The results of the study showed that the different processing techniques like two washing (70.93 %), four washing (73.97 %), soaking (23.99 %), soaking + two washing (76.04 %), soaking + four washing (79.71 %), cooking (90.92 %), two washing followed by cooking (98.37 %) and four washing + cooking (98.48 %) carried out 5 h after insecticide application reduced chlorpyriphos residues to a considerable level. The losses incurred due to different processing techniques 2 weeks after insecticide application were 41.30 (two washing), 45.21 (four washing), 19.43 (soaking), 63.80 (soaking + two washing) and 65.12 (soaking + four washing), 80.34 (cooking) and 88.99 (two washing + cooking) and 90.25 per cent (four washing + cooking).

4.3.3.4 *Quinalphos*

Treatment of insecticide emulsion on rice grains resulted in 4.00 mg kg^{-1} of quinalphos residues at 5 h after insecticide application which later dissipated to 3.46 mg kg^{-1} in 2 weeks resulting in reduction of 13.50 per cent (Table19). Percentage removal of quinalphos residues in rice grains when subjected to different processing techniques showed that all processing techniques significantly differed among each other. More than ninety per cent (97.78 % and 90.65 %) of the residues were removed when fortified rice grains were subjected to four washings in tap water for 2 min along with rubbing of grains followed by cooking, 5 h and 2 weeks after application and the technique was significantly superior over all other techniques.

The quinalphos residues was reduced to the extent of 72.34 per cent and 76.22 per cent by two washing and four washing respectively, 5 h after insecticidal application. Soaking in water reduced the residues by 22.57 per cent while cooking resulted in 91.73 per cent removal. Almost 47.83 and 54.79 per cent reduction was observed through soaking followed by two washings and soaking followed by four washings respectively while two

Table 21. Extent of removal of insecticide residues from rice grains by the use of different household processing techniques 2 weeks after spraying

Processing techniques	Mean per cent removal of insecticides (%) ± SD					
	Methyl parathion	Malathion	Chlorpyriphos	Quinalphos	Cypermethrin	Fenvalerate
Two washings in tap water for two minutes along with rubbing of grains	38.01 ± 1.21 (5.04)	46.16 ± 0.46 (0.25)	41.30 ± 0.47 (1.59)	42.01 ± 0.79 (2.00)	49.99 ± 0.79 (0.05)	52.11 ± 0.21 (0.69)
Four washings in tap water for two minutes along with rubbing of grains	44.94 ± 0.90 (4.48)	53.65 ± 0.90 (0.22)	45.21 ± 0.79 (1.48)	46.76 ± 1.34 (1.84)	56.10 ± 0.29 (0.04)	55.48 ± 1.79 (0.64)
Soaking of grains in water for six hours	22.25 ± 2.32 (6.32)	17.97 ± 0.13 (0.39)	19.43 ± 2.23 (2.18)	17.22 ± 1.00 (2.86)	26.59 ± 0.05 (0.07)	27.78 ± 2.64 (1.04)
Soaking (six hours) + two washings in tap water for two minutes along with rubbing of grains	57.30 ± 0.51 (3.47)	68.26 ± 0.21 (0.15)	63.80 ± 0.82 (0.98)	64.04 ± 0.59 (1.24)	74.76 ± 0.23 (0.03)	76.10 ± 0.09 (0.34)
Soaking (six hours) + four washings in tap water for two minutes along with rubbing of grains	62.46 ± 0.96 (3.05)	69.74 ± 3.22 (0.14)	65.12 ± 0.07 (0.94)	62.58 ± 0.93 (1.29)	70.94 ± 0.16 (0.03)	73.19 ± 0.30 (0.38)
Cooking followed by decanting rice gruel	79.98 ± 1.32 (1.62)	78.81 ± 1.36 (0.10)	80.34 ± 1.86 (0.53)	80.86 ± 0.91 (0.66)	79.90 ± 0.80 (0.02)	82.01 ± 1.04 (0.26)
Two washings in tap water for two minutes along with rubbing of grains + cooking	87.48 ± 0.80 (1.01)	88.28 ± 0.54 (0.05)	88.99 ± 0.49 (0.29)	88.55 ± 0.72 (0.39)	87.15 ± 0.09 (0.01)	88.14 ± 0.68 (0.17)
Four washings in tap water for two minutes along with rubbing of grains + cooking	89.92 ± 0.35 (0.82)	90.44 ± 0.20 (0.04)	90.25 ± 0.11 (0.26)	90.65 ± 0.17 (0.32)	88.36 ± 0.13 (0.01)	89.94 ± 0.22 (0.14)
CD (0.05%)	0.81					

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

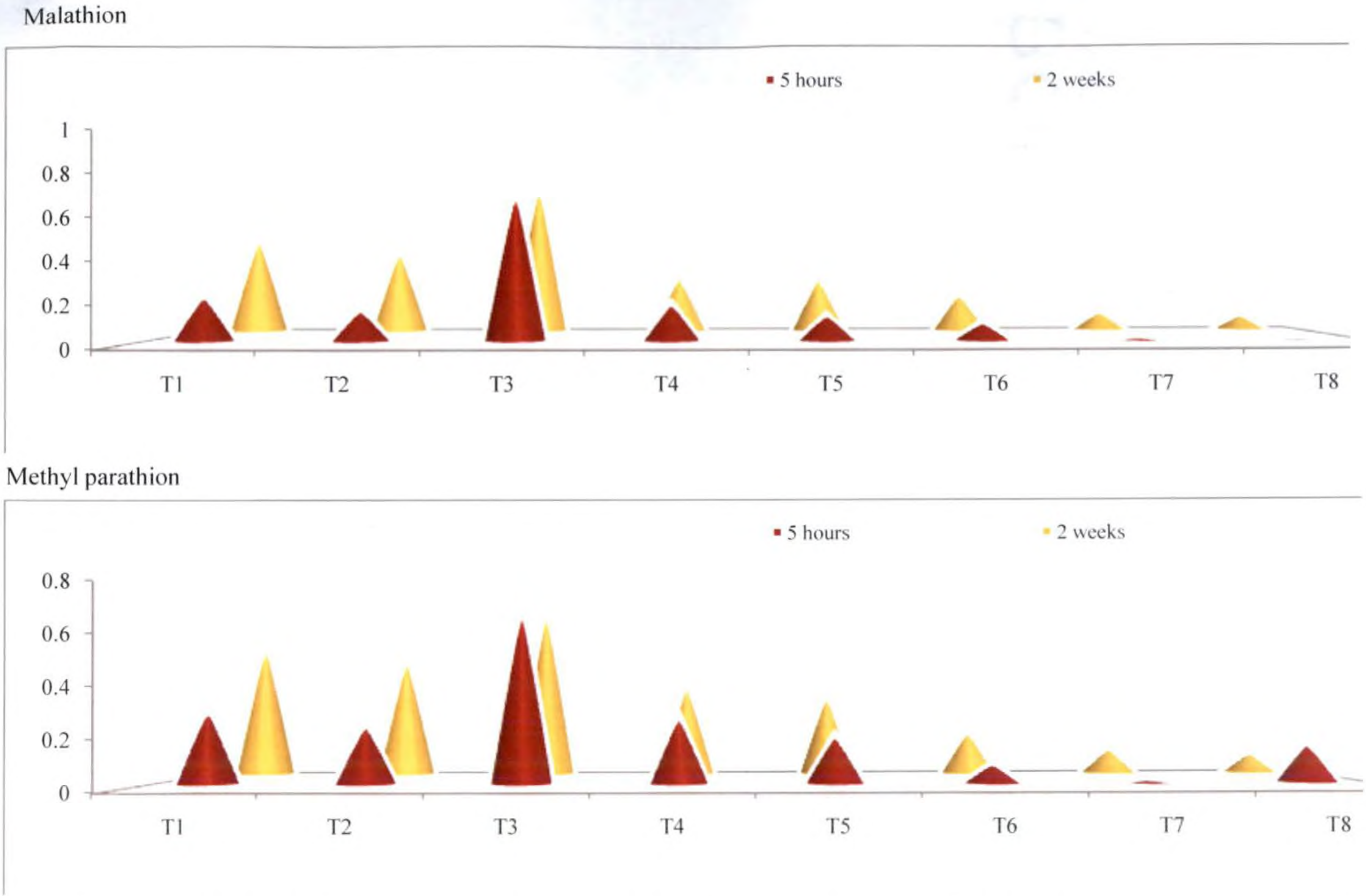
washings followed by cooking resulted in 84.74 per cent loss of residues. The percent removal of residues due to different processing techniques 2 weeks after insecticide application were 42.01 (two washings), 46.76 (four washings), 17.22 (soaking), 64.04 (soaking + washing), 62.58 (soaking + four washing), 80.86 (cooking) and 88.55 (two washing + cooking).

4.3.3.5 *Cypermethrin*

Concentration of cypermethrin in rice grains at 5 h after insecticide application was 0.10 mg kg^{-1} and the residue remain unchanged even after two weeks after insecticide application (Table19). Statistical analysis (CD, $p \leq 0.05$) proved that decontamination of cypermethrin residues by different household processing techniques except two *viz.,* two or four washings followed by cooking were significantly different as compared to control samples. These two techniques were found to be significantly superior over all the other techniques resulting in more than 85 per cent removal of cypermethrin residues.

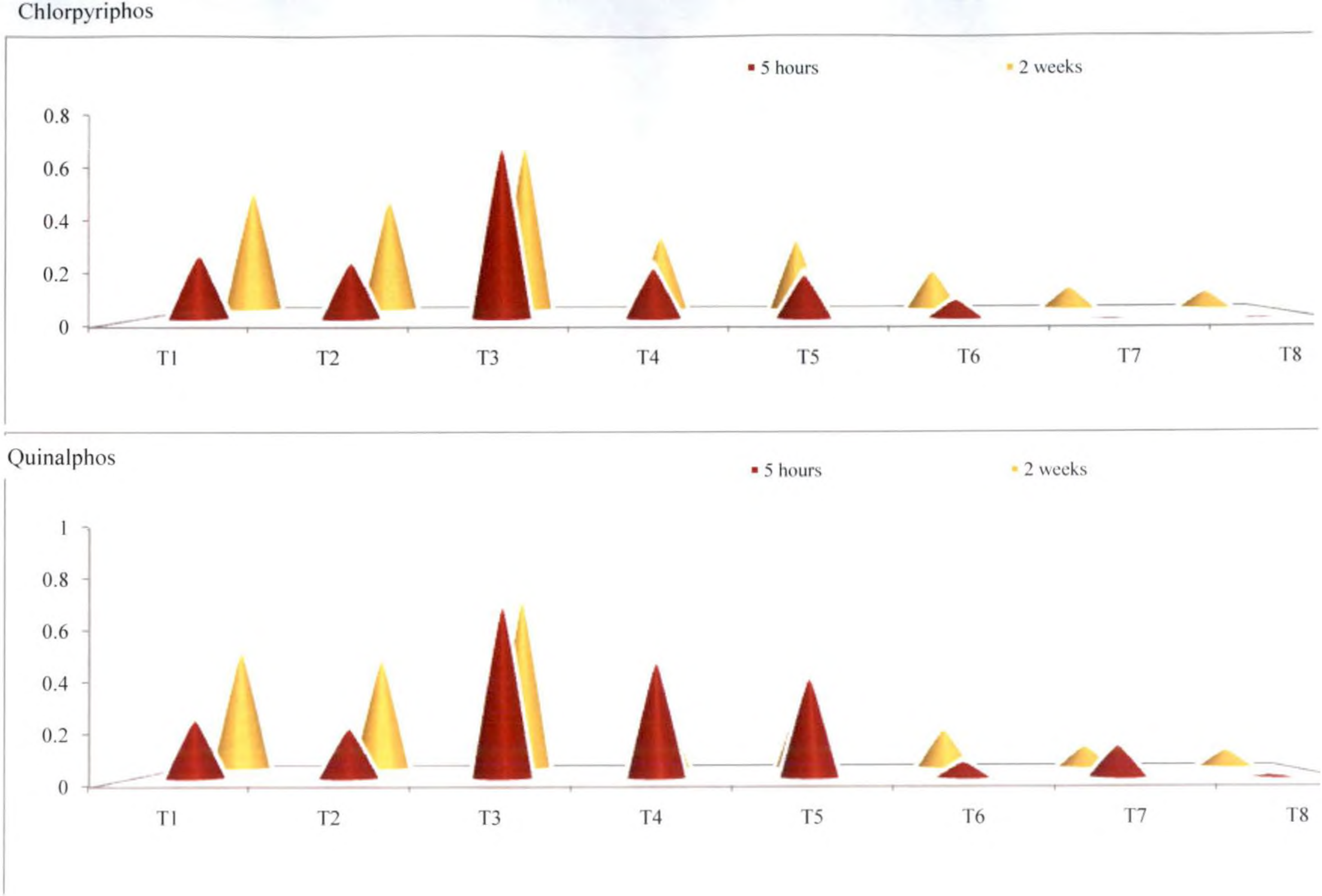
Analysis of rice samples, subjected to different processing techniques 5 h after insecticide application revealed that soaking followed by two washing and four washing reduced cypermethrin residues in rice grains by 85.61 and 88.63 per cent respectively, which was higher than with two washing (79.98 %), four washing (83.84 %) and soaking (34.08 %). After cooking and decanting rice gruel, the cypermethrin residues were reduced by 90.48 per cent. Two washing followed by cooking resulted in 96.49 % loss and four washing followed by cooking resulted in 96.59 per cent loss. The losses incurred due to different processing techniques 2 weeks after insecticide application were 49.99 (two washing), 56.10 (four washing), 26.59 (soaking), 74.76 (soaking + two washing), 70.94 (soaking + four washing),79.90 (cooking), 87.15 (two washing + cooking) and 88.36 per cent (four washing + cooking).

4.3.3.6 *Fenvalerate*



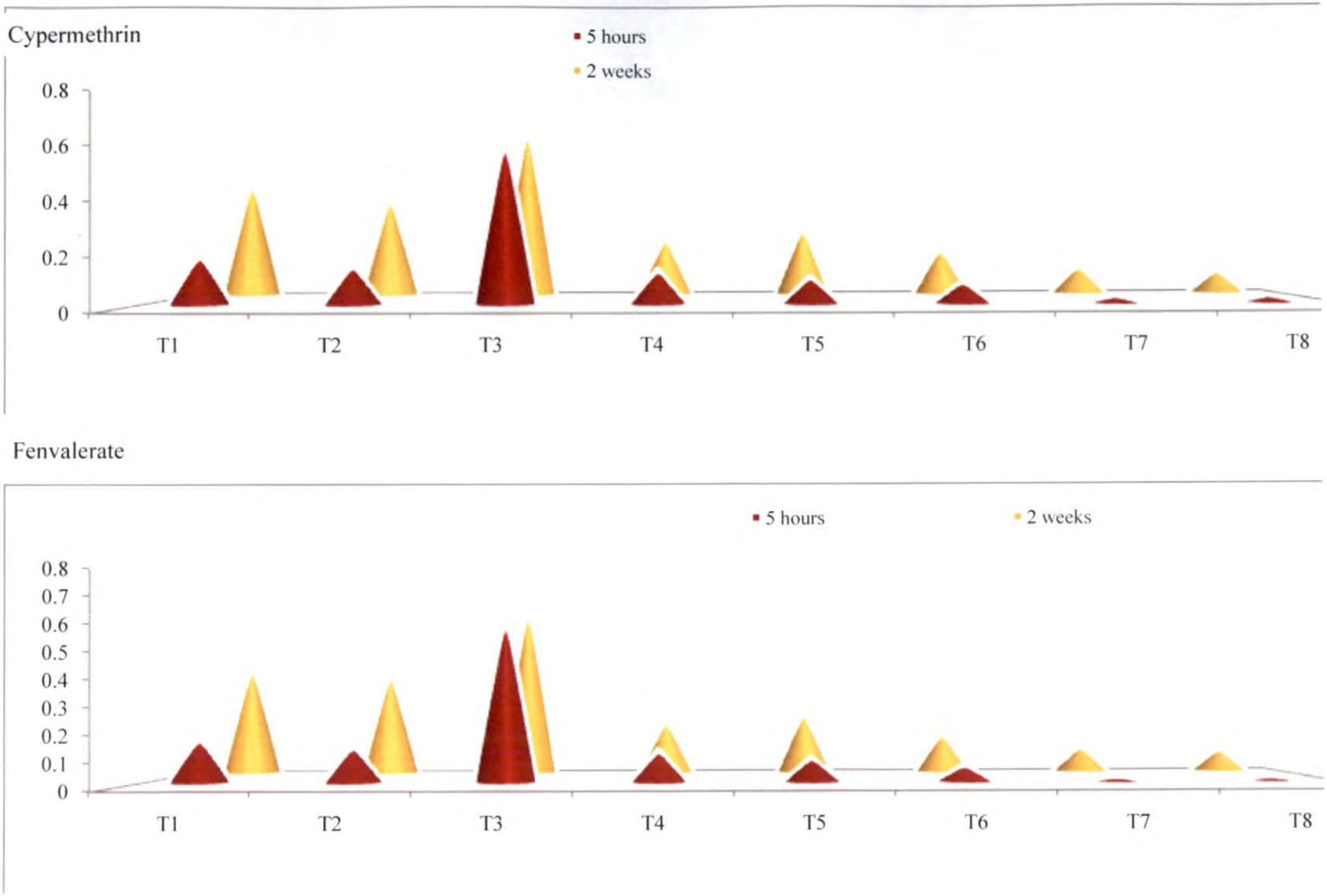
T1: 2 washing (2 min), T2: 4 washing (2 min), T3: soaking (6 h), T4: soaking + 2 washing, T5: soaking + 4 washing, T6: cooking, T7: 2 washing + cooking, T8: 4 washing + cooking. (X axis: Processing techniques; Y axis: Processing factor)

Fig. 3. Efficiency (processing factor) of decontamination of insecticide treated rice grains using different household processing techniques at 5 h and 2 weeks after insecticide spraying



T1: 2 washing (2 min), T2: 4 washing (2 min), T3: soaking (6 h), T4: soaking + 2 washing, T5: soaking + 4 washing, T6: cooking, T7: 2 washing + cooking, T8: 4 washing + cooking. (X axis: Processing techniques; Y axis: Processing factor)

Fig. 3. Efficiency (processing factor) of decontamination of insecticide treated rice grains using different household processing techniques at 5 h and 2 weeks after insecticide spraying



T1: 2 washing (2 min), T2: 4 washing (2 min), T3: soaking (6 h), T4: soaking + 2 washing, T5: soaking + 4 washing, T6: cooking, T7: 2 washing + cooking, T8: 4 washing + cooking. (X axis: Processing techniques; Y axis: Processing factor)

Fig. 3. Efficiency (processing factor) of decontamination of insecticide treated rice grains using different household processing techniques at 5 h and 2 weeks after insecticide spraying

Treatment of insecticide emulsion on rice grains resulted in 1.56 mg kg^{-1} of fenvalerate residues at 5 h after insecticide application which later dissipated to 1.45 mg kg^{-1} in 2 weeks resulting 7.05 per cent (Table19). Statistical analysis (CD, $p\leq 0.05$) proved that decontamination of fenvalerate residues by different household processing techniques except two *viz.,* two washing followed by cooking and four washing followed by cooking were significantly different as compared to control samples. The two techniques were found to be on par and significantly superior over all the other techniques resulting in more than 85 per cent removal of fenvalerate residues.

Fenvalerate residues when subjected to different processing techniques, 5 h after insecticide application (Table 20) were reduced by 75.66 (two washing), 82.18 (four washing), 23.22 (soaking), 79.50 (soaking + two washing), 85.43 (soaking + four washing), 89.40 (cooking), 97.83 (two washing + cooking) and 98.63 per cent (four washing + cooking).The losses incurred due to different processing techniques at 2 weeks after insecticide application were 46.16 (two washing), 53.65 (four washing), 17.97 (soaking), 68.26 (soaking + two washing), 69.74 (soaking + four washing), 78.81 (cooking) and 88.28 (two washing + cooking) and 90.44 per cent (four washing + cooking).

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of each processing techniques in removing the residues of insecticides at two intervals (5 h and 2 weeks after insecticide application).

4.4 ASSESSMENT OF THE EFFECT OF WASHING, SUNDRYING AND MILLING ON REMOVAL OF INSECTICIDE RESIDUES IN WHEAT GRAINS

Data pertaining to dissipation of insecticides in wheat grains during storage is presented in Table 22 and depicted in Fig. 4. The extent of removal of insecticide residues from wheat grains using different household processing techniques, 5 h and 2 weeks after insecticide application are presented in Table 23 to 24 and the processing factor for different technique in each insecticide is depicted in Fig. 5.

Table 22. Persistence of organophosphate and synthetic pyrethroid insecticides in wheat grains

Insecticides	Residues (mg kg^{-1}) ± SD		Dissipation (%)
	5 h after spraying	2 weeks	
Methyl parathion	13.58 ± 0.32	13.39 ± 1.27	1.39
Malathion	0.67 ± 0.08	0.66 ± 0.01	1.49
Chlorpyriphos	3.88 ± 0.36	3.49 ± 0.09	10.05
Quinalphos	5.80 ± 0.44	4.72 ± 0.09	18.62
Cypermethrin	0.21 ± 0.02	0.14 ± 0.01	33.33
Fenvalerate	2.58 ± 0.30	2.28 ± 0.71	11.62

4.4.1 Processing treatments

4.4.1.1 *Methyl parathion*

Concentration of methyl parathion in wheat grains at 5 h after insecticide application was 13.58 mg kg^{-1} and the residues reached to 13.39 mg kg^{-1} resulting in 1.39 per cent loss (Table 22). There was no significant reduction in the concentration of methyl parathion residues in wheat grains when subjected to residue analysis done at two weeks after spraying. Percentage removal of methyl parathion residues in wheat grains when subjected to different processing techniques showed that all the processing techniques except two *viz.*, two washing and two washing followed by sun drying and milling, significantly differed among each other in their efficiency in removing the residues. These two techniques were found to be significantly superior to all other techniques resulting in more than fifty five per cent removal of methyl parathion residues.

The percentage removal of methyl parathion residues when subjected

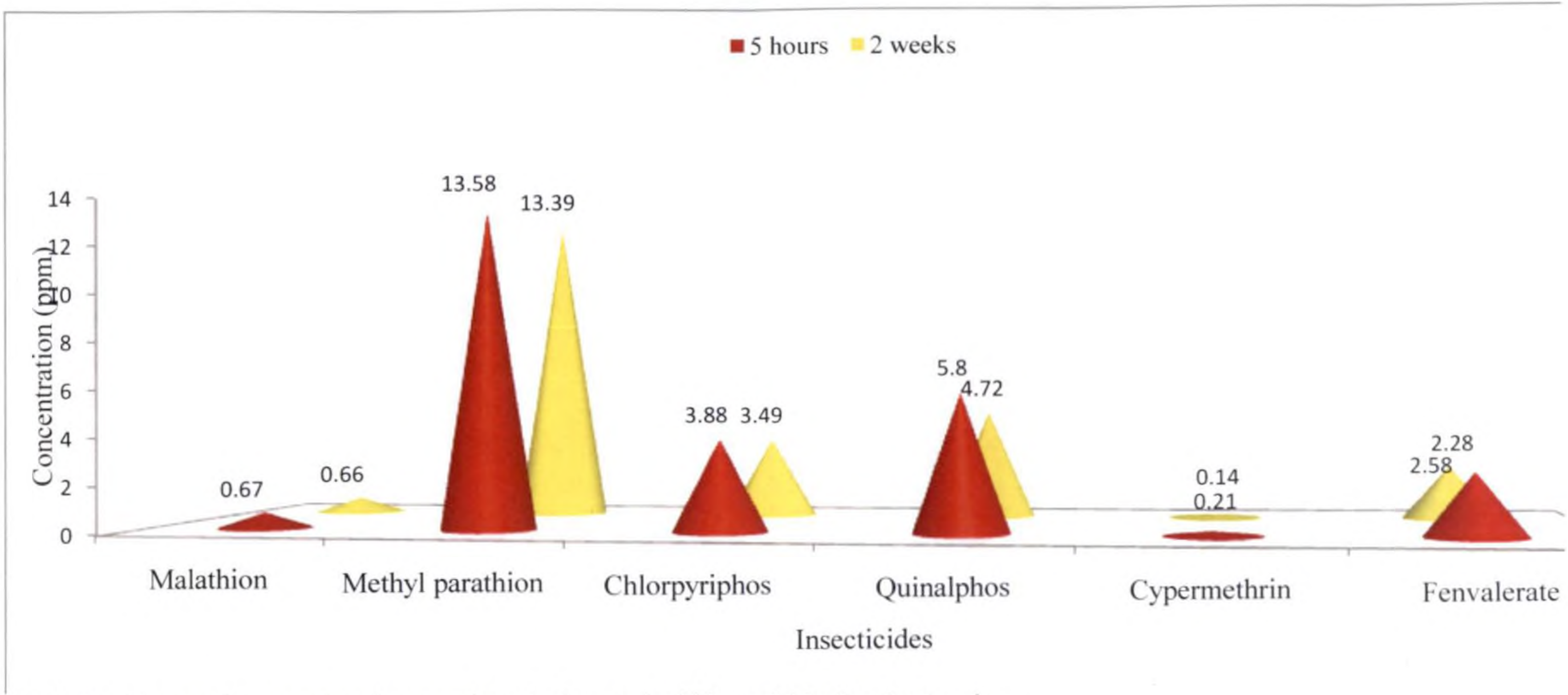


Fig. 4. Persistence of organophosphates and synthetic pyrethroid insecticides in wheat grains

to different processing techniques 5 h after insecticide application were 44.24 (two washing), 61.66 (four washing), 31.42 (sun drying), 42.91 (two washing + sun drying + milling) and 50.62 (four washing + sun drying + milling).The percentage removal of residues due to different processing techniques 2 weeks after insecticide application were 30.86 (two washing), 55.80 (four washing), 19.15 (sun drying), 31.81 (two washing + sun drying + milling) and 38.91 (four washing + sun drying + milling). Milling of wheat grains did not help in any pesticide removal.

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of each processing techniques in removing the methyl parathion residues at two intervals (5 h and 2 weeks after insecticide application).

4.4.1.2 *Malathion*

Treatment of insecticide emulsion on wheat grains resulted in 0.67 mg kg^{-1} of malathion, 5 h after insecticide application which later dissipated to 0.66 mg kg^{-1} resulting in 1.49 per cent loss (Table 22). There was no significant reduction in the concentration of malathion residues in wheat grains when subjected to residue analysis 2 weeks after spraying. Statistical analysis (CD, $p \leq 0.05$) proved that decontamination of malathion residues by different household processing techniques were significantly different as compared to control samples. More than seventy per cent(75.67 % and 72.47 %) of the residues were removed when wheat grains were subjected to four washings in tap water for two minutes along with rubbing of grains, 5 h and 2 weeks after insecticide application and the technique was significantly superior over all the other techniques.

Malathion residues when subjected to different processing techniques, 5 h after insecticide application were reduced by 56.87 (two washing), 75.67 (four washing), 30.69 (sun drying), 51.63 (two washing + sun drying +

Table 23. Extent of removal of insecticide residues from wheat grains by the use of different household processing techniques 5 h after spraying

Processing techniques	Mean per cent removal of insecticides (%) ± SD					
	Methyl parathion	Malathion	Chlorpyriphos	Quinalphos	Cypermethrin	Fenvalerate
Two washings in tap water for two minutes along with rubbing of grains	44.24 ± 2.57 (7.57)	56.87 ± 4.31 (0.28)	48.57 ± 2.10 (1.99)	50.02 ± 5.47 (2.89)	44.74 ± 1.98 (0.11)	49.03 ± 1.64 (1.31)
Four washings in tap water for two minutes along with rubbing of grains	61.66 ± 6.44 (5.20)	75.67 ± 3.54 (0.16)	66.40 ± 2.15 (1.30)	64.61 ± 1.40 (2.05)	51.92 ± 1.69 (0.10)	53.91 ± 2.46 (1.18)
Sun drying (five hours)	31.42 ± 0.49 (9.31)	30.69 ± 1.89 (0.46)	24.05 ± 2.36 (2.94)	26.19 ± 1.58 (4.28)	31.78 ± 7.63 (0.14)	34.10 ± 6.51 (1.70)
Milling	-95.67± 2.67 (26.50)	-87.60 ± 1.21 (1.25)	-94.33 ± 3.92 (7.54)	-82.19±1.53 (10.56)	-87.01 ±2.23 (0.39)	-91.64± 1.66 (0.21)
Two washings in tap water for two minutes along with rubbing of grains + sun drying (five hours) + milling	42.91 ± 1.61 (7.75)	51.63 ± 2.63 (0.32)	28.63 ± 2.05 (2.76)	34.17 ± 1.06 (3.81)	26.78 ± 1.49 (0.15)	28.35 ± 2.10 (1.84)
Four washings in tap water for two minutes along with rubbing of grains + sun drying (five hours) + milling	50.62 ± 2.13 (6.70)	60.81 ± 0.90 (0.26)	34.72 ± 2.53 (2.53)	44.22 ± 2.90 (3.23)	36.16 ± 1.44 (0.13)	38.21 ± 2.35 (1.59)
CD (5%)	2.31					

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

milling) and 60.81 (four washing + sun drying + milling) per cent. The percentage removal of residues due to different processing techniques at 2 weeks after insecticide application were 53.24 (two washing), 72.47 (four washing), 24.47 (sun drying), 38.76 (two washing + sun drying + milling) and 48.91 (four washing + sun drying + milling). Here also, milling of wheat grains did not help in any pesticide removal.

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of each processing techniques in removing the malathion residues at two intervals (5 h and 2 weeks after insecticide application).

4.4.1.3 *Chlorpyriphos*

Concentration of chlorpyriphos in wheat grains at 5 h after insecticide application was 3.88 mg kg^{-1} and the residues reached to 3.49 mg kg^{-1} after two weeks resulting in 10.05 per cent loss (Table 22). Similar scenario with respect to best processing technique, which was observed in malathion was found in the case of chlorpyriphos also.

The results of the study showed that the different processing techniques like two washing (48.57 %), four washing (66.40 %), sun drying (24.05 %), two washing + sun drying + milling (28.63 %) and four washing + sun drying + milling (34.72 %) carried out 5 h after insecticide application decrease the chlorpyriphos residues to a considerable level. The percentage removal of residues due to different processing techniques at 2 weeks after insecticide application were 31.24 (two washing), 51.09 (four washing), 22.98 (sun drying), 14.44 (two washing + sun drying + milling) and 26.96 (four washing + sun drying + milling). Milling of wheat grains didnot help in any pesticide removal.

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of each processing

Table 24. Extent of removal of insecticide residues from wheat grains by the use of different household processing techniques 2 weeks after spraying

Processing techniques	Mean per cent removal of insecticides (%) ± SD					
	Methyl parathion	Malathion	Chlorpyriphos	Quinalphos	Cypermethrin	Fenvalerate
Two washings in tap water for two minutes along with rubbing of grains	30.86 ± 3.25 (9.25)	53.24 ± 2.71 (0.30)	31.24 ± 2.68 (2.39)	34.84 ± 2.96 (3.07)	33.42 ± 4.09 (0.09)	38.55 ± 3.30 (1.40)
Four washings in tap water for two minutes along with rubbing of grains	55.80 ±1.73 (5.91)	72.47 ± 6.23 (0.18)	51.09 ±1.78 (1.70)	53.74 ± 6.98 (2.18)	60.40 ± 2.89 (0.05)	59.47 ±7.32 (0.92)
Sun drying (five hours)	19.15 ±1.85 (10.82)	24.47 ± 0.95 (0.49)	22.98 ± 3.30 (2.68)	25.02 ± 3.43 (3.53)	25.73 ± 3.12 (3.50)	31.14 ±1.83 (1.57)
Milling	-96.48 ± 3.06 (26.30)	-81.51 ± 2.02 (1.19)	-89.56 ± 3.84 (6.61)	-78.98 ± 4.61 (8.44)	-93.16 ±1.53 (0.27)	-93.01 ±2.33 (4.40)
Two washings in tap water for two minutes along with rubbing of grains + sun drying (five hours) + milling	31.81 ±1.41 (9.13)	38.76 ± 1.98 (0.40)	14.44 ±1.23 (2.98)	20.32 ±1.08 (3.76)	15.88 ±0.65 (0.11)	10.15 ±0.30 (2.04)
Four washings in tap water for two minutes along with rubbing of grains + sun drying (five hours) + milling	38.91 ±1.20 (8.17)	48.91 ± 2.72 (0.33)	26.96 ±2.95 (2.54)	23.34 ±1.51 (3.61)	30.77 ±2.09 (0.09)	20.19 ±2.99 (1.81)
CD (5%)	2.01					

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

techniques except sun drying in removing the chlorpyriphos residues at two intervals (5 h and 2 weeks after insecticide application).

4.4.1.4 *Quinalphos*

Treatment of insecticide emulsion on wheat grains resulted in 5.80 mg kg^{-1} of quinalphos at 5 h after insecticide application which later dissipated to 4.72 mg kg^{-1} resulting in 18.62 per cent loss (Table 22). The percentage removal of quinalphos residues in fortified wheat grains when subjected to different processing techniques showed that all processing techniques except sun drying and four washing followed by sun drying and milling significantly differed among each other in their efficiency in removing quinalphos residues. These two techniques were found to be significantly superior over all other techniques resulting in more than fifty per cent removal of quinalphos residues.

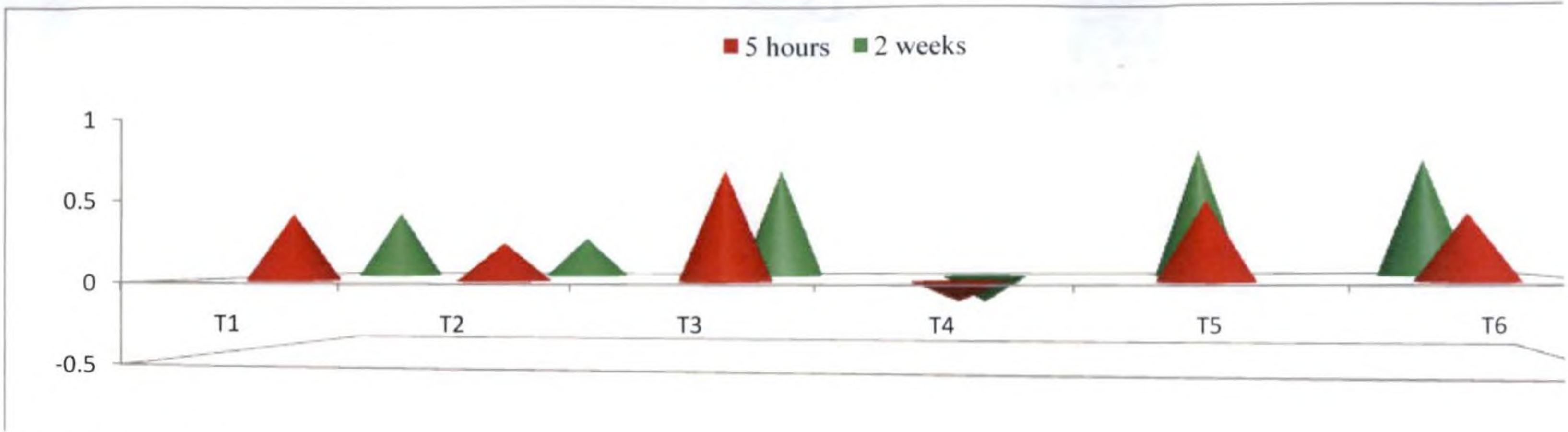
The quinalphos residues were reduced to the extent of 50.02 per cent by two washing and 64.61 per cent by four washing, 5 h after insecticidal application. Drying by sun reduced the residues by 26.19 per cent. 34.17 and 44.22 per cent reduction was observed through two washing and four washing followed by sun drying and milling respectively. The percentage removal of residues due to different processing techniques 2 weeks after insecticide application were 34.84 (two washing), 53.74 (four washing), 25.02 (sun drying), 20.32 (two washing + sun drying + milling) and 23.34 (four washing + sun drying + milling). Milling of wheat grains showed no significant effect on reduction of quinalphos residues.

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of each processing techniques except sun drying in removing the residues of quinalphos at two intervals (5 h and 2 weeks after insecticide application).

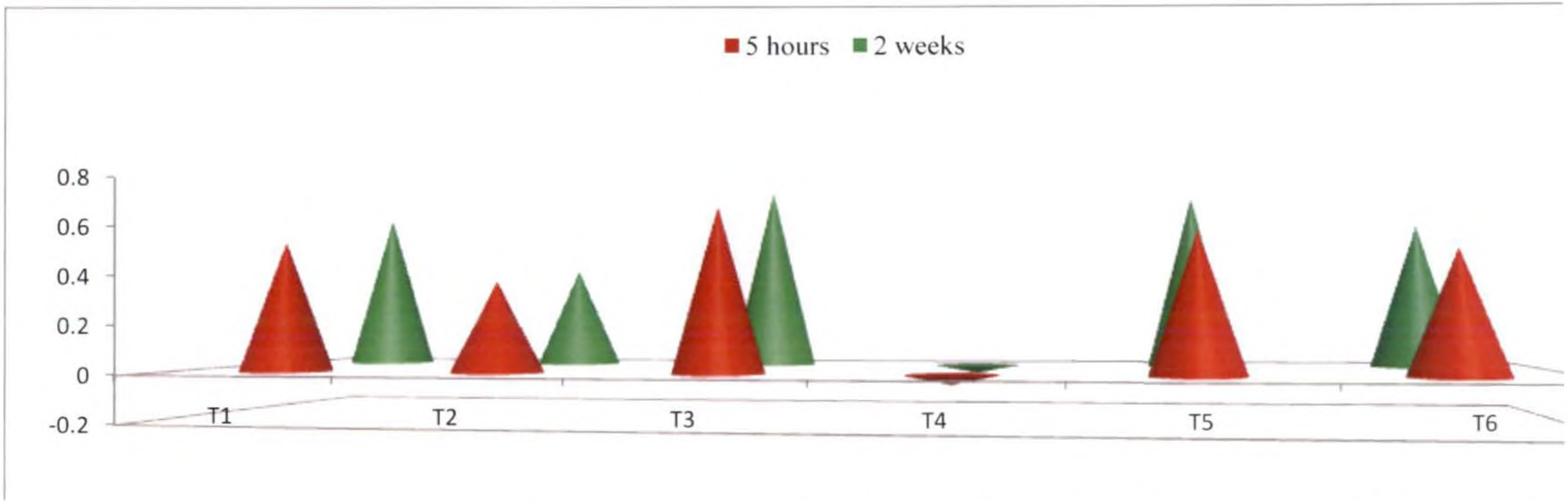
4.4.1.5 *Cypermethrin*

Concentration of cypermethrin (5 h after insecticide application) on

Malathion



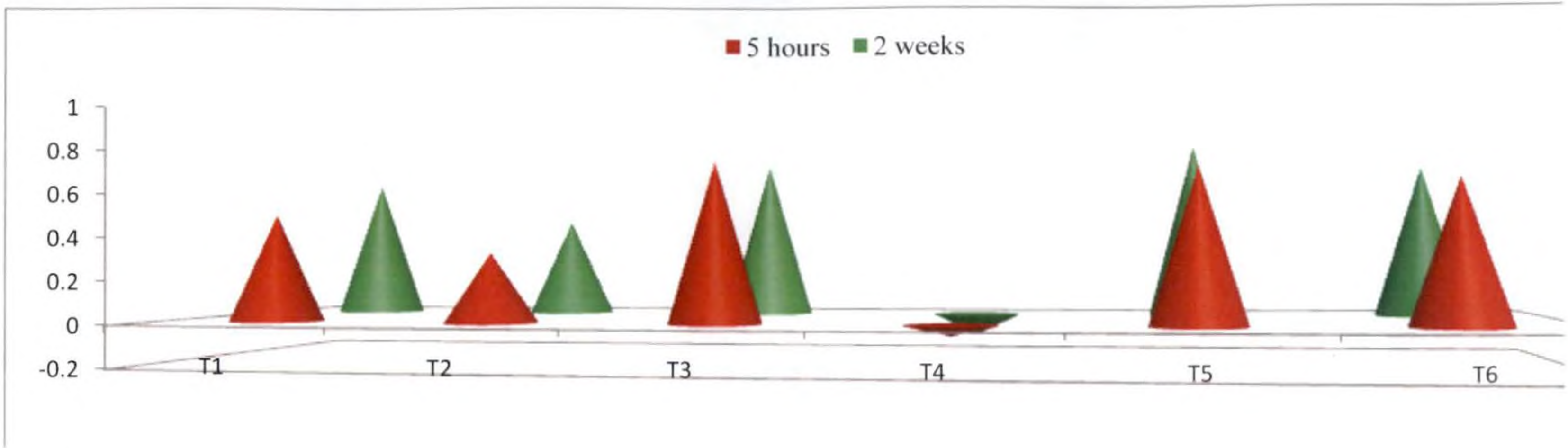
Methyl parathion



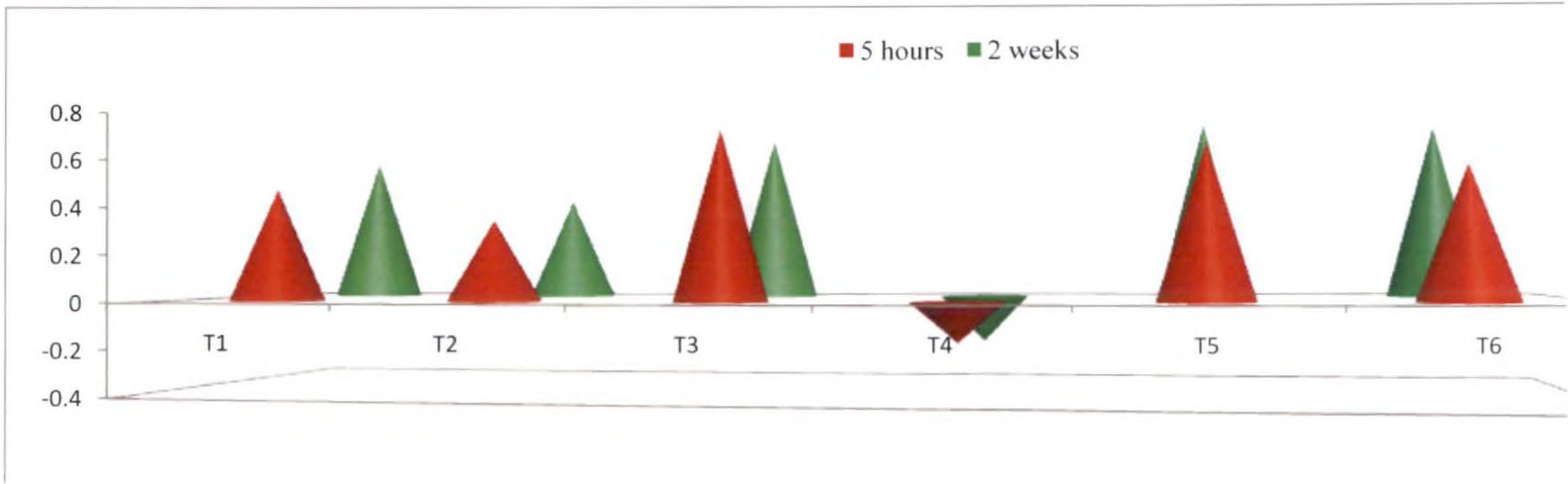
T1: 2 washing (2 min), T2: 4 washing (2 min), T3: sun drying (5 h), T4: milling, T5: 2 washing + sun drying + milling, T6: 4 washing + sun drying + milling (X axis: Insecticides; Y axis: Processing factor).

Fig. 5. Efficiency (processing factor) of decontamination of insecticide treated wheat grains using different household processing techniques at 5 h and 2 weeks after insecticide spraying

Chlorpyriphos



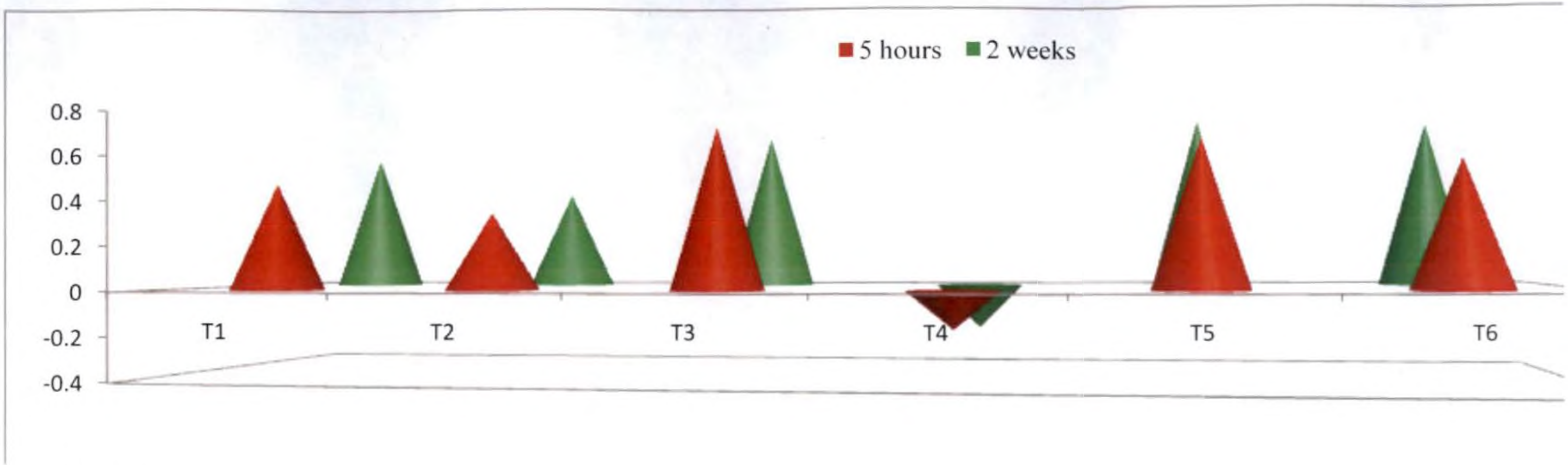
Quinalphos



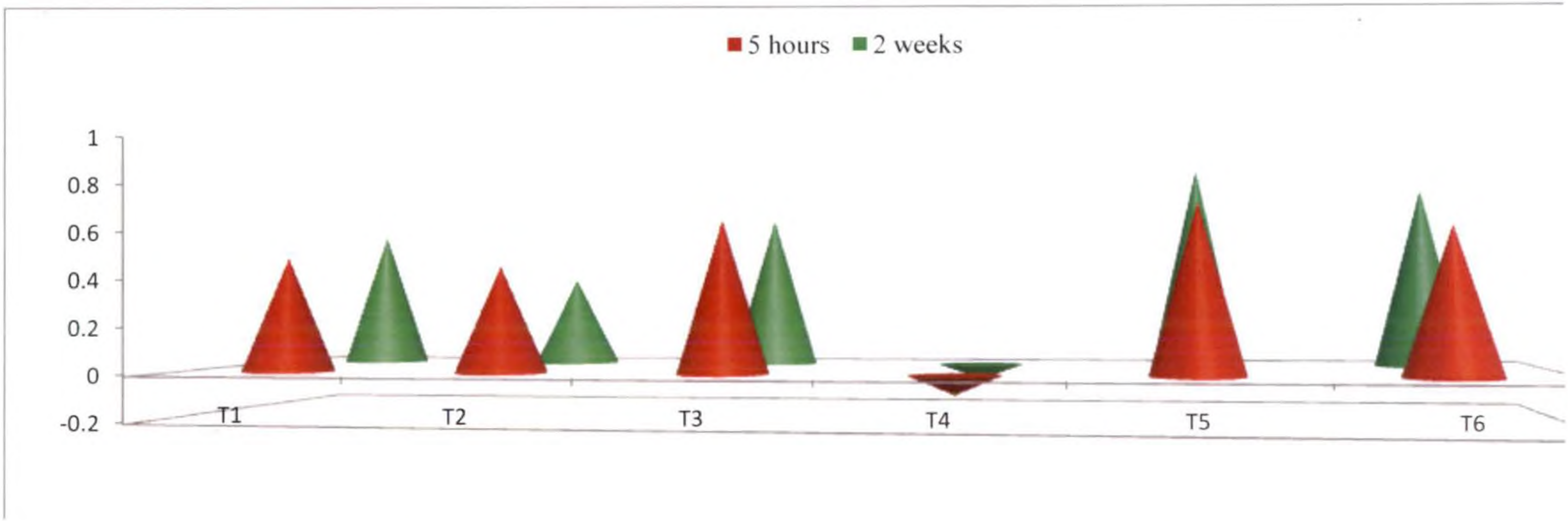
T1: 2 washing (2 min), T2: 4 washing (2 min), T3: sun drying (5 h), T4: milling, T5: 2 washing + sun drying + milling, T6: 4 washing + sun drying + milling (X axis: Insecticides; Y axis: Processing factor)

Fig. 5. Efficiency (processing factor) of decontamination of insecticide treated wheat grains using different household processing techniques at 5 h and 2 weeks after insecticide spraying

Cypermethrin



Fenvalerate



T1: 2 washing (2 min), T2: 4 washing (2 min), T3: sun drying (5 h), T4: milling, T5: 2 washing + sun drying + milling, T6: 4 washing + sun drying + milling (X axis: Insecticides; Y axis: Processing factor)

Fig. 5. Efficiency (processing factor) of decontamination of insecticide treated wheat grains using different household processing techniques at 5 h and 2 weeks after insecticide spraying

wheat grain was 0.21 mg kg^{-1} and the residues reached to 0.14 mg kg^{-1} at 2 weeks after insecticide application resulting 18.62 per cent loss (Table 22). The percentage removal of cypermethrin residues in fortified wheat grains when subjected to different processing techniques showed that all the processing techniques significantly differed among each other in their efficiency in removing the cypermethrin residues. Nearly sixty per cent (51.92`and 60.40 %) of the residues were eliminated from wheat grains subjected to four washings in tap water for 2 min along with rubbing of grains, 5 h and 2 weeks after insecticide application and the technique was significantly superior over all other techniques.

Analysis of wheat samples, subjected to different processing techniques 5 h after insecticide application revealed that two washing reduced cypermethrin residues in wheat grains by 44.74 per cent, which was higher than with two washing followed by sun drying and milling (26.78 %) and four washing followed by sun drying and milling (36.16 %). With sun drying, the cypermethrin residues were reduced by 31.78 per cent. The percentage removal of residues due to different processing techniques 2 weeks after insecticide application were 33.42 (two washing), 25.73 (sun drying), 15.88 (two washing + sun drying + milling) and 30.77 (four washing + sun drying + milling). Milling of wheat grains didnot help in reducing cypermethrin residues.

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of each processing techniques in removing the cypermethrin residues at two intervals (5 h and 2 weeks after insecticide application).

4.4.1.6 *Fenvalerate*

Concentration of fenvalerate in wheat grains at 5 h after insecticide application was 2.58 mg $kg^{-1}$and the residues reached to 2.28 mg kg^{-1} after 2 weeks resulting 11.62 per cent loss (Table 22). Similar scenario with respect to best processing technique, which was observed in cypermethrin was found in the case of fenvalerate also.

Percentage removal of fenvalerate residues when subjected to different processing techniques 5 h after insecticide application were 49.03 per cent (two washing), 53.91 per cent (four washing), 28.35 per cent (two washing + sun drying + milling) and 38.21 per cent (four washing + sun drying + milling). During sun drying, the residue level decreased significantly accounting to 34.10 per cent of the initial deposit. The losses incurred due to different processing techniques 2 weeks after insecticide application were 38.55 (two washing), 59.47 (four washing) 31.14 (sun drying), 10.15 (two washing + sun drying + milling) and 20.19 (four washing + sun drying + milling). Milling of wheat grains did not help in removing fenvalerate residues.

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of each processing techniques in removing the fenvalerate residues at two intervals (5 h and 2 weeks after insecticide application).

4.5 ASSESSMENT OF THE EFFECT OF DECORTICATION ON REMOVAL OF INSECTICIDE RESIDUES IN CARDAMOM

Cardamom samples which showed presence of more than one pesticide in the monitoring studies were subjected to decortications ie by removal of capsule cover. The same sample was divided into three portions and analysed as such, capsule cover alone and seeds alone. The result of decortication of six such cardamom samples with multiple residues representing six months of collection are presented in Table 25.

4.5.1 *Chlorpyriphos*

Chlorpyriphos was detected in five cardamom samples with a range of 0.057- 0.353 mg kg^{-1}. The level of residues of chlorpyriphos was 0.238, 0.057, 0.091, 0.353 and 0.087 mg kg^{-1}in whole cardamom capsule analyzed during January-June 2012. The corresponding values in capsule cover were 0.193, 0.046, 0.079, 0.260 and 0.074 mg kg^{-1} and in decorticated seeds were 0.045, 0.050, 0, 0.047 and 0 mg kg^{-1}. The percentage removal of chlorpyriphos residue as a result of decortication process was in the range of 73.65-86.05 per cent.

4.5.2 *Quinalphos*

Quinalphos was detected in five cardamom samples with a range of 0.137- 2.04 mg kg^{-1}. The level of quinalphos residues in cardamom capsules was 0.137, 0.150, 2.04, 1.19 and 1.62 mg kg^{-1}. In capsule cover, the level of residues were 0.115, 0.126, 1.46, 1.12 and 1.30 mg kg^{-1} and in decorticated seeds, the values were 0.047, 0.039, 0.267, 0.068 and 0.220 mg kg^{-1}. Decortication process removed the residues of quinalphos to a considerable extent of 71.42-93.41 per cent.

4.5.3 *Profenophos*

Monitoring of pesticide residues in cardamom samples during January to June 2012 revealed that out of six samples analyzed, all of them contained residues of profenophos with a range of 0.139-0.954 mg kg^{-1}. The level of profenophos residues in cardamom capsules were 0.268, 0.139, 0.540, 0.954, 0.509 and 0.166 mg kg^{-1}.On the other hand, residue level in cardamom capsule cover were 0.225, 0.102, 0.309, 0.850, 0.342 and 0.08 mg kg^{-1} and in decorticated seeds, the corresponding values were 0.017, 0.035, 0.092, 0.090, 0.01 and 0.055 mg kg^{-1}.The percentage removal of residues were 48.19-90.14 per cent as a result of decortication.

4.5.4 *Lambda cyhalothrin*

Lambda cyhalothrin was detected in all the six cardamom samples with a range of 0.058- 0.364 mg kg^{-1}. The level of lambda cyhalothrin residues was 0.058, 0.132, 0.225, 0.364, 0.077 and 0.133 mg kg^{-1} in whole cardamom capsule analyzed during January-June 2012. The corresponding values in capsule cover were 0.052, 0.127, 0.222, 0.345, 0.077 and 0.131 mg kg^{-1} and in decorticated seed the residues were Below Detectable Level. The percentage removal of lambda cyhalothrin residue as a result of decortication process was in the range of 90.25-100 per cent.

4.5.5 *Cypermethrin*

Monitoring of pesticide residues in cardamom samples during January to June 2012 revealed that out of six samples analyzed, all of them contained residues of cypermethrin with a range of 0.061-0.461 kg^{-1}. The level of cypermethrin residues in cardamom capsules was 0.266, 0.061, 0.071, 0.461,0.150 and 0.105 mg kg^{-1}. In capsule cover, the level of residue were 0.265, 0.060, 0.068, 0.458, 0.142 and 0.091 mg kg^{-1} and in decorticated seeds, residues were Below Detectable Level. Decortication process removed the cypermethrin residues to a considerable extent of 86.67-99.58 per cent.

4.5.6 *Ethion*

Ethion was detected in only one cardamom sample and the level of residue in cardamom capsule, capsule cover and decorticated seed was 0.344, 0.298 and 0.045 mg kg^{-1} respectively. The percentage removal of residue was 86.62 per cent as a result of decortication.

4.5.7 *Bifenthrin*

Like ethion, bifenthrin was detected in only one cardamom sample. The level of residue in cardamom capsule and capsule cover were 0.106 and 0.070 mg kg^{-1} respectively. In decorticated seeds the residue was Below Detectable Level. The percentage removal of residues was 66.61 per cent as a result of decortication.

It may be seen that most of the detected residues remained on the surface of capsule cover and highly systemic insecticides like profenophos had penetrated into the seed. Though negligible levels of quinalphos, chlorpyriphos and ethion were also detected in some samples even after decortication, their magnitude was much below the prescribed maximum levels (Maximum Residue Limits) for these insecticides.

Table 25. Insecticide residues in cardamom (whole capsule, husk and seed) and the extent of removal of residues through decortication.

Insecticides detected and the level of residues (mg kg^{-1}) in								
	whole capsule		husk (capsule cover)		decorticated seeds		Extent of removal of insecticides by decortication	
Sample details	Insecticides	Residue (mg kg^{-1})	Insecticides	Residue (mg kg^{-1})	Insecticides	Residue (mg kg^{-1})	Insecticides	Percent removal
Sample 1 January 2012	Chlorpyrifos	0.238	Chlorpyrifos	0.193	Chlorpyrifos	0.045	Chlorpyrifos	81.09
	Quinalphos	0.137	Quinalphos	0.115	Quinalphos	0.047	Quinalphos	83.94
	Profenophos	0.268	Profenophos	0.225	Profenophos	0.017	Profenophos	83.95
	Bifenthrin	0.106	Bifenthrin	0.070	-	-	Bifenthrin	66.03
	Lambda cyhalothrin	0.058	Lambda cyhalothrin	0.052	-	-	Lambda cyhalothrin	89.65
	Cypermethrin	0.266	Cypermethrin	0.265	-	-	Cypermethrin	99.62
Sample 2 February 2012	Chlorpyriphos	0.057	Chlorpyriphos	0.046	Chlorpyrifos	0.050	Chlorpyriphos	80.70
	Quinalphos	0.150	Quinalphos	0.126	Quinalphos	0.039	Quinalphos	84.00
	Profenophos	0.139	Profenophos	0.102	Profenophos	0.035	Profenophos	73.38
	Lambda cyhalothrin	0.132	Lambda cyhalothrin	0.127	-	-	Lambda cyhalothrin	96.21
	Cypermethrin	0.061	Cypermethrin	0.060	-	-	Cypermethrin	98.36

Table 25 continued

Insecticides detected and the level of residues (mg kg^{-1}) in								
Sample details	whole capsule		husk (capsule cover)		decorticated seeds		Extent of removal of insecticides by decortication	
	Insecticides	Residue (mg kg^{-1})	Insecticides	Residue (mg kg^{-1})	Insecticides	Residue (mg kg^{-1})	Insecticides	Percent removal
Sample 3 March 2012	Chlorpyriphos	0.091	Chlorpyriphos	0.079	-	-	Chlorpyriphos	86.81
	Quinalphos	2.044	Quinalphos	1.46	Quinalphos	0.267	Quinalphos	71.42
	Profenophos	0.540	Profenophos	0.309	Profenophos	0.092	Profenophos	57.29
	Lambda cyhalothrin	0.225	Lambda cyhalothrin	0.222	-	-	Lambda cyhalothrin	98.66
	Cypermethrin	0.071	Cypermethrin	0.068	-	-	Cypermethrin	95.77
Sample 4 April 2012	Chlorpyriphos	0.353	Chlorpyriphos	0.260	Chlorpyriphos	0.047	Chlorpyriphos	73.65
	Quinalphos	1.199	Quinalphos	1.120	Quinalphos	0.068	Quinalphos	94.11
	Profenophos	0.954	Profenophos	0.850	Profenophos	0.090	Profenophos	89.09
	Lambda cyhalothrin	0.364	Lambda cyhalothrin	0.345	-	-	Lambda cyhalothrin	94.78
	Cypermethrin	0.461	Cypermethrin	0.458	-	-	Cypermethrin	99.35

Table 25 continued

Sample details	Insecticides detected and the level of residues (mg kg^{-1}) in						Extent of removal of insecticides by decortication	
	whole capsule		husk (capsule cover)		decorticated seeds			
	Insecticides	Residue (mg kg^{-1})	Insecticides	Residue (mg kg^{-1})	Insecticides	Residue (mg kg^{-1})	Insecticides	Percent removal
Sample 5 May 2012	Chlorpyriphos	0.087	Chlorpyriphos	0.074	-	-	Chlorpyriphos	85.05
	Profenophos	0.509	Profenophos	0.342	Profenophos	0.010	Profenophos	67.19
	Lambda cyhalothrin	0.077	Lambda cyhalothrin	0.077	-	-	Lambda cyhalothrin	100
	Cypermethrin	0.150	Cypermethrin	0.142	-	-	Cypermethrin	94.66
Sample 6 June 2012	Quinalphos	1.625	Quinalphos	1.304	Quinalphos	0.220	Quinalphos	80.24
	Profenophos	0.166	Profenophos	0.08	Profenophos	0.055	Profenophos	48.19
	Ethion	0.344	Ethion	0.298	Ethion	0.045	Ethion	86.62
	Lamda cyhalothrin	0.133	Lamda cyhalothrin	0.131	-	-	Lamda cyhalothrin	98.50
	Cypermethrin	0.105	Cypermethrin	0.091	-	-	Cypermethrin	86.67

4.6 STANDARDISATION OF WASHING WITH SOLUTIONS OF HOUSE HOLD PRODUCTS TO REMOVE INSECTICIDE RESIDUES FROM SELECTED VEGETABLES

4.6.1.1 Capsicum

The effect of different decontaminating solutions of household products in removing the residues of different insecticides from capsicum fruits was studied and the data relating to this are summarized in Table 27 and processing factor for different treatment solutions for each insecticide is depicted in Fig. 6

Table 26. Residues of insecticides in/on capsicum fruits at 5 h after spraying

Insecticides	Residues (mg kg^{-1}) ± SD
	5 hr after spraying
Methyl parathion	2.46 ± 0.08
Malathion	2.44 ± 0.26
Chlorpyriphos	1.44 ± 0.23
Quinalphos	0.33 ± 0.03
Profenophos	3.29 ± 0.54
Ethion	3.74 ± 0.35
Cypermethrin	0.18 ± 0.02
Fenvalerate	0.56 ± 0.11

4.6.1.1.1 *Methyl parathion*

Treatment of insecticide emulsion on capsicum fruits resulted in 2.46 mg kg^{-1} of methyl parathion residues at 5 h after insecticide spraying (Table 26). The percentage removal of residues measured in capsicum fruits when subjected to different decontamination solutions showed that all the solutions except two *ie.* butter milk (2 %) and turmeric (1 %) significantly differed among each other in their efficiency in removing methyl parathion residues.

More than forty (42.40 %) of the residues were removed when the fruits were dipped in vinegar solution (2 %) for 15 min followed by washing in tap water, and the treatment was found to be significantly superior over all the other treatments. The percentage removal of residues due to dipping in common salt (2 %) solution was 35.86 per cent with a processing factor of 0.64. Dipping in turmeric solution (1 %) caused 22.71 per cent reduction in residues which was further reduced by 30.95 per cent due to dipping in tamarind solution (2 %). Almost 21:52 and 19.16 per cent of residues were removed from the treated samples through dipping in buttermilk solution (2 %) and luke warm water respectively, while washing with water alone resulted in a reduction of 13.74 per cent.

4.6.1.1.2 *Malathion*

Concentration of malathion on capsicum fruit was 2.44 mg kg^{-1} at 5 h after spraying (Table 26). Statistical analysis proved that decontamination of malathion residues in capsicum fruits by various decontaminating solutions was significant except two *ie.* butter milk (2 %) and turmeric (1 %)as compared to control samples. It has been found that dipping in vinegar solution (2 %) for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, residues could be reduced upto 48.46 percent. However, by dipping in common salt (2 %) solution for 15 min followed by washing in tap water, the residues were reduced to 42.50 per cent. The reduction in residue levels due to dipping in tamarind (2 %), turmeric (1 %), buttermilk solution (2 %) and luke warm water were 24.84, 22.41, 21.44 and 18.23 per cent and processing factors were 0.75, 0.77, 0.78 and 0.81 respectively. However, washing of treated capsicum fruits in tap water removed only 14.65 per cent, which was found to be the least effective treatment when compared to others.

Table 27. Extent of removal of insecticide residues from capsicum fruits collected at 5 h after spraying*

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	30.95 ± 1.33 (1.69)	42.40 ± 2.41 (1.41)	22.71 ± 2.19 (1.90)	35.86 ± 2.37 (1.57)	21.52 ± 1.75 (1.93)	19.16 ± 1.43 (1.98)	13.74 ± 1.30 (2.12)
Malathion	24.84 ± 3.77 (1.83)	48.46± 3.59 (1.25)	22.41 ±0.45 (1.89)	42.50 ± 1.48 (1.40)	21.44 ± 1.10 (1.91)	18.23 ± 1.11 (1.99)	14.65 ± 2.32 (2.08)
Chlorpyriphos	25.92 ± 1.77 (1.06)	35.80 ± 1.35 (0.95)	17.07 ± 3.30 (1.19)	33.09 ±1.32 (0.96)	23.69 ± 0.63 (1.09)	13.88 ± 1.60 (1.28)	13.81 ± 2.55 (1.28)
Quinalphos	28.10 ± 3.62 (0.23)	31.18 ± 2.74 (0.22)	18.63 ± 1.23 (0.26)	48.00 ±1.93 (0.17)	21.62 ± 0.75 (0.25)	18.35 ± 1.56 (0.26)	16.73 ± 1.73 (0.27)
Profenophos	33.46 ± 2.44 (2.18)	41.80 ± 2.51 (1.91)	17.78 ± 2.79 (2.70)	35.20 ± 2.55 (2.13)	23.91 ± 3.66 (2.50)	17.26 ± 1.22 (2.72)	12.31 ±1.76 (2.88)
Ethion	34.42 ± 6.22 (2.45)	46.13 ± 2.52 (2.01)	18.68 ± 4.12 (3.04)	37.54 ± 2.91 (2.33)	26.38 ± 3.31 (2.75)	11.89 ± 1.57 (3.29)	7.19 ± 2.79 (3.47)
Cypermethrin	37.73 ±0.96 (0.11)	57.70 ± 3.42 (0.076)	16.52 ± 2.78 (0.15)	53.26 ± 2.74(0.08)	22.02 ± 2.06 (0.14)	17.23 ± 1.66 (0.14)	12.94 ± 1.82 (0.15)
Fenvalerate	39.35 ± 2.88 (0.33)	74.88 ± 3.25 (0.14)	21.64 ± 1.07 (0.43)	54.74 ± 3.34(0.25)	33.28 ± 3.18 (0.37)	16.93 ± 1.45 (0.37)	11.50 ± 1.18 (0.49)
CD (5%)	0.95						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

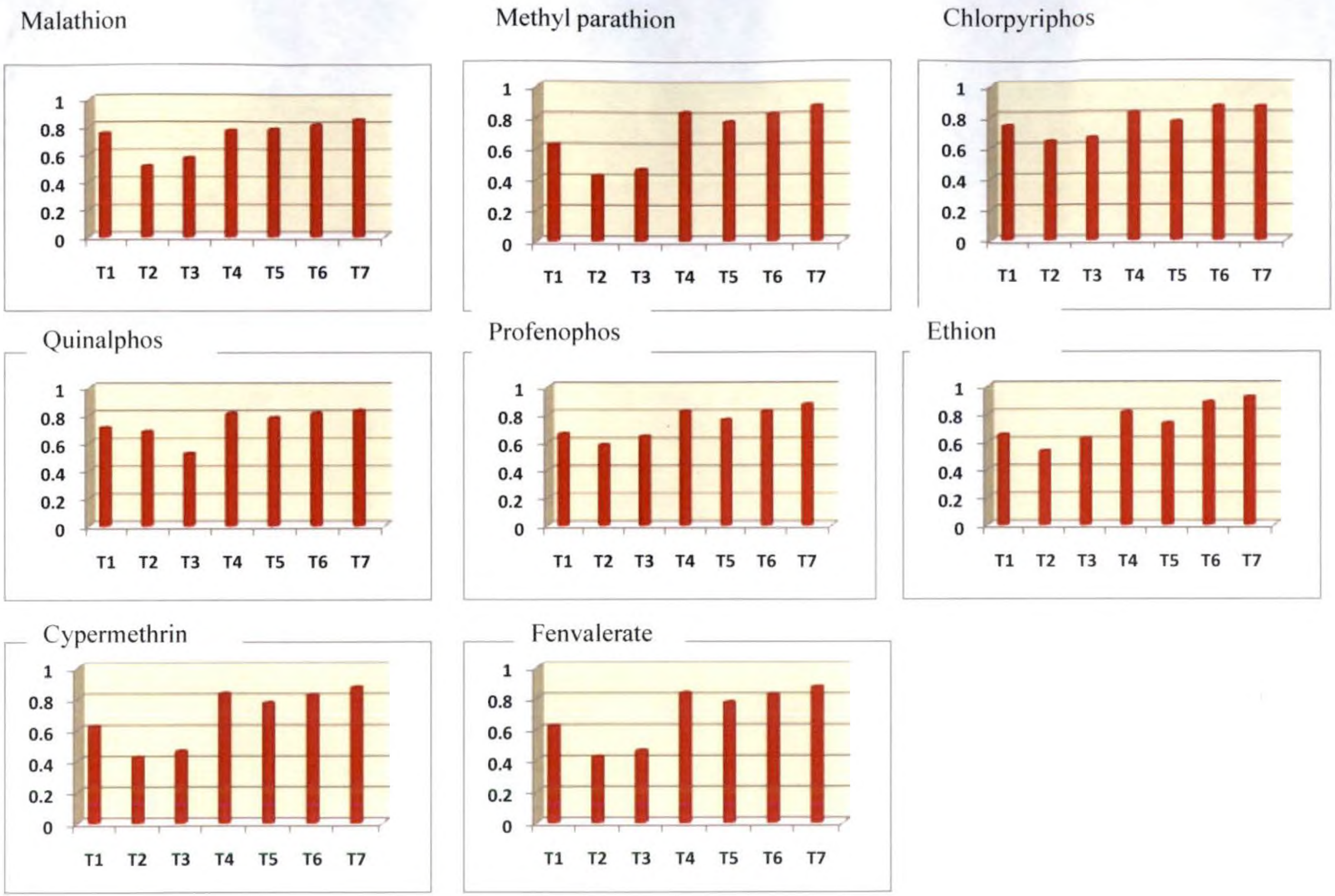
*dipping in different treatment solutions for 15 min.

4.6.1.1.3 *Chlorpyriphos*

Treatment of insecticide emulsion on capsicum fruits resulted in 1.44 mg kg^{-1} of chlorpyriphos residues (Table 26). The percentage removal of residues measured in capsicum fruits when subjected to different decontamination solutions showed that all the treatments except two *ie.* dipping in luke warm water and washing with tap water significantly differed among each other. More than thirty five (35.80 %) of the residues were removed when the fruits were dipped in vinegar solution (2 %) for 15 min followed by washing in tap water, and the treatment was found to be significantly superior over all the other treatments. The percentage removal of resides due to dipping in common salt solution (2 %) for 15 min followed by washing in tap water was 33.09 per cent with a processing factor of 0.66. Dipping in tamarind solution (2 %) caused 25.92 per cent reduction in residues which was further reduced by 23.69 per cent due to dipping in butter milk solution (2 %). Almost 17.07 percent of residues were removed from the treated samples through dipping in turmeric solution (1 %). There was no significant difference in the removal of chlorpyriphos residues when subjected to dipping in luke warm water (13.88 %) and washing with tap water (13.81 %).

4.6.1.1.4 *Quinalphos*

The initial concentration of quinalphos residues on capsicum fruit was 0.33 mg kg^{-1} at 5 h after spraying (Table 26). Statistical analysis proved that decontamination of quinalphos residues by various decontaminating solutions was significant except two *ie* turmeric solution (1 %)and luke warm water as compared to control samples. It has been found that dipping in common salt (2 %) solution for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, residues could be reduced upto 48.00 percent. However, by dipping in vinegar solution (2 %), the residues were reduced to 31.18 per cent. The reduction in residue levels



T1: 2% tamarind, T2: 2% vinegar, T3: 2% common salt, T4: 1% turmeric, T5: 2% buttermilk, T6: luke warm water, T7: water
(X axis: Decontaminating solution; Y axis: Processing factor)

Fig. 6. Efficiency (processing factor) of decontaminating solutions in removing insecticide residues from capsicum fruits five hours after insecticide spraying

due to dipping in tamarind (2 %), buttermilk (2 %), turmeric (1 %)solution and luke warm water were 28.10, 21.62, 18.63 and 18.35 per cent and processing factors were 0.71, 0.78, 0.81 and 0.82 respectively. However, washing of treated capsicum fruits in tap water removed only 16.73 per cent, which was found to be the least effective treatment when compared to others.

4.6.1.1.5 *Profenophos*

Treatment of insecticide emulsion on capsicum fruits resulted in 3.29 mg kg^{-1} of profenophos residues at 5 h after insecticide spraying (Table 26). The percentage removal of residues measured in capsicum fruits when subjected to different decontamination solutions showed that all the solutions except two *ie* luke warm water and turmeric (1 %) solution significantly differed among each other in their efficiency in removing profenophos residues. More than forty (41.80 %) of the residues were removed when the fruits were dipped in vinegar solution (2 %) for 15 min followed by washing in tap water, and the treatment was found to be significantly superior over all the other treatments. The losses incurred due to dipping in common salt (2 %) solution was 35.20 per cent with a processing factor of 0.64. Dipping in tamarind (2 %) solution caused 33.46 per cent reduction in residues which was further reduced by 17.78 per cent due to dipping in turmeric (1 %) solution. Almost 23.91 and 17.26 per cent of residues were removed from the treated samples through dipping in buttermilk (2 %) solution and luke warm water respectively, while washing with water alone resulted in a reduction of 12.31 per cent.

4.6.1.1.6 *Ethion*

Concentration of ethion on capsicum fruit was 3.74 mg kg^{-1} at 5 h after spraying (Table 26). Statistical analysis proved that decontamination of ethion residues in capsicum fruits by various decontaminating solutions was significant as compared to control samples. It has been found that dipping in 2 % vinegar solution for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, residues could be reduced upto 46.13 per cent. However, by dipping in common salt (2 %) solution, the residues were reduced to 37.54 per cent. The reduction in residue levels due to dipping in tamarind solution (2 %), buttermilk (2 %) solution, turmeric solution (1 %) and luke warm water were 34.42, 26.38, 18.68, and 11.89 per cent and processing factors were 0.65, 0.73, 0.81 and 0.88 respectively. However, washing of treated capsicum fruits in tap water removed only 7.19 per cent, which was found to be the least effective treatment when compared to others.

4.6.1.1.7 *Cypermethrin*

Treatment of insecticide emulsion on capsicum fruits resulted in 0.18 mg kg^{-1} of cypermethrin residues (Table 26). The percentage removal of residues measured in capsicum fruits when subjected to different decontamination solutions showed that all the treatments except two *ie* dipping in luke warm water and turmeric solution (1 %) significantly differed among each other in their efficiency in removing cypermethrin residues. More than fifty five (57.70 %) of the residues were removed when the fruits were dipped in vinegar solution (2 %) for 15 min followed by washing in tap water, and the treatment was found to be significantly superior over all the other treatments. The percentage removal of residues due to dipping in common salt (2 %) solution was 53.26 per cent with a processing factor of 0.46. Dipping in tamarind solution (2 %) caused 37.73 per cent reduction in residues which was further reduced by 22.02 per cent due to dipping in butter milk (2 %) solution. There was no significant difference in the removal of cypermethrin residues when subjected to dipping in luke warm water (17.23 %) and 1 % turmeric solution(16.52 %). Only 12.94 per cent of residues were removed from the treated samples through washing with tap water.

4.6.1.1.8 *Fenvalerate*

The initial concentration of fenvalerate residues on capsicum fruit was 0.56 mg kg^{-1} at 5 h after spraying (Table 26). Statistical analysis proved that decontamination of fenvalerate residues by various decontaminating solutions was significant in their efficiency in removing fenvalerate residues as compared to control samples. It has been found that dipping in vinegar solution (2 %) for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, residues could be reduced upto 74.88 percent. However, by dipping in common salt solution (2 %), the residues were reduced to 54.74 per cent. The reduction in residue levels due to dipping in tamarind solution (2 %), buttermilk solution (2 %), turmeric solution (1 %) and luke warm water were 39.35, 33.28, 21.64 and 16.93 per cent and processing factors were 0.60, 0.66, 0.78 and 0.83 respectively. However, washing of treated capsicum fruits in tap water removed only 11.50 per cent, which was found to be the least effective treatment when compared to others.

4.6.1.2. Okra

The results pertaining to the effect of different decontaminating solution of household products in removing the residues of different insecticides from okra are presented in Table 29 to 32 and processing factor for different treatment solutions for each insecticide is depicted in Fig. 7

4.6.1.2.1 *Methyl parathion*

Concentration of 2.72 mg kg^{-1} of methyl parathion at 5 h after spraying on okra dissipated to 1.96, 0.85 and 0.35 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 28). There was significant difference in the 'rate of degradation of residues during the study period.

The percentage removal of methyl parathion residues in okra when subjected to different decontaminating solutions at 5 h after spraying showed that all the treatments significantly differed among each other in their efficiency in removing methyl parathion residues. It has been found that dipping in tamarind solution (2 %) for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, the residues could be reduced upto 64.21 per cent. The mean percentage removal of methyl parathion residues in descending order in okra when dipped in different decontaminating solutions were common salt (2 %) (59.19 %) > 2 % vinegar (47.17 %) > 2 % buttermilk (45.68 %) > 1 % turmeric (39.94 %) > luke warm water (30.97 %). Overall, a significant reduction in methyl parathion residue was observed for all decontaminating solutions when compared with washing in tap water (23.43 %).

Dipping in common salt (2 %) solution for 15 min followed by washing in tap water showed higher reduction (54.22 %) in methyl parathion residues 1st day after spraying. All the decontaminating solutions significantly differed among each other. The losses incurred due to various decontaminating solutions in the descending order were 2 % tamarind (51.62 %) > 2 % vinegar (40.40 %) > 2 % buttermilk (34.43 %) > 1 % turmeric (31.33 %) > luke warm water (19.62 %). A significant reduction in methyl parathion residue was observed for all decontaminating solutions when compared with tap water washing (11.69 %).

Dipping in tamarind solution (2 %) for 15 min followed by washing in tap water resulted in more than thirty five percent (37.46 %) removal of methyl parathion residues three days after spraying and this treatment was significantly superior over all the other treatments. All the decontaminating solutions except two *ie* vinegar (2 %) and buttermilk (2 %) significantly differed among each other in their efficiency in removing residues. Other decontaminating solutions resulted in 2 % common salt (54.22 %) > 2 % vinegar (31.37 %) > 2 % buttermilk (31.34 %) > 1 % turmeric (24.71 %) > luke warm water (15.96 %) removal of methyl parathion residues. In the case

Table 28. Persistence of organophosphate and synthetic pyrethroid insecticides in/on okra fruits at different intervals (days) after spraying

Insecticides	5 h after spraying	1st day after spraying		3rd day after spraying		5th day after spraying	
	Residues (mg kg^{-1}) ± SD	Residues (mg kg^{-1}) ± SD	Dissipation (%)	Residues (mg kg^{-1}) ± SD	Dissipation (%)	Residues (mg kg^{-1}) ± SD	Dissipation (%)
Methyl parathion	2.72 ± 0.08	1.96 ± 0.15	27.94	0.85 ± 0.04	68.75	0.35 ± 0.01	87.13
Malathion	1.01 ± 0.03	0.80 ± 0.07	20.79	0.31 ± 0.02	69.31	0.19 ± 0.03	81.19
Chlorpyriphos	1.67 ± 0.02	1.45 ± 0.05	13.17	0.50 ± 0.02	70.06	0.35 ± 0.05	79.04
Quinalphos	1.41 ± 0.03	1.22 ± 0.03	13.48	0.58 ± 0.03	58.87	0.20 ± 0.02	85.82
Profenophos	3.56 ± 0.06	2.98 ± 0.05	16.29	1.04 ± 0.09	70.79	0.47 ± 0.03	86.80
Ethion	3.44 ± 0.03	3.20 ± 0.01	6.98	1.88 ± 0.10	45.35	0.75 ± 0.01	78.20
Cypermethrin	0.15 ± 0.01	0.11 ± 0.01	26.67	0.07 ± 0.01	53.33	0.05 ± 0.01	66.67
Fenvalerate	0.93 ± 0.01	0.73 ± 0.04	21.51	0.45 ± 0.02	51.61	0.13 ± 0.01	86.02

of 3rd day sample also, a significant reduction in methyl parathion residues was observed for all the decontaminating solutions when compared with tap water washing (11.70 %) was found as in the case of 1st day sample.

Same scenario was found in case of 5th day samples where dipping in tamarind (2 %) solution for 15 min followed by washing in tap water showed higher reduction (37.28 %). No significant reduction was observed in the case of vinegar (2 %) and common salt (2 %) solution. The losses incurred due to various decontaminating solutions were 20.09 (1 % turmeric), 21.47 (2 % vinegar), 23.55 (2 % common salt), 21.15 (2 % buttermilk) and 13.26 per cent (luke warm water). A significant reduction was observed in all the decontaminating treatments when compared with tap water washing (7.80 %).

Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of tamarind (2 %) solution in removing the residues of methyl parathion at 3rd day and 5th day after spraying. On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1stday, 3rd day and 5th day after spraying).

4.6.1.2.2 *Malathion*

The mean deposits of 1.01 mg kg^{-1} (5 h after spraying) of malathion in okra dissipated to 0.80, 0.31 and 0.19 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 28). There was significant difference in the rate of degradation of residues during the study period.

The percentage removal of malathion residues in okra when subjected to different decontaminating solutions at 5 h after spraying showed that all the treatment solutions except two *ie* turmeric (1 %) and tamarind (2 %) significantly differed among each other in their efficiency in removing malathion residue. Dipping in butter milk (2 %) solution for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, the residues could be reduced up to 81.96 per cent. The percentage removal of malathion residues in descending order in okra when dipped in different decontaminating solutions were 2 % vinegar (92.95 %) > 2 % tamarind (77.10 %) > 1 % turmeric (76.95 %) > 2 % common salt (71.86 %) > luke warm water (42.11 %). Overall, a significant reduction in malathion residue was observed for all the decontaminating solutions when compared with tap water washing (45.80 %).

Dipping in turmeric (1 %) solution for 15 min followed by washing in tap water showed higher reduction (70.56 %) in malathion residues one day after spraying. No significant difference in removal of residue was observed between tamarind (2 %), buttermilk (2 %) and vinegar (2 %), luke warm water, simple washing with tap water. The losses incurred due to various decontaminating solutions were 68.92 (2 % tamarind), 67.75 (2 % buttermilk), 62.37 (2 % common salt), 38.67 (2 % vinegar) and 37.53 per cent (luke warm water). A significant reduction in malathion residue was observed for all the decontaminating solutions when compared with tap water washing (37.67 %).

Dipping in buttermilk (2 %) solution for 15 min followed by washing in tap water resulted in nearly seventy percent (66.70 %) removal of malathion residues three days after spraying and this treatment was significantly superior over all the other treatments. The percentage removal of malathion residues in descending order in okra when dipped in different decontaminating solutions were 1 % turmeric (63.89 %) > 2 % common salt (62.37 %) > 2 % tamarind (57.10 %) > 2 % vinegar (41.77 %) > luke warm water (32.53 %). In the case of 3rd day sample also, a significant reduction in malathion residues was observed for all the decontaminating treatments when compared with tap water washing (25.88 %). Same scenario was found in the case of 5th day samples where dipping in tamarind (2 %) solution (52.68 %) for 15 min followed by washing in tap water showed higher reduction. Significant difference in percentage removal was observed for all

Table 29. Extent of removal of insecticide residues from okra fruits collected at 5 h after spraying*

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	64.21 ± 1.48 (0.97)	47.17 ± 2.23 (1.43)	39.94± 2.66 (1.63)	59.19 ± 3.23 (1.11)	45.68 ± 0.71 (1.47)	30.97 ± 3.10 (1.87)	23.43 ± 3.21 (2.08)
Malathion	77.10 ± 1.49 (0.23)	51.35 ± 1.85 (0.49)	76.95 ± 0.56 (0.23)	71.86 ± 2.12 (0.28)	81.96 ± 0.64 (0.18)	42.11 ± 1.22 (0.58)	45.80 ± 2.52 (0.54)
Chlorpyriphos	68.84 ± 1.40 (0.52)	56.58 ± 1.50 (0.72)	40.55 ± 2.06 (0.99)	58.83 ± 3.24 (0.41)	24.39 ± 1.37 (0.76)	23.88 ± 3.11 (0.76)	22.20 ± 2.43 (0.78)
Quinalphos	80.37 ± 0.42 (0.28)	63.51 ± 1.13 (0.51)	59.81 ± 1.84 (0.57)	73.23 ± 1.55 (0.38)	58.10 ± 2.64 (0.59)	48.22 ± 1.17 (0.73)	42.64 ± 4.23 (0.81)
Profenophos	80.21 ± 0.30 (0.70)	70.51 ± 0.61 (1.05)	64.87 ± 5.97 (1.25)	76.25 ± 2.38 (0.85)	61.44 ± 0.92 (1.37)	36.78 ± 2.67 (2.25)	31.90 ± 1.14 (2.42)
Ethion	73.27 ± 1.04 (0.92)	68.61 ± 1.18 (1.08)	51.76 ± 2.03 (1.66)	69.36 ± 2.48 (1.05)	56.49 ± 1.91 (1.50)	26.42 ± 2.15 (2.53)	10.18 ± 1.34 (3.09)
Cypermethrin	63.44 ± 1.38 (0.05)	63.16 ± 1.80 (0.06)	40.91 ± 2.42 (0.09)	64.36 ± 1.99 (0.05)	32.27 ± 2.46 (0.10)	29.55 ± 3.52 (0.11)	12.23 ± 1.01 (0.13)
Fenvalerate	68.93 ± 3.01 (0.29)	73.11 ± 4.26 (0.25)	54.77 ± 9.61 (0.42)	77.53 ± 5.26 (0.21)	30.56 ± 2.00 (0.65)	24.72 ± 1.89 (0.70)	20.43 ± 2.24 (0.74)
CD (5%)	1.54						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

decontaminating solutions. The losses incurred due to various decontaminating solutions were 33.17 (2 % vinegar), 23.69 (2 % common salt), 21.56 (2 % buttermilk), 15.05 (1 % turmeric) and 11.48 per cent (luke warm water). A significant reduction in malathion residue was observed in all the decontaminating treatment solutions when compared with tap water washing (11.44 %).

Based on the percentage removal of residues, it was statistically proved that there is significant difference in the efficiency of decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying).

4.6.1.2.3 *Chlorpyriphos*

The concentration of 1.67 mg kg^{-1} (5 h after spraying) of chlorpyriphos on okra dissipated to 1.45, 0.50 and 0.35 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 28). There was significant difference in the rate the rate of degradation of residues during the study period.

The percentage removal of chlorpyriphos residues in okra when subjected to different decontaminating solutions, 5 h after spraying showed that all the treatments except two *ie* butter milk (2 %) and common salt (2 %) solution significantly differed among each other in their efficiency in removing chlorpyriphos residues. It has been found that dipping in tamarind solution (2 %) for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, the residues could be reduced upto 68.84 per cent. The efficiency of other decontaminating solutions in descending order were 2 % common salt (58.83 %) > 2 % vinegar (56.58 %) > 1 % turmeric (40.55 %) > 2 % butter milk (24.39 %) > luke warm water (23.88 %). Overall, a significant reduction in chlorpyriphos residue was observed in all the decontaminating solutions when compared

Table 30. Extent of removal of insecticide residues from okra fruits collected at 1st day after spraying

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	51.62 ± 1.83 (0.95)	40.40 ± 1.62 (1.17)	31.33 ± 0.89 (1.35)	54.22 ± 1.41 (0.90)	34.43 ± 0.96 (1.29)	19.62 ± 1.16 (1.58)	11.69 ± 1.18 (1.78)
Malathion	68.92 ± 1.44 (0.25)	38.67 ± 2.83 (0.49)	70.56 ± 1.27 (0.24)	62.37 ± 1.36 (0.30)	67.75 ± 1.42 (0.26)	37.53 ± 1.67 (0.50)	37.67 ± 1.55 (0.50)
Chlorpyriphos	62.52 ± 3.29 (0.54)	50.67 ± 0.70 (0.72)	32.14 ± 1.19 (0.98)	54.38 ± 2.36 (0.66)	13.90 ± 1.48 (1.25)	18.68 ± 1.32 (1.18)	9.48 ± 0.40 (1.31)
Quinalphos	65.30 ± 3.69 (0.42)	54.79 ± 3.67 (0.55)	52.88 ± 2.88 (0.57)	63.14 ± 2.10 (0.45)	44.46 ± 1.15 (0.68)	39.67 ± 0.78 (0.74)	33.24 ± 2.20 (0.81)
Profenophos	73.25 ± 4.12 (0.80)	63.76 ± 3.01 (1.08)	50.60 ± 1.26 (1.47)	68.24 ± 2.41 (0.95)	52.71 ± 2.52 (1.41)	27.23 ± 1.67 (2.17)	23.64 ± 2.89 (2.28)
Ethion	64.03 ± 3.94 (1.15)	56.06 ± 3.07 (1.41)	41.39 ±1.51 (1.88)	59.73 ± 1.67 (1.29)	48.53 ± 1.38 (1.65)	16.96 ± 1.93 (2.66)	5.32 ± 1.58 (3.03)
Cypermethrin	54.46 ± 1.22 (0.05)	57.23 ± 1.32 (0.05)	32.28 ± 1.16 (0.07)	54.61 ± 2.09 (0.05)	25.63 ± 1.17 (0.08)	18.17 ± 1.82 (0.09)	6.70 ± 3.04 (0.10)
Fenvalerate	56.15 ± 4.98 (0.32)	63.67 ±4.04 (0.27)	37.88 ± 2.01 (0.45)	73.21 ± 2.09 (0.20)	21.32 ± 1.42 (0.57)	13.67 ± 0.77 (0.63)	9.70 ± 1.22 (0.66)
CD (5%)	1.31						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

with washing in tap water (22.20 %).

Dipping in tamarind solution (2 %) for 15 min followed by washing in tap water (62.52 %) showed higher reduction in chlorpyriphos residues one day after spraying. The losses incurred due to various decontaminating solutions were 54.38 (2 % common salt), 50.67 (2 % vinegar), 32.14 (1 % turmeric), 18.68 (luke warm water) and 13.90 per cent (2 % buttermilk). A significant difference in percentage removal was observed for all the decontaminating solutions when compared with washing with tap water (9.48 %).

Dipping in tamarind solution (2 %) for 15 min followed by washing in tap water resulted in more than sixty percent (60.22 %) removal of chlorpyriphos residues three days after spraying and this treatment was significantly superior over all the other treatments. There was no significant difference between dipping in butter milk solution (2 %) and washing with water. The different decontaminating solutions resulted in 2 % common salt (54.38 %) > 2 % vinegar (47.30 %) > luke warm water (17.84 %) > 2 % buttermilk (11.44 %) > 1 % turmeric (8.90 %) removal of chlorpyriphos residues. Similarly in the case of 1st day samples, a significant reduction was observed in all the decontaminating solutions except vinegar (2 %) when compared with washing in tap water (10.80 %).

Same scenario was also found in case of 5th day samples where dipping in tamarind solution (2 %) for 15 min followed by washing in tap water showed higher reduction (44.77 %). The losses incurred due to various decontaminating solutions were 41.95 (2 % vinegar), 32.11 (2 % common salt), 24.96 (2 % buttermilk), 22.87 (1 % turmeric) and 11.07 per cent (luke warm water). A significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (12.36 %).

Based on the percentage removal of residues, it was statistically proved that there is significant difference in the efficiency of different decontaminating solutions in removing the residues at different intervals (5h, 1stday, 3rd day and 5th day after spraying).

4.6.1.2.4 *Quinalphos*

The mean initial deposits of 1.41 mg kg^{-1} (5 h after spraying) of quinalphos on okra dissipated to 1.22, 0.58 and 0.20 mg kg^{-1} on 1st, 3rd and 5th day after spraying. There was significant difference in the rate of degradation of residues during the study period.

The percentage removal of quinalphos residues in okra when subjected to different decontaminating solutions, 5 h after spraying showed that all the treatments significantly differed among each other. It has been found that dipping in tamarind solution (2 %) for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, the residues could be reduced upto 80.37 per cent. The percentage removal of quinalphos residues when dipped in other decontaminating solutions were 73.23 (2 % common salt), 63.51 (2 % vinegar), 59.81 (1 % turmeric), 58.10 (2 % buttermilk) and 48.22 per cent (luke warm water). Overall, a significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (42.64 %).

Dipping in tamarind (2 %) solution (65.30 %) showed higher reduction in quinalphos residues one day after spraying. The losses incurred due to various decontaminating solutions were 63.14 (2 % common salt), 54.79 (2 % vinegar), 52.88 (1 % turmeric), 44.46 (2 % buttermilk) and 39.67 per cent (luke warm water). A significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (33.24 %).

Similarly dipping in tamarind (2 %) solution was found to be the best one in removing (61.31 %) quinalphos residues three days after spraying and

Table 31. Extent of removal of insecticide residues from okra fruits collected at 3rd day after spraying

	Mean per cent removal of insecticides (%) ± SD						
Insecticides	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	37.46 ± 1.37 (0.53)	31.37 ± 0.82 (0.58)	24.71 ± 2.29 (0.64)	54.22 ± 1.41 (0.39)	31.34 ± 0.78 (0.58)	15.96 ± 1.68 (0.71)	11.70 ± 1.17 (0.75)
Malathion	57.10 ± 1.67 (0.13)	41.77 ± 1.56 (0.18)	63.89 ± 3.75 (0.11)	62.37 ± 1.36 (0.12)	66.70 ± 1.59 (0.10)	32.53 ± 2.89 (0.21)	25.88 ± 3.31 (0.23)
Chlorpyriphos	60.22 ± 1.15 (0.20)	47.30 ± 1.00 (0.26)	8.90 ± 1.36 (0.46)	54.38 ± 2.36 (0.23)	11.44 ± 1.34 (0.44)	17.84 ± 1.89 (0.41)	10.80 ± 0.40 (0.45)
Quinalphos	61.31 ± 1.09 (0.22)	51.48 ± 0.82 (0.28)	36.40 ± 1.39 (0.37)	56.14 ± 2.10 (0.25)	41.86 ± 1.15 (0.34)	32.41 ± 0.79 (0.39)	18.59 ±1.22 (0.47)
Profenophos	65.65 ± 2.48 (0.36)	52.77 ±1.44 (0.49)	41.68 ± 1.62 (0.61)	68.24 ± 2.41 (0.33)	48.33 ± 1.90 (0.54)	27.66 ± 2.64 (0.75)	21.66 ± 0.69 (0.81)
Ethion	59.62 ± 0.73 (0.76)	52.52 ± 0.68 (0.84)	42.38 ±1.26 (1.08)	59.73 ± 1.67 (0.76)	44.31 ± 0.94 (1.05)	11.48 ± 1.35 (1.66)	6.31 ± 2.26 (1.76)
Cypermethrin	52.18 ± 1.16 (0.03)	50.25 ± 1.63 (0.03)	19.59 ± 1.06 (0.06)	45.61 ± 2.09 (0.04)	22.74 ± 1.77 (0.05)	15.49 ± 2.90 (0.06)	8.19 ± 2.65 (0.06)
Fenvalerate	50.97 ± 1.45 (0.22)	49.13 ±1.84 (0.23)	16.97 ± 1.72 (0.37)	73.21 ± 2.09 (0.12)	19.73 ± 1.28 (0.36)	1 1.55± 1.77 (0.40)	8.82 ± 1.83 (0.41)
CD (5%)	0.98						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

this treatment was significantly superior over all the other treatments. The different decontaminating solutions resulted in 56.14 (2 % common salt), 51.48 (2 % vinegar), 41.86 (2 % buttermilk), 36.40 (1 % turmeric) and 32.41 per cent (luke warm water) removal of quinalphos residues. Similarly in the case of 1st day samples, a significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (18.59 %).

Same scenario was also found in case of 5th day samples where dipping in tamarind (2 %) solution showed higher reduction (50.36 %). There was no significant difference between dipping in luke warm water and washing with water. The losses incurred due to various decontaminating solutions were 47.87 (2 % vinegar), 43.28 (2 % common salt), 17.54 (1 % turmeric), 21.65 (2 % buttermilk) and 11.07 per cent (luke warm water). A significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (12.36 %).

Based on the percentage removal of residues, it was statistically proved that there was significant difference in the efficiency of all decontaminating solutions except butter milk (2 %) on 3rd and 5th day after spraying in removing the residues at different intervals (5h, 1stday, 3rd day and 5th day after spraying)

4.6.1.2.5 *Profenophos*

The mean initial deposits of 3.56 mg kg^{-1} (5 h after spraying) of profenophos on okra dissipated to 2.98, 1.04 and 0.47 mg kg^{-1} on 1st, 3rd and 5th day after spraying. There was significant difference in the rate of degradation of residues during the study period.

The percentage removal of profenophos residues in okra when subjected to different decontaminating solutions, 5 h after spraying showed that all the treatments significantly differed among each other. It has been found that dipping in tamarind (2 %) solution for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, the residues could be reduced upto 80.21 per cent. The percentage removal of profenophos residues when dipped in other decontaminating solutions were 76.25 (2 % common salt), 70.51 (2 % vinegar), 64.87 (1 % turmeric), 61.44 (2 % buttermilk) and 36.78 per cent (luke warm water). Overall, a significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (31.90 %).

Dipping in tamarind (2 %) solution showed higher reduction in profenophos residues (73.25 %) one day after spraying. No significant difference was observed between washing in luke warm water and tap water. The losses incurred due to various decontaminating solutions were 68.24 (2 % common salt), 63.76 (2 % vinegar), 52.71 (2 % buttermilk), 50.60 (1 % turmeric) and 27.23 per cent (luke warm water).A significant reduction of residue was observed in all the decontaminating solutions when compared with washing in tap water (23.64 %).

Similarly, dipping in tamarind (2 %) solution resulted in more than 65.65 percent removal of profenophos residues three days after spraying and this common salt), 52.77 (2 % vinegar), 48.33 (2 % buttermilk), 41.68 (1 % turmeric) and 27.66 per cent (luke warm water) removal of profenophos residues. Similarly in the case of 1st day samples, a significant reduction was observed in all the decontaminating solutions compared with washing in tap water (21.66 %).

No significant difference in percentage removal was observed in turmeric (1 %) and buttermilk (2 %). The extent of residue removal due to various decontaminating solutions were 62.99 (2 % tamarind), 29.28 (1 % turmeric), 25.02 (2 % common salt), 17.80 (2 % buttermilk), 16.95 (2 % vinegar) and 14.61 per cent (luke warm water).A significant reduction was observed in all the decontaminating solutions when compared with washing

Table 32. Extent of removal of insecticide residues from okra fruits collected at 5th day after spraying

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	37.28 ± 1.63 (0.22)	21.47 ± 1.88 (0.27)	20.09 ± 1.99 (0.28)	23.55 ± 1.57 (0.27)	21.15 ± 1.07 (0.28)	13.26 ± 2.25 (0.30)	7.80 ± 2.38 (0.32)
Malathion	52.68 ± 1.91 (0.09)	33.17 ± 2.42 (0.13)	15.05 ± 1.89 (0.16)	23.69 ± 1.66 (0.14)	21.56 ± 1.25 (0.15)	11.48 ± 0.59 (0.17)	11.44 ± 0.97 (0.17)
Chlorpyriphos	44.77 ± 4.07 (0.19)	41.95 ± 2.22 (0.20)	22.87 ± 2.49 (0.27)	32.11 ± 1.66 (0.24)	24.96 ± 2.43 (0.26)	19.44 ± 2.03 (0.28)	6.76 ± 1.93 (0.33)
Quinalphos	50.36 ± 1.09 (0.10)	47.87 ± 3.02 (0.10)	17.54 ± 1.04 (0.16)	43.28 ± 1.86 (0.11)	21.65 ± 0.58 (0.16)	11.07 ± 1.01 (0.18)	12.36 ± 2.69 (0.18)
Profenophos	62.99 ± 2.47 (0.17)	29.28 ± 1.59 (0.33)	16.95 ± 4.25 (0.39)	25.02 ± 1.42 (0.35)	17.80 ± 0.69 (0.39)	14.61 ± 2.26 (0.40)	11.14 ± 4.66 (0.42)
Ethion	51.67 ± 2.16 (0.36)	21.63 ± 1.94 (0.59)	17.91 ±2.50 (0.62)	20.21 ± 1.76 (0.60)	20.72 ± 0.84 (0.59)	9.93 ± 1.19 (0.68)	5.65 ± 1.16 (0.71)
Cypermethrin	42.35± 3.09 (0.03)	37.45 ± 1.54 (0.03)	25.40 ± 3.06 (0.04)	31.14 ± 0.36 (0.03)	31.76 ± 1.34 (0.03)	18.83 ± 1.97 (0.04)	11.17 ± 0.80 (0.04)
Fenvalerate	42 ± 2.55 (0.08)	43.63 ± 2.23 (0.07)	30.06 ± 2.18 (0.09)	33.65 ± 2.14 (0.09)	33.42 ± 1.52 (0.09)	21.11 ± 2.02 (0.10)	10.68 ± 1.50 (0.12)
CD (5%)	1.20						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

in tap water (11.14 %).

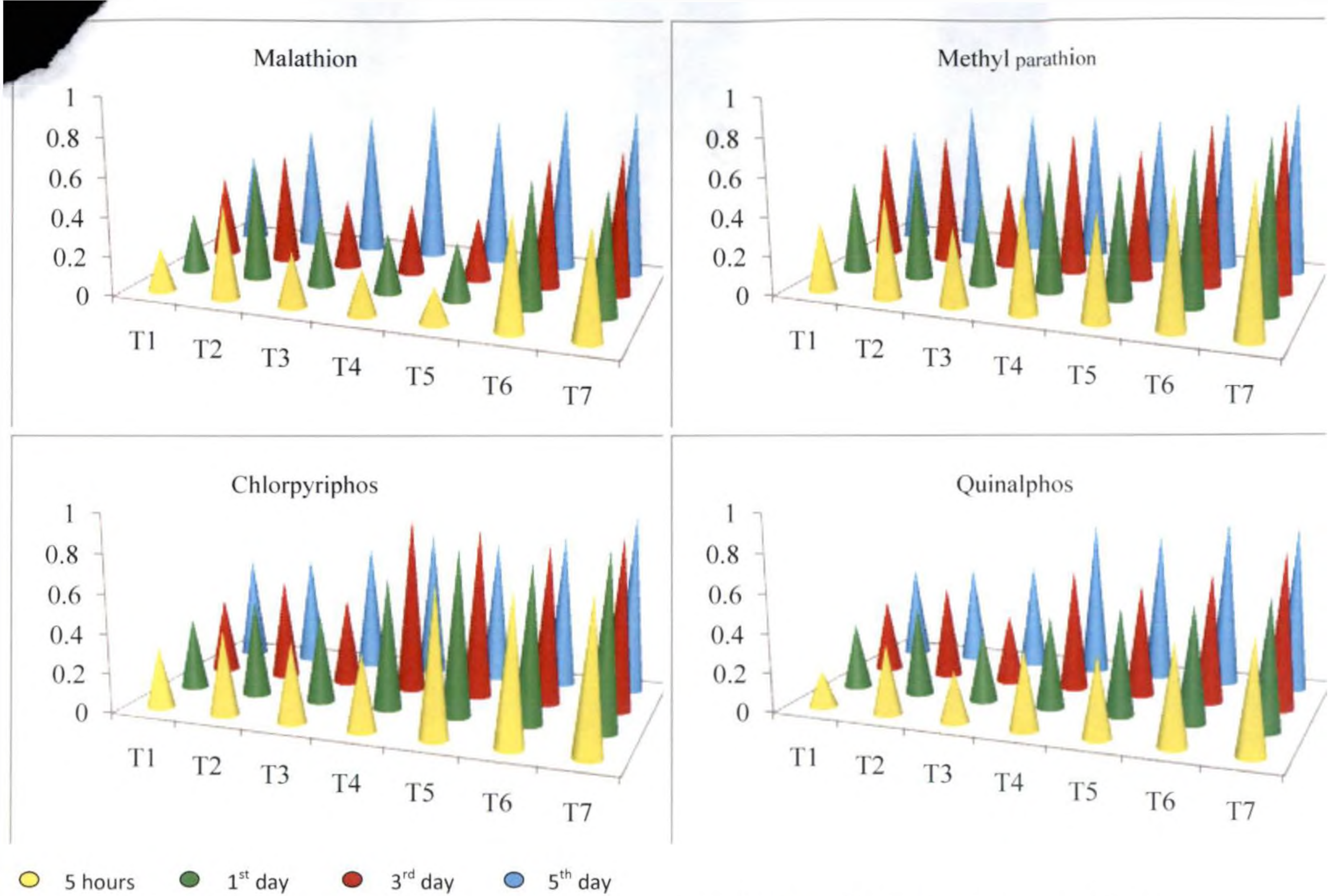
Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of simple washing with tap water in removing the residues of profenophos 1st day and 3rd day after spraying. On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1stday, 3rd day and 5th day after spraying)

4.6.1.2.6 *Ethion*

The concentration of 3.44 mg kg^{-1} (5 h after spraying) of ethion on okra dissipated to 3.20, 1.88 and 0.75 mg kg^{-1} on 1st, 3rd and 5th day after spraying. There was significant difference in the rate of degradation of residues during the study period.

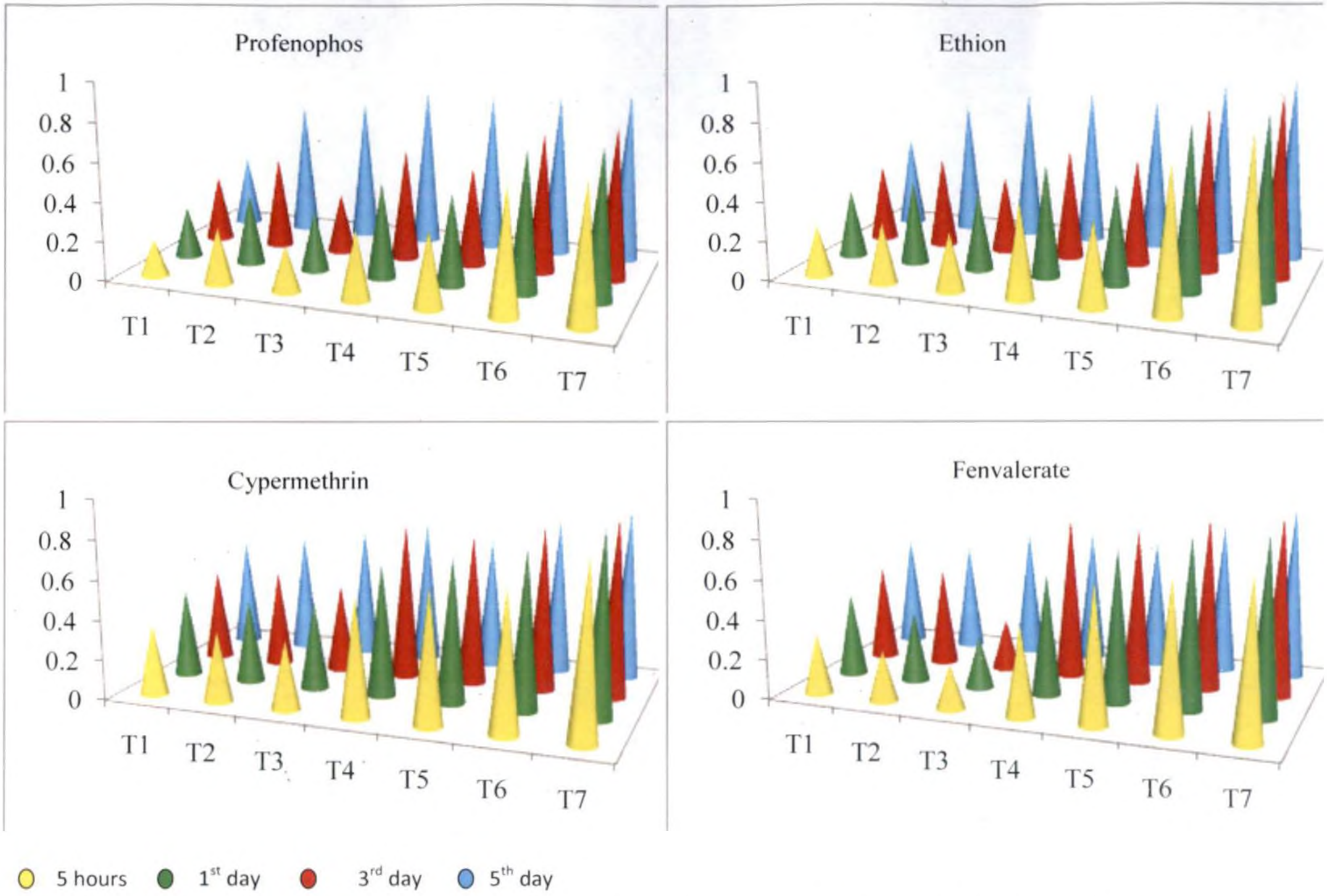
The percentage removal of ethion residues in okra when subjected to different decontaminating solutions 5 h after spraying showed that all the treatments except vinegar (2 %) and common salt (2 %) significantly differed among each other. It has been found that dipping in tamarind (2 %) solution was found to be more effective than other treatments. In this process, the residues could be reduced upto 73.27 per cent. The percentage removal of ethion residues in okra when subjected to other decontaminating solutions were 69.36 (2 % common salt), 68.61 (2 % vinegar), 56.49 (2 % buttermilk), 51.76 (1 % turmeric) and 26.42 (luke warm water). Overall, a significant reduction in ethion residue was observed in all the decontaminating solutions when compared with washing in tap water (10.18 %).

Dipping in tamarind (2 %) solution showed higher reduction in ethion residues (64.03 %) one day after spraying. All the decontaminating solutions significantly differed in their efficiency in removing ethion residues among each other. The losses incurred due to various decontaminating solutions were 59.73 (2 % common salt), 56.06 (2 % vinegar), 48.53 (2 % buttermilk), 41.39 (1 % turmeric) and 16.96 per cent (luke warm water). A significant



T1: 2% tamarind, T2: 2% vinegar, T3: 2% common salt, T4: 1% turmeric, T5: 2% buttermilk, T6: luke warm water, T7: water
(X axis: Decontaminating solutions; Y axis: Processing factor)

Fig. 7. Efficiency (processing factor) of decontaminating solutions in removing insecticide residues in okra fruit at different time intervals after insecticide spraying



T1: 2% tamarind, T2: 2% vinegar, T3: 2% common salt, T4: 1% turmeric, T5: 2% buttermilk, T6: luke warm water, T7: water
(X axis: Decontaminating solutions; Y axis: Processing factor)

Fig. 7. Efficiency (processing factor) of decontaminating solutions in removing insecticide residues in okra fruit at different time intervals after insecticide spraying

reduction in ethion residues was observed in all the decontaminating solutions when compared with washing in tap water (5.32 %).

Dipping in tamarind solution (2 %) resulted in more than fifty five per cent (59.62 %) removal of ethion residues three days after spraying and this treatment was significantly superior over all the other treatments. It was statistically proved that all the decontaminating solutions significantly differed among each other. Other decontaminating solutions resulted in 59.73 (2 % common salt), 52.52 (2 % vinegar), 44.31 (2 % buttermilk), 42.38 (1 % turmeric) and 11.48 per cent (luke warm water) removal of ethion residues. Similarly in the case of 1st day samples, a significant reduction in ethion residue was observed in all the decontaminating techniques when compared with washing in tap water (6.31 %).

Same scenario was also found in case of 5th day samples where dipping in tamarind (2 %) solution showed higher reduction (51.67 %). Significant difference in percentage removal of ethion residues was observed in all decontaminating solutions except common salt (2 %) and butter milk (2 %). The losses incurred due to various decontaminating solutions were 21.63 (2 % vinegar), 20.72 (2 % buttermilk), 20.21 (2 % common salt), 17.91 (1 % turmeric) and 9.93 per cent (luke warm water). A significant reduction in ethion residues was observed in all the decontaminating solutions when compared with washing in tap water (5.65 %).

Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of simple washing with tap water 1st day, 3rd day and 5th day after spraying. On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1stday, 3rd day and 5th day after spraying).

4.6.1.2.7 *Cypermethrin*

Treatment of insecticidal emulsion on okra fruits resulted in 0.15 mg kg^{-1} (5 h after spraying) of cypermethrin which dissipated to 0.11, 0.07 and 0.05 mg kg^{-1} on 1st, 3rd and 5th day after spraying. There was significant difference in the rate of degradation of residues during the study period.

No significant difference in percentage removal was observed between tamarind (2 %), vinegar (2 %) and common salt (2 %). In this processes, the residues could be reduced upto 63.44, 63.16 and 64.36 per cent respectively. The percentage removal of cypermethrin residues when dipped in other decontaminating solutions were 40.91 (1 % turmeric), 32.27 (2 % buttermilk) and 29.55 per cent (luke warm water). Overall, a significant reduction in cypermethrin residue was observed in all the decontaminating solutions when compared with washing in tap water (12.23 %).

Dipping in vinegar (2 %) solution (57.23 %) showed higher reduction in cypermethrin residues one day after spraying. No significant difference was observed between common salt (2 %) and tamarind (2 %). The losses incurred due to various decontaminating solutions were 54.61 (2 % common salt), 54.46 (2 % tamarind), 32.28 (1 % turmeric), 25.63 (2 % buttermilk) and 18.17 per cent (luke warm water). Overall, a significant reduction in cypermethrin residue was observed in all the decontaminating solutions when compared with washing in tap water (6.70 %).

Dipping in tamarind solution (2 %) resulted in more than fifty percent (52.18 %) removal of cypermethrin residues three days after spraying and this treatment was significantly superior over all the other treatments. The different decontaminating solutions resulted in 50.25 (2 % vinegar), 45.61 (2 % common salt), 22.74 (2 % buttermilk), 19.59 (1 % turmeric) and 15.49 per cent (luke warm water) removal of cypermethrin residues. Similarly in the case of 1st day samples, a significant reduction in cypermethrin residue was observed in all the decontaminating solutions when compared with washing in tap water (8.19 %).

Same scenario was also found in case of 5th day samples where dipping in tamarind (2 %) solution showed higher reduction (42.35 %). There was no significant difference between common salt (2 %) and butter milk (2 %). The losses incurred due to various decontaminating solutions were 37.45 (2 % vinegar), 31.76 (2 % buttermilk), 31.14 (2 % common salt), 25.40 (1 % turmeric) and 18.83 per cent (luke warm water). A significant reduction in cypermethrin residue was observed in all the decontaminating solutions when compared with washing in tap water (11.17 %).

Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of simple washing with tap water in removing the residues of cypermethrin 1st and 3rd day after spraying. On the other hand, there is significant difference in the efficiency of all decontaminating solutions in removing the residues at different intervals (5h, 1stday, 3rd day and 5th day after spraying)

4.6.1.2.8 *Fenvalerate*

Concentration of 0.93 mg kg^{-1} (5 h after spraying) of fenvalerate on okra dissipated to 0.73, 0.45 and 0.13 mg kg^{-1} on 1st, 3rd and 5th day after spraying. There was significant difference in the rate of degradation of residues during the study period.

It has been found that dipping in common salt (2 %) for 15 min followed by washing in tap water was found to be more effective than other treatments. In this process, the residues could be reduced upto 77.53 per cent. The percentage removal of fenvalerate residues when dipped in other decontaminating solutions were 73.11 (2 % vinegar), 68.93 (2 % tamarind), 54.77 (1 % turmeric), 30.56 (2 % buttermilk) and 24.72 per cent (luke warm water). Overall, a significant reduction in fenvalerate residue was observed in all the decontaminating solutions when compared with washing in tap water (20.43 %).

Dipping in common salt (2 %) solution showed higher reduction in fenvalerate residues (73.21 %) one day after spraying. The losses incurred due to various decontaminating solutions were 63.67 (2 % vinegar), 56.15 (2 % tamarind), 37.88 (1 % turmeric), 21.32 (2 % buttermilk) and 13.67 per cent (luke warm water). A significant reduction in fenvalerate residue was observed in all the decontaminating solutions when compared with washing in tap water (9.70 %).

Dipping in tamarind (2 %) solution resulted in more than fifty percent (50.97 %) removal of fenvalerate residues three days after spraying and this treatment was significantly superior over all the other treatments. The different decontaminating solutions resulted in 73.21 (2 % common salt), 49.13 (2 % vinegar), 19.73 (2 % buttermilk), 16.97 (1 % turmeric) and 11.55 per cent (luke warm water) removal of fenvalerate residues. Similarly in the case of 1st day samples, a significant reduction in fenvalerate residue was observed in all the decontaminating solutions when compared with washing in tap water (8.82 %).

Same scenario was found in case of 5th day samples where dipping in tamarind (2 %) solution showed higher reduction (42.00 %). There was no significant difference between dipping in common salt (2 %) and butter milk (2 %). The losses incurred due to various decontaminating solutions were 43.63 (2 % vinegar), 33.65 (2 % common salt), 33.42 (2 % buttermilk), 30.06 (1 % turmeric) and 21.11 per cent (luke warm water). A significant reduction in fenvalerate residue was observed in all the decontaminating solutions when compared with washing in tap water (10.68 %).

Based on the percentage removal of residues, it was statistically proved that there is significant difference in the efficiency of all decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying)

4.6.1.3 Curry leaf

The results pertaining to the effect of different decontaminating solution of household products in removing the residues of different insecticides from curry leaf are presented in Table 34 - 37 and processing factor for different treatment solutions for each insecticide is depicted in Fig. 8.

4.6.1.3.1 *Methyl parathion*

Concentration of 19.20 mg kg^{-1} of methyl parathion at 5 h after spraying on curry leaf dissipated to 8.51, 3.39 and 1.92 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 33). There was significant difference in the rate of degradation of residues during the study period.

The percentage removal of methyl parathion residues in curry leaf when subjected to different decontaminating solutions at 5 h after spraying showed that all the treatments significantly differed among each other in their efficiency in removing methyl parathion residues. It has been found that dipping in turmeric solution (1 %) was found to be more effective than other treatments. In this process, the residues could be reduced upto 86.83 per cent. The percentage removal of methyl parathion residues in curry leaf when dipped in other decontaminating solutions were 86.77 (2 % vinegar), 81.95 (2 % common salt), 75.24 (2 % tamarind), 70.74 (2 % buttermilk) and 62.80 per cent (luke warm water). Overall, a significant reduction in methyl parathion residue was observed for all decontaminating solutions when compared with washing in tap water (52.12 %).

Dipping in turmeric (1 %) solution showed higher reduction in methyl parathion residues (74.43 %) one day after spraying. All the decontaminating solutions except two *ie* vinegar (2 %) and common salt (2 %) significantly differed among each other. The losses incurred due to various decontaminating solutions were 70.79 (2 % common salt), 69.46 (2 % vinegar), 64.20 (2 % buttermilk) 61.22 (2 % tamarind),and 58.41 per cent (luke warm water). A significant reduction in methyl parathion residue was observed for all decontaminating solutions when compared with washing in tap water (50.68 %).

Dipping in tamarind solution (2 %) resulted in more than forty percent (43.23 %) removal of methyl parathion residues three days after spraying and this treatment was significantly superior over all the other treatments. All the decontaminating solutions except two *ie* vinegar (2 %) and turmeric (1 %) significantly differed among each other. Other decontaminating solutions resulted in 24.02 (2 % common salt), 21.77 (2 % vinegar), 20.70 (1 % turmeric), 10.91 (2 % buttermilk) and 31.87 per cent (luke warm water) removal of methyl parathion residues. Similarly in the case of 1st day samples, a significant reduction in methyl parathion residue was observed for all decontaminating solutions when compared with washing in tap water (9.24 %).

Same scenario was found in case of 5th day samples, where dipping in tamarind solution (2 %) showed higher reduction (38.70 %). No significant reduction in methyl parathion residues was observed in the case of vinegar (2 %), common salt (2 %) and turmeric (1 %). The losses incurred due to various decontaminating solutions were 23.97 (luke warm water), 19.26 (2 % vinegar), 19.01 (2 % common salt), 18.71 (1 % turmeric) and 9.30 per cent (2 % buttermilk). A significant reduction in methyl parathion residues was observed for all the decontaminating solutions when compared with washing in tap water (16.35 %).

Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of turmeric (1 %) in removing the residues of methyl parathion 3rd day and 5th day after spraying. On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying).

4.6.1.3.2 *Malathion*

Table 33: Persistence of organophosphate and synthetic pyrethroid insecticides in/on curry leaf at different intervals (days) after spraying

Insecticides	5 h after spraying	1st day after spraying		3rd day after spraying		5th day after spraying	
	Residues (mg kg^{-1}) ± SD	Residues (mg kg^{-1}) ± SD	Dissipation (%)	Residues (mg kg^{-1}) ± SD	Dissipation (%)	Residues (mg kg^{-1}) ± SD	Dissipation (%)
Methyl parathion	19.20 ± 2.84	8.51 ± 1.17	55.60	3.39 ± 0.35	82.34	1.92 ± 0.22	90.00
Malathion	1.53 ± 0.17	1.10 ±0.15	28.10	0.36 ± 0.04	76.47	0.21 ± 0.02	86.27
Chlorpyriphos	7.59 ± 0.34	3.26 ± 0.42	57.04	0.73 ± 0.08	90.38	0.41 ± 0.04	94.59
Quinalphos	8.20 ± 0.58	5.34 ± 0.69	34.87	1.96 ± 0.20	76.09	1.11 ± 0.13	86.46
Profenophos	51.23 ± 6.79	37.47 ± 5.35	26.85	19.80 ± 2.03	61.35	11.20 ± 1.30	78.13
Ethion	43.29 ± 1.89	31.40 ± 4.43	27.46	19.79 ± 2.01	54.28	11.18 ± 1.26	74.17
Cypermethrin	0.27 ± 0.01	0.21 ± 0.04	22.22	0.18 ± 0.02	33.33	0.10 ± 0.02	62.96
Fenvalerate	4.43 ± 0.11	3.59 ± 0.49	18.96	2.37 ± 0.26	46.50	1.33 ± 0.14	69.97

Treatment of insecticide emulsion on curry leaf resulted in 1.53 mg kg^{-1} of malathion residues at 5 h after insecticide spraying which later dissipated to 1.10, 0.36 and 0.21 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 33). There was significant difference in the rate of degradation of residues during the study period.

Statistical analysis (CD, $p \leq 0.05$) proved that decontamination of malathion residues in curry leaf 5 h after spraying by different decontaminating solutions except two *ie* turmeric (1 %) and tamarind (2 %) significantly differed among each other. It has been found that dipping in turmeric solution (1 %) and tamarind solution (2 %) was found to be more effective than other treatments. In this processes, the residues could be reduced upto 97.36 and 98.05 per cent respectively. The percentage removal of malathion residues in curry leaf when dipped in other decontaminating solutions were 94.39 (2 % common salt), 92.95 (2 % vinegar), 92.39 (2 % buttermilk) and 89.10 per cent (luke warm water). Overall, a significant reduction in malathion residues was observed for all the decontaminating solutions when compared with washing in tap water (83.19 %).

Dipping in turmeric (1 %) solution showed higher reduction in malathion residues (95.78 %) one day after spraying. No significant difference was observed in the case of tamarind (2 %), common salt (2 %),vinegar (2 %) and buttermilk (2 %). The losses incurred due to various decontaminating solutions were 94.01 (2 % common salt), 93.24 (2 % vinegar), 93.09 (2 % buttermilk), 91.80 (2 % tamarind) and 87.80per cent (luke warm water). A significant reduction in malathion residues was observed for all the decontaminating solutions when compared with washing in tap water (84.25 %).

Table 34. Extent of removal of insecticide residues from curry leaf collected at 5 h after spraying*

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	75.24 ± 2.23 (4.75)	86.77 ± 1.43 (2.54)	86.83 ± 1.65 (2.52)	81.95 ± 0.62 (3.46)	70.74 ± 0.82 (5.61)	62.80 ± 0.47 (7.14)	52.12 ± 1.21 (9.19)
Malathion	98.05 ± 1.82 (0.03)	92.95 ± 0.25 (0.10)	97.36 ± 0.45 (0.04)	94.39 ± 0.94 (0.08)	92.39 ± 2.06 (0.12)	89.10 ± 0.82 (0.16)	83.19 ± 3.14 (0.25)
Chlorpyriphos	68.59 ± 1.32 (2.38)	68.71 ± 0.58 (2.37)	87.15 ± 1.74 (1.15)	71.63 ± 1.59 (2.15)	70.33 ± 0.65 (2.25)	54.47 ± 1.14 (3.45)	47.43 ±1.46 (3.99)
Quinalphos	81.76 ± 1.98 (1.49)	71.45 ± 1.01 (2.34)	87.70 ± 2.23 (1.00)	79.06 ± 3.15 (1.71)	76.66 ± 0.68 (1.91)	66.10 ± 0.22 (2.77)	56.46 ± 1.04 (3.57)
Profenophos	82.09 ± 1.51 (9.17)	74.99 ± 0.45 (12.81)	90.79 ± 0.31 (4.71)	90.40 ± 0.38 (4.91)	82.02 ± 0.80 (9.21)	72.10 ± 1.22 (14.29)	52.04 ± 1.32 (24.56)
Ethion	79.84 ± 0.99 (8.72)	70.92 ± 1.59 (12.58)	87.84 ± 0.41 (5.26)	82.83 ± 0.50 (7.43)	76.23 ± 0.86 (10.29)	64.44 ± 1.08 (15.39)	52.78 ± 2.73 (20.44)
Cypermethrin	87.53 ± 1.28 (0.03)	86.27 ± 1.19 (0.03)	90.93 ± 0.21 (0.02)	87.26 ± 1.72 (0.03)	86.51 ± 1.49 (0.03)	71.76 ± 1.56 (0.07)	51.84 ±0.16 (0.13)
Fenvalerate	86.97 ± 1.31 (0.57)	87.09 ± 0.14 (0.57)	92.61 ± 0.72 (0.32)	91.34 ± 0.89 (0.38)	92.15 ± 1.18 (0.34)	87.05 ± 1.16 (0.57)	47.33 ± 1.49 (2.33)
CD (5%)	0.89						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

Dipping in tamarind solution (2 %) resulted in nearly ninety per cent (89.04 %) removal of malathion residues three days after spraying and this treatment was significantly superior over all the other treatments. There was no significant difference between dipping in buttermilk (2 %) and washing with water. The different decontaminating solutions resulted in 83.48 (luke warm water), 81.34 (1 % turmeric), 78.84 (2 % common salt), 76.36 (2 % vinegar) and 69.93(2 % buttermilk) removal of malathion residues. Similarly in the case of 1st day samples, a significant reduction was observed in all the decontaminating solutions except butter milk (2 %) when compared in washing with tap water (69.64 %).

Same scenario was also found in case of 5th day samples where dipping in 2 % tamarind solution showed higher reduction (79.57 %). Significant difference in percentage removal was observed for all decontaminating solutions. The losses incurred due to various decontaminating solutions were 71.63 (2 % vinegar), 62.64 (2 % common salt), 61.60 (1 % turmeric), 51.49 (2 % buttermilk) and 35.16 (luke warm water). A significant reduction in malathion residue was observed for all the decontaminating solutions when compared with washing in tap water (46.45 %).

Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of vinegar (2 %), 2 % common salt (2 %), luke warm water and simple washing with tap water in removing the residues of malathion at 5 h and 1st day after spraying. On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying)

Table 35. Extent of removal of insecticide residues from curry leaf collected at 01st day after spraying*

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	61.22 ± 0.69 (3.30)	69.46 ± 0.14 (2.59)	74.43 ± 0.28 (2.17)	70.79 ± 3.47 (2.48)	64.20 ± 1.06 (3.04)	58.41 ± 3.10 (3.53)	50.68 ± 1.49 (4.19)
Malathion	91.80 ± 0.24 (0.09)	93.24 ± 0.04 (1.02)	95.78 ± 0.09 (0.05)	94.01 ± 1.21 (0.06)	93.09 ± 0.19 (0.08)	87.80 ± 0.92 (0.13)	84.25 ±0.60 (0.17)
Chlorpyriphos	66.05 ± 0.93 (1.10)	58.61 ± 0.33 (1.34)	82.93 ± 0.28 (0.55)	69.36 ± 3.28 (0.99)	69.07 ± 5.05 (1.00)	47.98 ± 3.62 (1.69)	43.59 ±0.82 (1.83)
Quinalphos	74.00 ± 1.42 (2.13)	70.67 ± 0.23 (1.38)	85.16 ± 0.29 (0.79)	77.35 ± 2.39 (1.20)	74.10 ± 0.78 (1.38)	61.46 ± 2.49 (2.05)	54.23 ±0.65 (2.44)
Profenophos	77.25 ± 0.47 (8.52)	68.94 ± 0.18 (11.63)	87.59 ± 0.09 (4.65)	88.52 ± 0.98 (4.30)	73.74 ± 3.22 (9.83)	61.46 ± 7.88 (14.40)	51.06 ± 2.41 (18.33)
Ethion	71.26 ± 0.79 (9.02)	60.37 ± 0.58 (12.44)	86.99 ± 0.31 (4.08)	70.88 ± 2.77 (9.14)	72.35 ± 0.26 (8.68)	57.25 ± 1.63 (13.40)	39.94 ± 1.43 (18.85)
Cypermethrin	71.98 ±0.70 (0.06)	66.82 ± 0.49 (0.07)	89.37 ± 0.20 (0.02)	68.14 ± 7.06 (0.07)	78.46 ± 2.99 (0.05)	58.84 ±12.69 (0.09)	48.58 ± 2.31 (0.10)
Fenvalerate	70.39 ±0.46 (1.06)	64.95 ± 0.17 (1.25)	87.88 ± 0.16 (0.43)	90.25 ± 1.88 (0.35)	90.22 ± 1.48 (0.35)	84.86 ±1.76 (0.54)	44.08 ±2.70 (2.00)
CD (5%)	1.59						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

4.6.1.3.3 *Chlorpyriphos*

Concentration of 7.59 mg kg^{-1} (5 h after spraying) of chlorpyriphos on curry leaf dissipated to 3.26, 0.73 and 0.41 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 33). There was significant difference in the rate of degradation of residues during the study period.

The percentage removal of chlorpyriphos residues in curry leaf when subjected to different decontaminating solutions 5 h after spraying showed that all the treatments except two *ie* vinegar (2 %) and tamarind (2 %) significantly differed among each other in their efficiency in removing chlorpyriphos residues. It has been found that dipping in turmeric solution (1 %) was found to be more effective than other treatments. In this process, the residues could be reduced upto 87.15 per cent. The percentage removal of chlorpyriphos residues in curry leaf when dipped in other decontaminating solutions were 71.63 (2 % common salt), 70.33 (2 % buttermilk), 68.71 (2 % vinegar), 68.59 (2 % tamarind) and 54.47 per cent (luke warm water). Overall, a significant reduction in chlorpyriphos residues was observed for all the decontaminating solutions when compared with washing in tap water (47.43 %).

Dipping in 1 % turmeric solution (1 %) showed higher reduction in chlorpyriphos residues (82.93 %) one day after spraying. No significant difference was observed in the case of common salt (2 %) and butter milk (2 %). The losses incurred due to various decontaminating solutions were 69.36 (2 % common salt), 69.07 (2 % buttermilk), 66.05 (2 % tamarind), 58.61 (2 % vinegar), and 47.98 per cent (luke warm water). Overall, a significant reduction in chlorpyriphos residues was observed for all the decontaminating solutions when compared with washing in tap water (43.59 %).

Dipping in tamarind solution (2 %) resulted in more than sixty percent (62.01 %) removal of chlorpyriphos residues three days after spraying and this treatment was significantly superior over all the other treatments. There was no significant difference in percentage removal of chlorpyriphos residues in curry leaf when dipped in vinegar (2 %) and washing with water. The different decontaminating solutions resulted in 47.38 (1 % turmeric), 45.72 (luke warm water), 38.86 (2 % common salt), 34.12 (2 % vinegar) and 21.85 % (2 % buttermilk) removal of chlorpyiphos residues. Similarly in the case of 1st day samples, a significant reduction in chlorpyriphos residues was observed for all the decontaminating solutions except vinegar (2 %) when compared with washing in tap water (34.20 %).

Same scenario was also found in case of 5th day samples where dipping in tamarind (2 %) solution showed higher reduction (60.24 %). There was no significant difference in percentage removal of chlorpyriphos residues in curry leaf when dipped in vinegar (2 %) and washing with water. The losses incurred due to various decontaminating solutions were 42.84 (1 % turmeric), 39.48 (luke warm water), 33.13 (2 % common salt), 30.69 (2 % vinegar) and 18.50 per cent (2 % buttermilk). Overall, a significant reduction in chlorpyriphos residues was observed for all the decontaminating solutions when compared with washing in tap water (29.92 %).

Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of butter milk (2 %) in removing the residues of chlorpyriphos 5 h and one day after spraying. On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying).

4.6.1.3.4 *Quinalphos*

Treatment of insecticide emulsion on curry leaf resulted in 8.20 mg kg^{-1} of quinalphos residues at 5 h after insecticide spraying which later dissipated to 5.34, 1.96 and 1.11 mg kg^{-1} on 1st, 3rd and 5th day after spraying

Table 36. Extent of removal of insecticide residues from curry leaf collected at 3rd day after spraying*

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	43.23 ± 3.17 (1.92)	21.77 ± 1.52 (2.65)	20.70 ± 0.94 (2.68)	24.02 ± 2.12 (2.57)	10.91 ± 1.02 (3.02)	31.87 ± 2.66 (2.30)	9.24 ± 1.04 (3.07)
Malathion	89.04 ±0.79 (0.04)	76.36 ± 1.53 (0.09)	81.34 ± 0.44 (0.07)	78.84 ± 0.16 (0.08)	69.93 ± 2.50 (0.10)	83.48 ± 0.19 (0.06)	69.64 ± 2.09 (0.10)
Chlorpyriphos	62.01 ±2.31 (0.27)	34.12 ± 2.60 (0.48)	47.38 ± 1.45(0.38)	38.86 ±1.17 (0.44)	21.85 ± 2.15 (0.57)	45.72 ± 0.06 (0.39)	34.22± 0.81 (0.48)
Quinalphos	69.30 ±1.85 (0.60)	45.65 ± 3.53(1.06)	57.86 ± 1.03 (0.82)	50.90 ± 0.37 (2.97)	40.40 ± 1.57 (1.16)	58.53 ± 0.58 (0.81)	40.55 ± 1.26 (1.96)
Profenophos	67.52 ±1.74 (6.43)	50.95 ± 2.06 (9.71)	59.50 ± 0.66 (8.01)	48.88 ± 1.40 (10.12)	47.25 ± 1.12 (10.44)	59.75 ± 1.78 (7.96)	44.55 ± 0.87 (10.97)
Ethion	67.00 ±2.11 (6.53)	51.71 ± 0.49 (9.55)	60.98 ± 0.52 (7.72)	43.34 ± 1.98 (11.21)	50.19 ± 0.65 (9.85)	57.15 ± 1.40 (8.48)	43.91 ± 0.59 (11.10)
Cypermethrin	59.51 ±3.19 (0.07)	53.70 ± 3.07 (0.08)	56.79 ± 1.68 (0.07)	36.26 ± 3.44 (0.11)	47.64 ± 1.20 (0.09)	48.63 ± 3.23 (0.09)	49.17 ± 5.18 (0.09)
Fenvalerate	56.16 ±2.72 (1.03)	52.69 ± 1.70 (1.12)	45.32 ± 10.41 (1.29)	36.44 ± 1.49 (1.50)	37.75 ± 5.75 (1.47)	49.09 ± 2.78 (1.20)	39.9 ±0.82 (1.42)
CD (5%)	1.42						

Value in parentheses are concentration of residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

(Table 33). There was significant difference in the rate of degradation of residues during the study period.

Statistical analysis (CD, $p \leq 0.05$) proved that decontamination of quinalphos residues in curry leaf 5 h after spraying by different decontaminating solutions showed that all the treatments significantly differed among each other in their efficiency in removing quinalphos residues. It has been found that dipping in turmeric solution (1 %) was found to be more effective than other treatments. In this process, the residues could be reduced upto 87.70 per cent. The percentage removal of quinalphos residues when dipped in other decontaminating solutions were 81.76 (2 % tamarind), 79.06 (2 % common salt),76.66 (2 % buttermilk), 71.45 (2 % vinegar), and 66.10 (luke warm water). Overall, a significant reduction in quinalphos residues was observed for all the decontaminating solutions when compared with washing in tap water (56.46 %).

Dipping in turmeric solution (1 %) showed higher reduction in quinalphos residues (85.16 %) one day after spraying. No significant difference was observed in the case of common salt (2 %) and vinegar (2 %). The losses incurred due to various decontaminating solutions were 77.35 (2 % common salt), 74.10 (2 % buttermilk), 74.00 (2 % tamarind), 70.67 (2 % vinegar) and 61.46 per cent (luke warm water). Overall, a significant reduction in quinalphos residues was observed for all the decontaminating solutions when compared with washing in tap water (54.23 %).

Dipping in tamarind solution (2 %) resulted in more than sixty five per cent (69.30 %) removal of quinalphos residues three days after spraying and this treatment was significantly superior over all the other treatments. There was no significant difference in percentage removal of quinalphos residues in curry leaf when subjected to dipping in turmeric (1 %), luke warm water and buttermilk (2 %), washing with water. The different decontaminating solutions resulted in 58.53 (luke warm water), 57.86 (1 % turmeric), 50.90 (2

% common salt), 45.65 (2 % vinegar) and 40.40 per cent (2 % buttermilk) removal of quinalphos residues. Similarly in the case of 1st day samples, a significant reduction in quinalphos residues was observed for all the decontaminating solutions when compared with washing in tap water (40.55 %).

Same scenario was also found in case of 5th day samples where dipping in tamarind solution (2 %) showed higher reduction (62.80 %). There was no significant difference between dipping in common salt (2 %) and luke warm water and buttermilk (2 %) and washing in water. The losses incurred due to various decontaminating solutions were 49.21 (1 % turmeric), 46.53 (luke warm water), 46.35 (2 % common salt), 43.45 (2 % vinegar) and 30.37 per cent (2 % buttermilk). Overall, a significant reduction in quinalphos residues was observed for all the decontaminating solutions when compared with washing in tap water (36.52 %).

Based on the percentage removal of residues, it was statistically proved that there is significant difference in the efficiency of all decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying)

4.6.1.3.5 *Profenophos*

Concentration of 51.23 mg kg^{-1} (5 h after spraying) of profenophos on curry leaf dissipated to 37.47, 19.80 and 11.20 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 33). There was significant difference in the rate of degradation of residues during the study period.

The percentage removal of profenophos residues in curry leaf when subjected to different decontaminating solutions 5 h after spraying showed that there was no significant difference in percentage removal of profenophos residues in curry leaf when dipped in common salt (2 %), turmeric (1 %) and tamarind (2 %), buttermilk (2 %).

Table 37. Extent of removal of insecticide residues from curry leaf collected at 5th day after spraying*

Insecticides	Mean per cent removal of insecticides (%) ± SD						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	38.70 ± 1.45 (1.17)	19.26 ± 1.08 (1.55)	18.71± 1.30 (1.56)	19.01 ± 1.23 (1.55)	9.30 ± 0.73 (1.74)	23.97 ± 1.46 (1.45)	16.35 ± 1.02 (1.60)
Malathion	79.57 ± 1.39 (0.04)	71.63 ± 1.99 (0.06)	61.60 ± 2.86 (0.08)	62.64 ± 2.02 (0.08)	51.49 ± 1.72 (0.10)	35.16 ± 1.67 (0.13)	46.45 ± 1.27 (0.11)
Chlorpyriphos	60.24 ± 2.09 (0.18)	30.69 ± 1.29 (0.28)	42.81± 2.14 (0.23)	33.13 ± 0.72 (0.27)	18.50 ± 0.99 (0.33)	39.48 ± 1.13 (0.25)	29.92 ± 0.86 (0.28)
Quinalphos	62.80 ± 0.92 (0.41)	43.45 ± 0.88 (0.62)	49.21± 1.90 (0.56)	46.35 ±1.14 (0.60)	30.37 ± 1.53 (0.77)	46.53 ± 2.01 (0.59)	36.52 ± 6.14 (0.70)
Profenophos	53.54 ± 5.87 (5.20)	46.93 ± 1.56 (5.94)	53.63± 1.95 (5.19)	32.98 ± 1.22 (7.53)	32.58 ± 4.56 (7.55)	47.32 ± 1.88 (5.90)	34.97 ± 1.28 (7.28)
Ethion	59.56 ± 9.22 (4.52)	48.34 ± 2.18 (5.77)	50.38 ± 0.90 (5.54)	41.25 ± 0.63 (6.56)	34.29 ± 0.63 (7.29)	56.26 ± 1.24 (4.81)	38.04 ± 1.19 (6.92)
Cypermethrin	53.93 ± 1.43 (0.05)	46.83 ± 1.80 (0.05)	48.27± 2.42 (0.05)	30.09 ± 0.45 (0.07)	30.57 ± 0.45 (0.07)	38.42 ± 2.08 (0.06)	32.04 ± 1.96 (0.06)
Fenvalerate	51.22 ± 4.89 (0.64)	45.79 ± 1.03 (0.72)	38.49± 2.24 (0.82)	30.40 ± 0.78 (0.92)	27.65 ± 0.78 (0.96)	45.33 ± 1.22 (0.73)	31.58 ± 0.50 (0.90)
CD (5%)	1.30						

Value in parentheses are concentration of insecticide residues in mg kg^{-1}

*subjected to dipping in different treatment solutions for 15 min.

The percentage removal of profenophos residues in curry leaf when dipped in decontaminating solutions were 90.40 (2 % common salt), 82.09 (2 % tamarind), 82.02 (2 % buttermilk), 74.99 (2 % vinegar) and 72.10 per cent (luke warm water). Overall, a significant reduction in profenophos residues was observed for all the decontaminating solutions when compared with washing in tap water (52.04 %).

Dipping in common salt (2 %) solution showed higher reduction in profenophos residues (88.52 %) one day after spraying. No significant difference was observed between turmeric (1 %) and common salt (2 %). The losses incurred due to various decontaminating solutions were 87.59 (1 % turmeric), 77.25 (2 % tamarind), 73.74 (2 % buttermilk), 68.94 (2 % vinegar) and 61.46 per cent (luke warm water). A significant reduction in profenophos residues was observed for all the decontaminating solutions when compared with washing in tap water (51.06 %).

Dipping in tamarind solution (2 %) resulted in more than sixty per cent (67.52 %) removal of profenophos residues three days after spraying this treatment was significantly superior over all the other treatments. There was no significant difference between turmeric (1 %) and washing with luke warm water. The different decontaminating solutions resulted in 59.75 (luke warm water), 59.50 (1 % turmeric), 50.95 (2 % vinegar), 48.88 (2 % common salt) and 47.25 per cent (2 % buttermilk) removal of profenophos residues. Similarly in the case of 1st day samples, a significant reduction in profenophos residues was observed for all the decontaminating solutions when compared with washing in tap water (44.55 %).

No significant difference in percentage removal was observed between tamarind (2 %) and common salt solution (2 %), vinegar (2 %) and luke warm water and common salt (2 %) and buttermilk (2 %). The losses incurred due to various decontaminating solutions were 53.63 (1 % turmeric), 53.54 (2 %

tamarind), 47.32 (luke warm water), 46.93 (2 % vinegar), 32.98 (2 % common salt) and 32.58 per cent (2 % buttermilk). A significant reduction in profenophos residues was observed for all the decontaminating solutions when compared with washing in tap water (34.97 %).

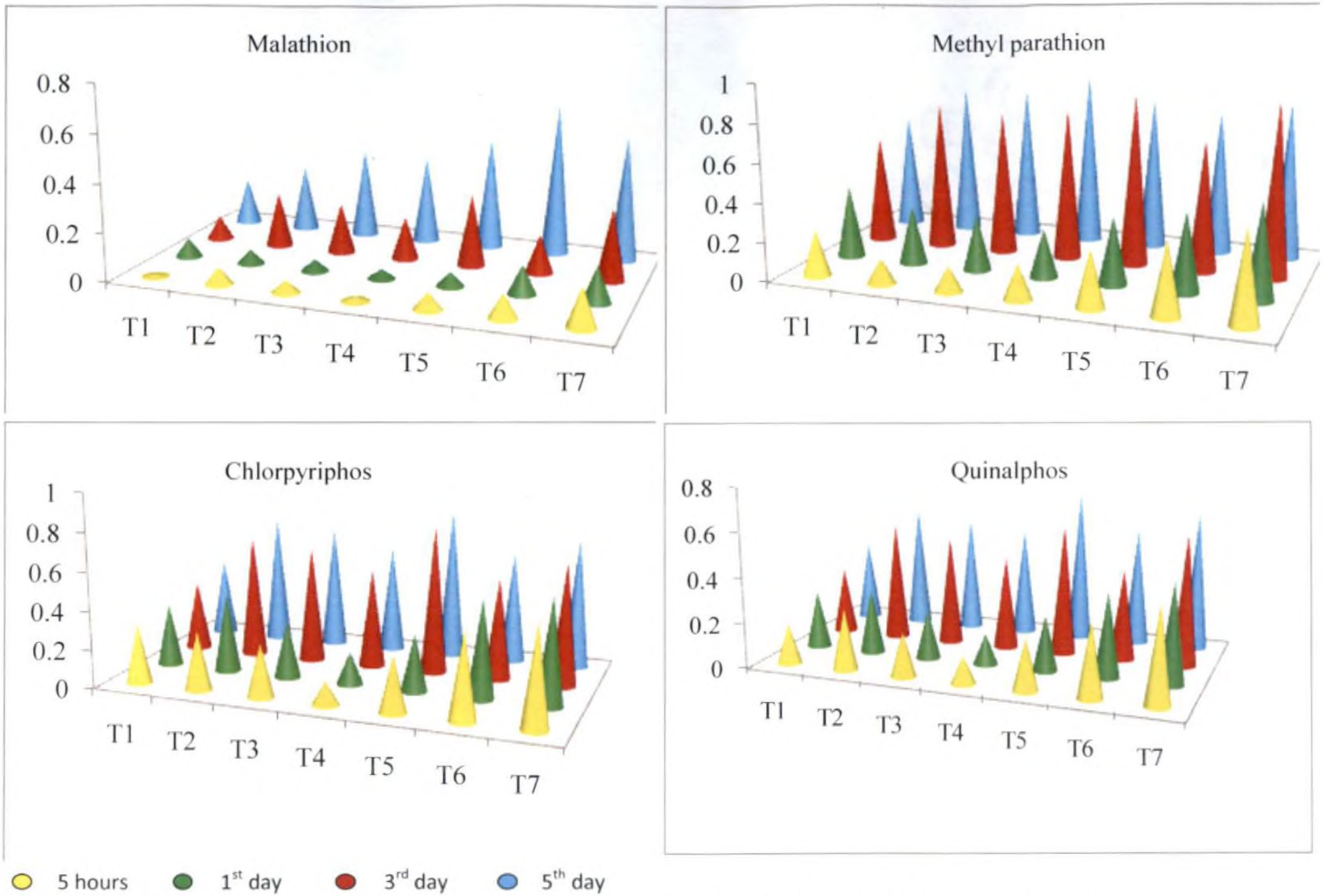
Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of luke warm water and simple washing in tap water in removing the residues of profenophos 1st day and 3rd day and 5 h and one day after spraying. On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying).

4.6.1.3.6 *Ethion*

Concentration of 43.29 mg kg^{-1} (5 h after spraying) of ethion on curry leaf dissipated to 31.40, 19.79and 11.18 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 33). There was significant difference in the rate of degradation of residues during the study period.

The percentage removal of ethion residues in curry leaf when subjected to different decontaminating solutions 5 h after spraying showed that all the treatments significantly differed among each other. It has been found that dipping in turmeric solution (1 %) was found to be more effective than other treatments. In this process the residues could be reduced upto 87.84 per cent. The percentage removal of ethion residues when dipped in other decontaminating solutions were 82.83 (2 % common salt), 79.84 (2 % tamarind), 76.23 (2 % buttermilk), 70.92 (2 % vinegar) and 64.44 per cent (luke warm water). Overall, a significant reduction in ethion residues was observed in all the decontaminating solutions when compared with washing in tap water (52.78 %).

Dipping in turmeric solution (1 %) showed higher reduction in ethion


Malathion

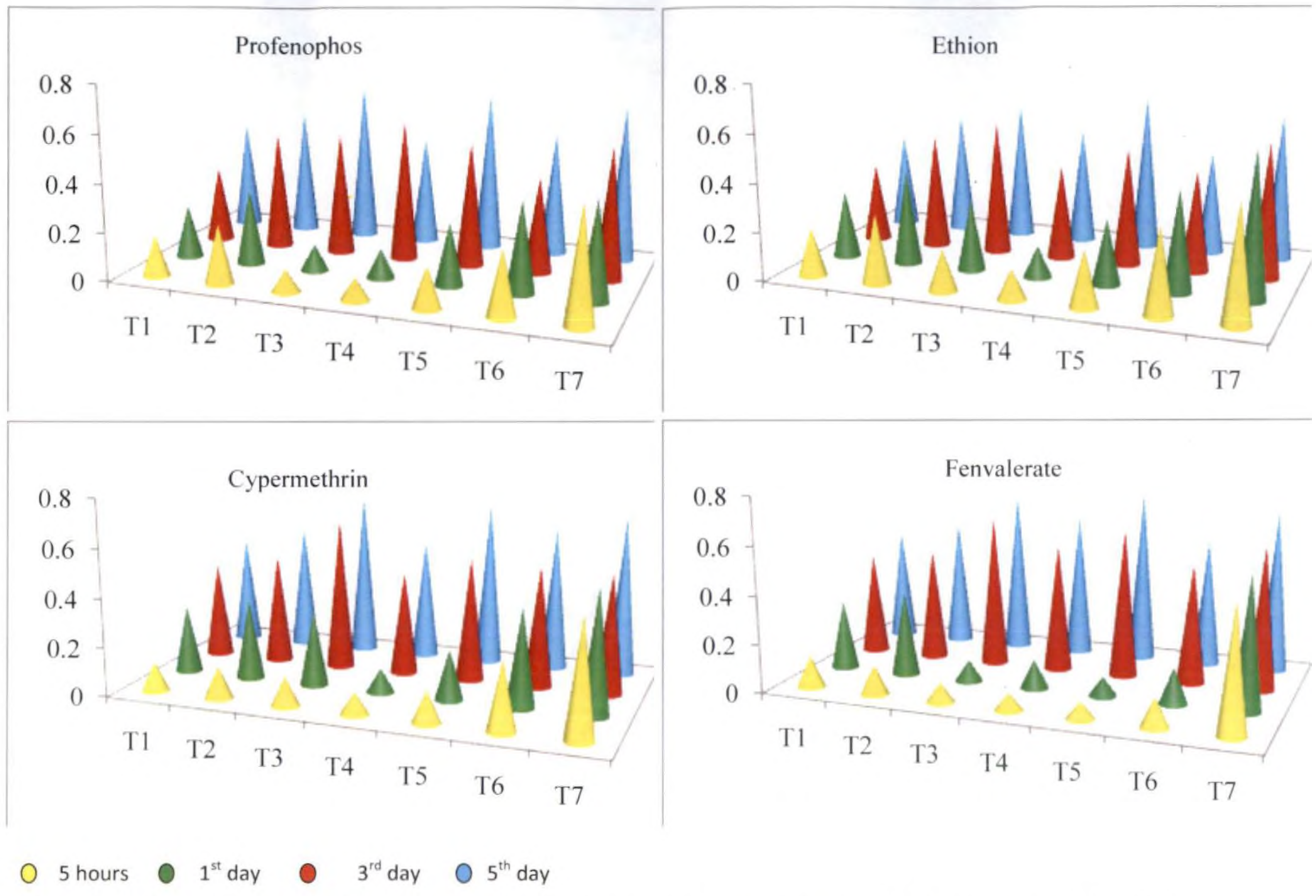
Methyl parathion

Chlorpyriphos

Quinalphos

T1: 2% tamarind, T2: 2% vinegar, T3: 2% common salt, T4: 1% turmeric, T5: 2% buttermilk, T6: luke warm water, T7: water
(X axis: Decontaminating solutions; Y axis: Processing factor)

Fig. 8. Efficiency (processing factor) of decontaminating solutions in removing insecticide residues from curry leaf at different time intervals after insecticide spraying



T1: 2% tamarind, T2: 2% vinegar, T3: 2% common salt, T4: 1% turmeric, T5: 2% buttermilk, T6: luke warm water, T7: water
(X axis: Decontaminating solutions; Y axis: Processing factor)

Fig. 8. Efficiency (processing factor) of decontaminating solutions in removing insecticide residues from curry leaf at different time intervals after insecticide spraying

residues (86.99 %) one day after spraying. All the decontaminating solutions except three *ie* tamarind (2 %), buttermilk (2 %) and common salt (2 %) significantly differed among each other in their efficiency in removing the residues. The losses incurred due to various decontaminating solutions were were 72.35 (2 % buttermilk), 71.26 (2 % tamarind), 70.88 (2 % common salt), 60.37 (2 % vinegar) and 57.25 per cent (luke warm water). A significant reduction in ethion residues was observed in all the decontaminating solutions when compared with washing in tap water (39.94 %).

Dipping in tamarind solution (2 %) resulted in more than sixty five percent (67.00 %) removal of ethion residues three days after spraying and this treatment was significantly superior over all the other treatments. All the decontaminating solutions except two *ie* common salt (2 %) and washing with water significantly differed among each other in their efficiency in removing residues. Other decontaminating solutions resulted in 60.98 (1 % turmeric), 57.15 (luke warm water), 51.71 (2 % vinegar), 50.19 (2 % buttermilk) and 43.34 per cent (2 % common salt) removal of ethion residues. Similarly in the case of 1st day samples, a significant reduction in ethion residues was observed in all the decontaminating solutions except common salt (2 %) when compared with washing in tap water (43.91).

Same scenario was also found in case of 5th day samples where dipping in tamarind solution (2 %) showed higher reduction (59.56 %). Significant difference in percentage removal of ethion residues was observed in all decontaminating solutions. The losses incurred due to various decontaminating solutions were 56.26 (luke warm water), 50.38 (1 % turmeric), 48.34 (2 % vinegar), 41.25 (2 % common salt) and 34.29 per cent (2 % buttermilk). A significant reduction in ethion residues was observed in all the decontaminating solutions when compared with washing in tap water (38.04 %).

Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of turmeric (1 %) in removing the residues of ethion 5 h and 1st day after spraying and in luke warm water 1st day, 3rd day and 5th day after spraying On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying).

4.6.1.3.7 *Cypermethrin*

The concentration of 0.27 mg kg^{-1} (5 h after spraying) of cypermethrin on curry leaf dissipated to 0.21, 0.18 and 0.10 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 33). There was significant difference in the rate of degradation of residues during the study period.

No significant difference in percentage removal of cypermethrin residue was observed between tamarind (2 %) and vinegar (2 %), common salt (2 %) and buttermilk (2 %). It has been found that dipping in turmeric solution (1 %) was found to be more effective than other treatments. In this process, the residues could be reduced upto 90.93 per cent.The percentage removal of cypermethrin residues when dipped in other decontaminating solutions were 87.53 (2 % tamarind), 87.26 (2 % common salt), 86.51 (2 % buttermilk) 86.27 (2 % vinegar) and 71.76 per cent (luke warm water). Overall, a significant reduction in cypermethrin residues was observed in all the decontaminating solutions when compared with washing in tap water (51.84 %).

Dipping in turmeric solution (1 %) showed higher reduction in cypermethrin residues (89.37 %) one day after spraying. No significant difference was observed in the case of common salt (2 %) and vinegar (2 %). The losses incurred due to various decontaminating solutions were 78.46 (2 % buttermilk), 71.98 (2 % tamarind), 68.14 (2 % common salt), 66.82 (2 %

vinegar), and 58.84 per cent (luke warm water). A significant reduction in cypermethrin residues was observed in all the decontaminating solutions when compared with washing in tap water (48.58 %).

Dipping in tamarind solution (2 %) resulted in nearly sixty percent (59.51 %) removal of cypermethrin residues three days after spraying and this treatment was significantly superior over all the other treatments. There was no significant difference between dipping in butter milk (2 %), luke warm water and washing with tap water. The different decontaminating solutions resulted in 56.79 (1 % turmeric), 53.70 (2 % vinegar), 48.63 (luke warm water), 47.64 (2 % buttermilk) and 36.26 per cent (2 % common salt) removal of cypermethrin residues. Similarly in the case of 1st day samples, a significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (49.17 %).

Same scenario was also found in case of 5th day samples where dipping in tamarind solution (2 %) showed higher reduction (53.93 %). There was no significant difference between common salt (2 %) and butter milk (2 %). The losses incurred due to various decontaminating solutions were 48.27 (1 % turmeric), 46.83 (2 % vinegar), 38.42 (luke warm water), 30.57 (2 % buttermilk) and 30.09 per cent (2 % common salt). A significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (32.04 %).

Based on the percentage removal of residues, it was statistically proved that there is no significant difference in the efficiency of simple washing with tap water in removing the residues of cypermethrin 5 h and one day after spraying. On the other hand, there is significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying).

4.6.1.3.8 *Fenvalerate*

Concentration of 4.43 mg kg^{-1} (5 h after spraying) of fenvalerate on curry leaf dissipated to 3.59, 2.37 and 1.33 mg kg^{-1} on 1st, 3rd and 5th day after spraying (Table 33). There was significant difference in the rate of degradation of residues during the study period.

No significant difference in percentage removal of fenvalerate in curry leaf was observed in tamarind solution (2 %) and luke warm water, turmeric solution (1 %) and buttermilk (2 %) solution. It has been found that dipping in turmeric (1 %) solution and 2 % buttermilk (2 %) solution was found to be more effective than other treatments since there is no significant difference in percentage removal of residues between these two treatments. In this process, the residues could be reduced upto 92.61 and 92.15 per cent respectively. The percentage removal of fenvalerate residues in curry leaf when dipped in other decontaminating solutions were 91.34 (2 % common salt), 87.09 (2 % vinegar), 87.05 (luke warm water) and 86.97 per cent (2 % tamarind). Overall, a significant reduction was observed in all the decontaminating solutions when compared with washing in tap water (47.33 %).

Dipping in turmeric solution (1 %) for 15 min followed by washing in tap water showed higher reduction in fenvalerate residues (87.88 %) one day after spraying. No significant difference in percentage removal was observed in the case of common salt (2 %) and butter milk solution (2 %). The losses incurred due to various decontaminating solutions were 90.25 (2 % common salt), 90.22 (2 % buttermilk), 84.86 (luke warm water), 70.39 (2 % tamarind) and 64.95 (2 % vinegar). A significant reduction in fenvalerate residue was observed in all the decontaminating solutions when compared in washing with tap water (44.08 %).

Dipping in tamarind solution (2 %) for 15 min followed by washing in tap water resulted in more than fifty percent (56.16 %) removal of fenvalerate residues three days after spraying and this treatment was significantly superior over all the other treatments. There was no significant difference between butter milk (2 %) and common salt (2 %)solution. The different decontaminating solutions resulted in 52.69 (2 % vinegar), 49.09 (luke warm water), 45.32 (1 % turmeric), 37.75 (2 % buttermilk) and 36.44 per cent (2 % common salt) removal of fenvalerate residues. Similarly in the case of 1st day samples, a significant reduction in fenvalerate residue was observed in all the decontaminating solutions when compared with washing in tap water (39.90 %).

Same scenario was found in case of 5th day samples where dipping in tamarind solution (2 %) for 15 min followed by washing in tap water showed higher reduction (51.22 %). There was no significant difference between 2 % vinegar (2 %) and luke warm water. The losses incurred due to various decontaminating solutions were 45.79 (2 % vinegar), 45.33 (luke warm water), 38.49 (1 % turmeric), 30.40 (2 % common salt) and 27.65 per cent (2 % buttermilk). A significant reduction in fenvalerate residue was observed for all the decontaminating solutions when compared in washing with tap water (31.58 %).

Based on the percentage removal of residues, it was statistically proved that there was no significant difference in the efficiency of common salt (2 %) in removing the residues of fenvalerate 5 h and one day after spraying. On the other hand, there was significant difference in the efficiency of all other decontaminating solutions in removing the residues at different intervals (5h, 1st day, 3rd day and 5th day after spraying).

Discussion

5. DISCUSSION

Investigation carried out to monitor the level of pesticide residues in different agricultural commodities and to assess the effect of washing, soaking and cooking in rice, washing, sun drying and milling in wheat, decortication in cardamom on the removal of pesticide residues are discussed hereunder. Studies on validation of multi residue method for the estimation of pesticide residues and the standardization of washing solutions of household product to remove the residues from vegetables like capsicum, okra and curry leaf are also discussed below.

5.1 VALIDATION OF MULTI RESIDUE METHODS (MRM) FOR PESTICIDE RESIDUE ANALYSIS IN AGRICULTURAL COMMODITIES

Analytical methods that are used to monitor pesticide residue levels in food should be capable of measuring pesticide residues at very low levels (Taylor *et al.*, 2002). In addition, these methods should be capable to identify and quantify the types of pesticides found in food products (Sannino *et al.*, 2004). Furthermore, these methods should be fast, robust and simple. Multi residue methods are ideally suited to satisfy these requirements for pesticides, since they are typically simple, robust and rapid.

In this study, Multi Residue Methods (MRM) for pesticide residue analysis of rice flour, wheat flour (atta and maida), rice, wheat, cardamom, cumin seed, capsicum, okra and curry leaf were validated by conducting recovery studies. The method satisfying requirements of Limit of Detection, Limit of Quantification, Linearity, Recovery and Repeatability was selected for the estimation of multiple pesticide residues. The results demonstrated that the method followed for each commodity had a satisfactory analytical performance in terms of selectivity and linearity. Good linearity was found within the range of 0.01-0.5 mg kg^{-1} for the 21 pesticides belonging to OC, OP and SP insecticide groups (Appendix I). Satisfactory recoveries and RSDs were achieved for most of the pesticides evaluated even at the lowest level of fortification. The mean recovery of all the 21 pesticides under study were in the range 70 - 110 per cent and the repeatability of the recovery results, as indicated by the RSD < 20 %

confirmed that the method is sufficiently reliable for pesticide residue analysis in different agricultural commodities (Table 7 - Table 16). The optimized methods developed for each specific commodity in this study allowed rapid quantification and identification of low levels of pesticide residues.

5.2 MONITORING OF PESTICIDE RESIDUES IN AGRICULTURAL COMMODITIES

Pesticides are recognised as important for food production, but their use might cause potential health risks from both occupational and non-occupational exposures. For example, different pesticides have been implicated in chronic neurotoxicity, endocrine disruption, immune impacts, genotoxicity, mutagenicity and carcinogenesis through routes that include consumption of dietary residues. So constant monitoring of pesticide residues in agricultural commodity is needed for ensuring food safety to consumers. In this study, agricultural commodities like rice (parboiled, raw and basmathi), branded rice flour, wheat, wheat flour (atta and maida), cardamom, cumin seed, capsicum, okra and curry leaf were tested for the presence of pesticide residues. Results of the monitoring study conducted in Thiruvananthapuram district during January - June 2012 (Table 17) are discussed below.

Out of the 72 samples analysed, 33 samples showed the presence of various pesticides, whereas 39 samples were free of residues. Among the total 72 samples, 11 samples showed residues of single pesticide while 22 samples showed residues of multiple pesticides. Monitoring of pesticide residues in agricultural commodity in Thiruvananthapuram district during January-June 2012 revealed the presence of 14 different pesticide molecules *viz.*, malathion, chlorpyriphos, fenvalerate, methyl parathion, cypermethrin, quinalphos, profenophos, bifenthrin, lambda cyhalothrin, ethion, alpha endosulphan, triazophos, fenpropathrin and cyfluthrin belonging to organophosphate (7), synthetic pyrethroid (6) and organochlorine (1) group. Among the different pesticides, chlorpyriphos (O, O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate) was the most frequently detected insecticide. It was detected in 20 samples out of the 72 samples analyzed (Table 38). The most likely explanation for the presence of chlorpyriphos in agricultural commodity is due to its preference by farmers because of its broad spectrum activity as insecticide, acaricide and nematicide and its lesser price. Its high preference is clear from its high production rate (3887 MT/year) (Arora *et al.*, 2011).

Table 38. Frequency of occurrence of insecticides in different agricultural commodities like rice(basmathi, parboiled and raw rice), rice flour, wheat, wheat flour (atta and maida), cardamom, cumin seed, capsicum, okra and curry leaf.

Sl No	Pesticides	No, of samples analyzed	No, of samples with detected pesticides
1	Chlorpyriphos	72	20
2	Profenophos	72	19
3	Cypermethrin	72	12
4	Quinalphos	72	10
5	Malathion	72	7
6	Lambda cyhalothrin	72	6
7	Methyl parathion	72	3
8	Alpha endosulphan	72	3
9	Triazophos	72	3
10	Fenpropathrin	72	2
11	Bifenthrin	72	2
12	Ethion	72	2
13	Fenvalerate	72	1

Profenophos (O-(4-bromo-2-chlorophenyl) O-ethyl S-propyl phosphorothioate) has been the second frequently detected organophosphate (19 samples) pesticide, registered for use only in cotton and tea in India. Along with the contact and stomach action, profenophos exhibits a translaminar action by penetrating into leaf tissues, that make it more effective against sucking pest complex including insects and mites in tea and cotton (Mathew, 2012). Because of its translaminar, ovicidal and growth stimulating nature, it is widely used by the farmers. It may be the reason for the frequent occurrence of profenophos residues in agricultural commodities. Being a pesticide banned for sale and use in Kerala state, its presence in vegetables to the tune of 0.033 to 25.63 mg kg^{-1} has to be viewed seriously. Continued use of profenophos in vegetable crops cultivated in the neighbouring states inspite of not having any label claim or recommendation is evident from present studies.

Cypermethrin (12 samples) and quinalphos (10 samples) were the next most frequently detected pesticide, but at substantially lower frequency than chlorpyriphos and profenophos. The present findings on the occurrence of chlorpyriphos and profenophos residues in agricultural commodities is in agreement with that of Marasinghee and his co workers (2011) who reported the occurrence of residues of chlorpyriphos and profenophos in different agricultural commodities in Srilanka.

Considering pesticide groups, it may be concluded that insecticides belonging to organophosphate group predominated over synthetic pyrethroid and organochlorine compounds. This trend is supported by the consumption pattern of pesticides which also indicated greater use of organophosphates when compared with synthetic pyrethroids and organochlorines (Adityachaudhury *et al.*, 1997). From this study it is clear that organophosphate insecticides are the compounds of most concern for health risk, with the intake coming mainly from consumption of cereals, spices and vegetables. Dietary exposure to organophosphate insecticides is of health concern due to potential cumulative effects of these pesticides that act through a common mechanism of toxicity, the inhibition of acetyl cholinesterase (Ecobichon, 1995).

The study revealed the presence of pesticide residues in cereals like basmathi rice and wheat. Five samples each of basmathi rice and wheat was found to be contaminated with residues of insecticides like chlorpyriphos (0.025 - 0.31 mg kg^{-1}), malathion (0.025 - 0.19 mg kg^{-1}), methyl parathion (0.024 - 0.065 mg kg^{-1}), quinalphos (0.039 - 0.046 mg kg^{-1}), cypermethrin (0.011 mg kg^{-1}) and fenvalerate (0.052 mg kg^{-1}). Among the different insecticides, chlorpyriphos (3/12) and malathion (5/12) were the major contaminants. Organophosphates like malathion, chlorpyriphos, dichlorovos (DDVP), fenitrothion and synthetic pyrethroids like cypermethrin are reported to be misused widely as grain protectants during storage (Zhang, 2010). Basmathi rice being the most expensive brand of rice, grain protectants are more likely to be applied which might have resulted in pesticide residue. In contrary to this, none of the samples of raw rice and parboiled rice showed the residues of any pesticide. This indicated a low level of pesticide usage in stores keeping raw and parboiled rice, obviously due to lower level of infestation by storage pests.

In the present investigation, none of the samples of rice flour and wheat flour (atta and maida) showed presence of pesticide residues. Fractionation of residues in different wheat and rice portions (bran, germ, semolina, grout and flour) during milling and polishing could be the reason for the absence of pesticide residues in atta, maida and rice flour. Our findings are in line with those of Uygun and co workers (2005) who reported that the reduction of malathion residues was about 95 per cent in wheat through milling (to flour). In the case of wheat, pesticides are retained on the seed coat and tent to concentrate in the bran and germ which contain high levels of triglycerides and the transfer of residues to flour will be low (Holland *et al.*, 1994).

The data generated through monitoring studies in cardamom have established the overdependence and abuse of pesticides as evident from the range of chemically different pesticides like chlorpyriphos, quinalphos, profenophos, cypermethrin, lambda cyhalothrin, ethion and bifenthrin identified and quantified. Presence of multiple residues has undoubtedly established rotational spraying of these pesticides directly on capsules. All the cardamom samples analyzed during the study period contained residues above MRLs fixed by FSSAI and all the insecticides detected except quinalphos were not at all registered for use in cardamom (Table 39). Usha (2007) reported that there has been an increase in the pesticide consumption in cardamom during the last ten years and the results of a survey showed an unscientific and non judicious use of pesticides by farmers in Kattapana block of Idukki district. The present finding on the occurrence of various insecticide residues in cardamom is also in agreement with the findings of Seena (2013) who reported occurrence of residues of pesticides like quinalphos, chlorpyriphos, profenophos, lambda cyhalothrin, ethion, cypermethrin and bifenthrin in cardamom samples collected from cardamom growing tracts of Idukki district.

Cumin seed samples tested in the present study were found to be frequently contaminated with residues of profenophos, chlorpyriphos, quinalphos and alpha endosulphan for which no FSSAI MRL exists which means none of the pesticides detected were registered for use in this commodity. It was reported that residues of organophosphate pesticides like malathion (4.1 mg kg^{-1}) and diazinon (7.6 mg kg^{-1}) (Sarkhail, *et al.,* 2012) and organochlorine pesticides like DDT (0.055 mg kg^{-1}) and HCH (0.0467 mg kg^{-1}) have been detected in cumin seed collected from the local markets of Lucknow, India (Srivastava *et al.,* 2001). Cumin seed is an important spice consumed by Keralites as an important constituent of masala powder and also for making the drink, Jeera water. However, the insecticides detected in the samples were not found to be transferred to Jeera water, when boiled with water and the residues were found retained in the cumin seed fraction only (Mathew, personal communication, 2012)

Monitoring of pesticide residues in curry leaf revealed the presence of 12 different pesticide molecules *viz.*, chlorpyriphos, quinalphos, profenophos, triazophos, methyl parathion, cypermethrin, alpha endosulphan, malathion, fenpropathrin, cyfluthrin, bifenthrin and ethion at varying levels. A level as high as 25.63 mg kg^{-1} of profenophos was detected in one sample of curry leaf. Eventhough it is not registered for use in curry leaf, it is widely used against psyllids, citrus butterfly and citrus leaf roller in curry leaf because of its high bioefficacy, translaminar and growth promoting action (Sreedharan, personal communication, 2013). Shaji (n.d) reported that curry leaves cultivated in villages in and around Mettupalayam near Coimbatore was sprayed with endosulphan several times, a banned pesticide that is facing a global phase out because of its toxicity Viju (2012) quoted the results generated by AINP (PR) Vellayani, that curry leaves (47 of 79 samples) collected from different markets of Kerala had traces of pesticides like profenophos and triazophos which should not have been used in that crop. Yadav (2013) reported that curry leaves from India have been banned in UAE since June 2010 due to high level of pesticide residues. Nair (2013) reported that European Union Rapid Alert System for Food and Feed alert notification claimed the reinforced controls for pesticide residues in 2011 and identified two food items from India – curry leaves and okra – as having multi-residue of pesticides in consignments that were checked. So, Spices Board has made it mandatory for exporters to get the export consignments of curry leaves to the European Union be subjected to Cleared Analytical Reports on pesticides such as profenophos, triazophos and endosulphan from January 18, 2013. Mohan (n.d.) reported that curry leaves have received red alert message from the European Union who are the major importers where, the pesticide residue limits were found beyond the permissible levels. It was reported that specific conditions are applicable for the import of curry leaves and okra from India due to high pesticide load (Anonymous, 2013b).

Among the three different commodities viz. cereals, vegetables and spices, highest pesticide residue accumulation was observed in spices and it may be due to the greater scope of pesticide application in spices considering high economic value they posses in the domestic and international markets.

Most of the samples tested in the present study had multiple residues with some samples containing three to six pesticides. However, most of these detected pesticides were not registered for use in India by CIB(RC) in that specific commodity (Table 39). All the cardamom, cumin seed and curry leaf samples showed multiple pesticide residues at varying levels. None of the pesticides detected in curry leaf and cumin seed were registered for use in these commodities. Another important factor to consider is the presence of pesticides like methyl parathion, profenophos and endosulphan in basmathi rice, cardamom, cumin seed, curry leaf, capsicum and okra samples tested which were banned for sale and use in Kerala state.

Human beings are exposed to pesticide through the consumption of treated food that contain their residues. So assessment of dietary exposure to pesticides which combines both food consumption data and data on the concentration of pesticides in food are essential. In this study, long term (chronic) and short term

Table 39. Categorization of detected pesticides in agricultural commodities in relation to label claim

Commodity	Registered pesticide	Unregistered pesticide	Commodity	Registered pesticide	Unregistered pesticide
Basmathi rice	Malathion	Methyl parathion	Curry leaf		Profenophos
	Chlorpyriphos	Cypermethrin			Chlorpyriphos
		Fenvalerate			Quinalphos
Wheat	Malathion	Quinalphos			Alpha endosulphan
	Chlorpyriphos	Methyl parathion			Triazophos
Cardamom	Quinalphos	Chlorpyriphos			Ethion
		Profenophos			Bifenthrin
		Ethion			Cypermethrin
		Lambda cyhalothrin			Fenpropathrin
		Bifenthrin			Malathion
		Cypermethrin			Methyl parathion
Cumin seed		Profenophos	Capsicum	Chlorpyriphos	Profenophos
		Chlorpyriphos	Okra	Malathion	Profenophos
		Quinalphos			
		Alpha endosulphan			

(acute) health risk to consumers by pesticide through intake of contaminated food were estimated in terms of ADI and ARfD values for each commodity using the highest detected pesticide residue levels, based on methods recommended by the WHO (WHO, 2003). WHO has recommended to compare highest detected level of pesticide with percentage of ARfD and percentage of ADI for assessing acute and chronic health risk. If pesticides detected resulted in an intake of >50 per cent of percentage of ARfD and >4 per cent of percentage of ADI value, it can be considered to cause acute and chronic health risk (Dalvie and London, 2009)

Highest detected level of the pesticides like lambda cyhalothrin and ethion in cardamom, chlorpyriphos, profenophos and alpha endosulphan in cumin seed and chlorpyriphos, profenophos, malathion, cypermethrin, ethion and bifenthrin in curry leaf exceed the ARfD values (Table 40). However, none of the detected pesticides resulted in an intake of >50 % of ARfD value which gave an impression of no acute health risk, as per the guidelines of WHO.

Among the different agricultural commodity like cardamom, cumin seed and curry leaf, highest detected level of pesticides like (lambda cyhalothrin and ethion in cardamom, profenophos in cumin seed and chlorpyriphos, profenophos and ethion in curry leaf) exceeded >4 % of ADI value fixed for the representative insecticides (Table 40). Among the different pesticides studied, profenophos was present in levels >85.00 % of the ADI which represented a very high level of a chronic health risk to consumers as indicated by more than 20 times that of the safe margin prescribed by Dalvie and London (2007). Among the pesticides detected in the study, there are four possible carcinogens (cypermethrin, methyl parathion, malathion and quinalphos) and one suspected endocrine disruptor (fenvalerate), one reproductive and developmental toxins (chlorpyriphos) and five neurotoxins (profenophos, malathion, methyl parathion, ethion and quinalphos) (Table 1) but these effects are accounted for in ADI setting (EFSA, 2008). So it may be concluded that consumption of cardamom, curry leaf and cumin seed for a longer period of time can cause chronic health risk to consumers.

Table 40. Risk assessment of pesticides detected in different agricultural commodities.

Commodity	*Amount consumed per day (g/day/person)	Pesticides detected (mg kg^{-1})	Highest residue level (mg kg^{-1})	Average daily intake (mg /kg bodyweight)	**ADI(mg/kg body weight)	% of ADI based on highest residue level	**ARfD (mg/kg bw)	% of ARfD based on highest residue level
Basmathi rice	275.00	Malathion	0.08	3.6 x 10^{-4}	0.03	0.26	0.3	0.02
		Methyl parathion	0.046	2.1 x10^{-4}	0.003	1.53	0.3	0.015
		Chlorpyriphos	0.025	1.14 x10^{-4}	0.01	0.25	0.1	0.025
		Cypermethrin	0.011	5.04 x10^{-5}	0.05	0.02	0.2	0.005
		Fenvalerate	0.052	2.38 x10^{-4}	0.02	0.26	NA	-
Wheat	172.80	Malathion	0.19	5.4 x10^{-4}	0.03	0.63	0.3	0.06
		Methyl parathion	0.065	1.8x10^{-4}	0.003	2.16	0.3	0.021
		Chlorpyriphos	0.31	8.9 x10^{-4}	0.01	3.1	0.1	0.31
		Quinalphos	0.039	1.12 x10^{-5}	NA	-	NA	-
Cardamom	0.8	Chlorpyriphos	0.353	4.7 x10^{-9}	0.01	3.53	0.1	0.353
		Quinalphos	2.044	2.72 x10^{-5}	NA	-	NA	-
		Profenophos	0.954	1.27 x10^{-6}	0.03	3.18	1.0	0.09

Table 40. continued

Commodity	*Amount consumed per day (g/day/person)	Pesticides detected (mg kg^{-1})	Highest residue level (mg kg^{-1})	Average daily intake (mg /kg bodyweight)	**ADI(mg/kg body weight)	% of ADI based on highest residue level	**ARfD (mg/kg bw)	% of ARfD based on highest residue level
Cardamom	0.8	Lambda cyhalothrin	0.364	4.85 x\`10^{-6}	0.005	7.28	0.0074	11.50
		Cypermethrin	0.461	6.14 x10^{-6}	0.05	0.92	0.2	0.23
		Ethion	0.344	4.58 x10^{-6}	0.002	17.20	0.015	2.29
		Bifenthrin	0.106	1.41 x10^{-6}	0.015	0.70	0.03	0.35
Cumin seed	*0.8*	Chlorpyriphos	0.27	3.6 x10^{-6}	0.01	2.7	0.1	0.27
		Quinalphos	0.139	1.85 x10^{-6}	NA	-	NA	-
		Profenophos	1.45	1.33 x10^{-5}	0.03	4.83	1.0	0.14
		Alpha endosulphan	0.135	1.80 x10^{-5}	0.006	2.25	0.02	0.67
Capsicum	8.7	Profenophos	0.033	4.7 x10^{-6}	0.03	0.11	1.0	0.033
		Chlorpyriphos	0.047	6.81 x10^{-6}	0.01	0.47	0.1	0.047
Okra	4.1	Profenophos	0.121	8.26 x10^{-6}	0.03	0.40	1.0	0.012
		Malathion	0.038	2.59 x10^{-6}	0.03	0.12	0.3	0.012

Table 40. continued

Commodity	*Amount consumed per day (g/day/person)	Pesticides detected (mg kg^{-1})	Highest residue level (mg kg^{-1})	Average daily intake (mg /kg bodyweight)	**ADI(mg/kg body weight)	% of ADI based on highest residue level	**ARfD (mg/kg bw)	% of ARfD based on highest residue level
Curry leaf	2	Chlorpyriphos	1.34	4.46x10^{-5}	0.01	13.40	0.1	1.34
		Malathion	0.439	1.46x10^{-5}	0.03	1.46	0.3	0.14
		Quinalphos	0.259	8.63x10^{-6}	NA	-	NA	-
		Methyl parathion	0.113	3.76x10^{-6}	0.003	3.76	0.3	0.037
		Profenophos	25.63	8.54x10^{-4}	0.03	85.43	1.0	2.56
		Cypermethrin	1.44	4.8x10^{-5}	0.05	2.88	0.2	0.72
		Ethion	1.15	3.8x10^{-5}	0.002	57.50	0.015	7.66
		Bifenthrin	0.104	3.46x10^{-6}	0.015	0.69	0.03	0.34
		Fenpropathrin	0.143	4.76x10^{-6}	0.03	0.47	NA	-
		Alpha endosulphan	0.015	5x10^{-7}	0.006	0.25	0.02	0.075

*Assuming a 60 kg person, total intake of each commodity is estimated from cluster diets compiled by the Global Environment Monitoring System–Food Contamination Monitoring and Assessment Programme (WHO/GEMS/FOODS) on http://www.who.int/foodsafety/chem/gems/en/index1.html. ** PPDB: Pesticide http://sitem.herts.ac.uk/aeru/footprint/en/index.html

5.3 ASSESSMENT OF THE EFFECT OF WASHING, SOAKING AND COOKING ON REMOVAL OF INSECTICIDE RESIDUES IN RICE

Based on the monitoring data, insecticides *viz.*, malathion, methyl parathion, chlorpyriphos, quinalphos, cypermethrin and fenvalerate were selected for assessing the effect of washing, soaking and cooking on the removal of insecticide residues in rice and the results were summarized in Table 20 to 21.

A significant reduction (38.01 - 84.27 %) in the level of pesticide residues was observed during washing processes evaluated. Washing reduced significantly the levels of residue that could be dislodged by the mechanical action of rubbing of grains in presence of water. Miyahara and Saito (1994) reported that washing of soybeans twice with water reduced the pesticides like dichlorvos, malathion, chlorpyriphos and captan by 80 - 90 per cent. They suggest that sprayed pesticide remain as microparticles on the surface of the soyabean and are easily removed by mechanical stirring in water. In a study, organophosphate residues were reduced by 9 - 40 per cent by washing tomatoes and peppers in water, depending upon the type of matrix and pesticide (Celik *et al.*, 1995). It was reported that removal of pesticide residues through washing depended on the physiochemical property of the pesticides *ie* degree of degradation in water and octanol/water partition coefficient of the pesticides (Weiner, 2001). In their study, maximum percentage removal in capsicum fruits was observed in the case of malathion which had highest degree of degradation (45 %), while minimum percentage removal was reported in methyl parathion which had lowest degree of degradation (22 %). In the present study, highest removal was observed in malathion and lower in the case of methyl parathion. The results are in line with the findings of Satpathy (2011), who reported that degree of degradation of pesticides in water play a major role in determining the fate of residues during washing. Although water solubility of pesticide is an important factor during washing process, yet it has not been highlighted by some researchers (Cabras *et al.*, 1998a; Walter *et al.*, 2000) and they concluded that water solubility of pesticide is not an important parameter in the removal of pesticide residues from food crops. In the present study also, water solubility was not found to be the important factor during washing process and the results from the current study are consistent with an earlier study which showed that residues of six pesticides on olives decreased after washing with no correlation to water solubility of the pesticides (Cabras *et al.*, 1998b). The results are also in line with some recent findings, where washing decreased profenophos, cypermethrin and ethylenebisdithiocarbamates residues in asparagus by 24, 35 and 52 per cent, respectively (Chavarri *et al.*, 2005)

There was significant difference in the percentage removal of residues subjected to two and four washings in tap water along with rubbing of grains (Table 20 to 21). Four washings in tap water resulted in 44.94 - 84.27 per cent removal of residues where as two washings resulted in 38.01 - 81.93 per cent. Therefore increasing the number of washings had better performance in decontamination which might have contributed cumulative effects in improving the efficiency of washing.

Almost 62.46 - 86.80 per cent of the pesticide residues were removed from fortified rice samples through soaking followed by washing four times with rubbing (Table 20 to 21). Soaking followed by washing twice resulted in a reduction of 47.83 - 86.80 per cent. Soaking alone contributed only 17.22 - 34.56 per cent removal. Wen and his co workers (1995) studied the effect of soaking on the removal of pesticide residues in fortified potato tubers and reported that soaking resulted in only 11.2-18.1 per cent removal of dimethoate, malathion and pirimiphos methyl pesticides. However in the present study, soaking of grains had contributed an additive effect on washing in reducing the pesticide residues.

Reduction of pesticides in rice during cooking process was studied to simulate the practical exposure to the pesticide residues, and to estimate the actual concentration of exposure at the final stage of consumption. The present data revealed significant reduction in the levels of pesticides due to cooking process. The level of reduction due to cooking ranged between 78.81 - 92.59 per cent (Table 20 to 21). These findings clearly indicated that heat treatment had a significant effect on decomposition and elimination of pesticide residues. Similar results were also stated by Wen and co workers (1995) and Lalah and Wandiga (2002) who have determined the stability of toxic residues after the rice grains were subjected to cooking in boiling water. They reported that the total residues removed by cooking were 69.70 per cent from rice grains and 75.00 per cent from beans. Balinova and co workers (2006) have explained the processes that normally occur during cooking as volatilization, hydrolysis and thermal breakdown at elevated temperature, which depends on different parameters, such as vapour pressure, boiling point, and susceptibility of pesticide to hydrolysis. In this study, malathion which had the highest vapour pressure (Table 2) among the different pesticides degraded easily when compared to other insecticides.

In the present investigation, it was found that almost 98.63 - 89.92 per cent pesticide residues could be removed from fortified rice samples through washing four times with rubbing followed by cooking and draining of rice gruel from cooked grains (Table 20 to 21). Washing twice followed by cooking resulted in a reduction of 87.15 - 98.37 per cent. Washing contributed an additive effect on cooking in reducing the pesticide residues.

In the present study, it was also observed that there was no significant difference in the concentration of six pesticides belonging to organophosphates and synthetic pyrethroids, when analyzed at five hours and two weeks after insecticide application, indicating stability of the residues adhering to the grains during the period of storage (Table 19). Synthetic pyrethroids were found to be more stable when compared to organophosphates and this result is in line with the findings of Afridi and co workers (2001).

When the fortified rice samples were analyzed two weeks after spraying, though the residue levels remained almost unchanged, an overall reduction in the efficiency of different processing techniques except soaking was observed probably due to the ageing of residues which might have given stronger binding over the grain surface. Guardian-Rubio and co workers (2007) found that it was easier to wash off the pesticide residues from olives one day after spraying than from the fruits harvested after one week. Krol and co workers (2000) also indicated that some pesticides that could translocate into inner plant tissues were inaccessible to water rinsing. Therefore, the status of pesticide residues whether occuring on the surface or penetrated affects the removal of pesticide residue from agricultural commodity.

5.4 ASSESSMENT OF THE EFFECT OF WASHING, SUNDRYING AND MILLING ON REMOVAL OF INSECTICIDE RESIDUES IN WHEAT

In the case of wheat also, a similar trend in dissipation of pesticides at two intervals was found as in the case of rice (Table 22). Comparing the two matrices *viz.* rice and wheat, wheat grains were found to be less amenable to removal of pesticide residues through different processing techniques. Reynolds (2005) reported that there is a possibility for the physical entrapment of pesticide residue in the fibrous layers of wheat grains and that may be the reason for lesser efficiency of processing techniques in wheat when compared to rice. This indicated that there was stronger biochemical binding of pesticide residues in wheat than in rice.

Considerable reduction of 30.86 - 75.67 per cent was observed during washing processes (Table 23 to 24) and there was no correlation between water solubility and the level of degradation of pesticides. Here also, increasing the number of washing improved the efficiency of removal of pesticide residues.

Regarding sun drying, this process did not reduce residues to a great extent when compared to other processing techniques. The removal of pesticides varied only to the tune of 19.15 - 34.10 per cent (Table 23 to 24) as a result of sun drying alone. This was consistent with the earlier study which showed that the reduction due to sundrying was negligible in the case of organophosphate pesticides like acephate, methamidophos and chlorpyriphos in rice (Zhang *et al.*, 2010; Kong *et al.*, 2012). However almost all pesticides were susceptible to photodegradation to some degree, their reduction depended on intensity and spectrum of sunlight, length of exposure, and properties of the pesticide (Kaushik *et al.*, 2009). Taking into consideration that photodegradation as the basic process acting on pesticide residues during sun drying, lesser exposure time could be the reason for lesser removal.

In this study, pesticide emulsion was sprayed on wheat grains (without bran) and the mixer grinder and sieve used did not help in the fractionation of wheat into different portions. In the case of wheat, most of the residues were retained on the seed coat and tend to concentrate on the bran and germ and milling resulted in distribution of this residues in various fractions especially on bran and germ (Balinova *et al.*, 2006). Here the entire process was different from the real industrial process which leads to maximum recovery of residues from fortified wheat grains. This means that the experiment error preclude drawing any conclusion on milling.

Almost 20.19 - 60.81 per cent pesticide residues could be removed from fortified wheat samples through washing four times with rubbing followed by sun drying and milling (Table 23 to 24). Washing twice followed by sun drying and milling resulted in a reduction of 10.15 - 51.63 per cent. Sun drying contributed a cumulative effect on washing whereas milling reduced the removal of pesticide residues.

5.5 ASSESSMENT OF THE EFFECT OF DECORTICATION ON REMOVAL OF INSECTICIDE RESIDUES IN CARDAMOM

Multiple residues of pesticides deposited during plant protection operations in cardamom are a major concern of today and it was reported that pesticide use in cardamom plantations in Idukki was one of the world's highest (Mishra, 2011). Presence of multiple residues in cardamom samples analyzed during monitoring study has undoubtedly established rotational spraying of these pesticides directly on cardamom capsules (Table 17). In another monitoring study conducted by Seena (2013) revealed that out of 180 cardamom samples analyzed, 173 were detected with pesticide residues, of which 160 samples showed multiple residues. In order to tackle the problem of pesticide residues in cardamom, an experiment was conducted to assess the effect of decortication (removal of capsule cover) on removal of pesticide residues left in cardamom seeds. In this study, cardamom samples with presence of more than one insecticide during the monitoring period (January - June 2012) were subjected to decortication. Samples (10 g) from each cardamom lot was taken and divided into three portions and analysed as such (5 g) capsule cover alone (1 g) and seed alone (4 g) and the samples were analyzed separately.

Results from the study revealed that decortication process had a significant effect on the removal of pesticide residues (48.19 - 100 %) in cardamom (Table 25). The level of residues of chlorpyriphos was 0.238, 0.057, 0.091, 0.353 and 0.087 mg kg^{-1} in whole cardamom capsule analyzed and the corresponding values in decorticated seeds were 0.045, 0.050, 0, 0.047 and 0 mg kg^{-1}. Hence it was observed that the level of residues got depleted in the range of 73.65 - 86.05 per cent in decorticated seed. The data clearly indicated that pesticide residues practically remained on the capsule cover, as only small amounts were identified in the seed. It may be because of lower penetration power of the pesticides studied, which is evident from their contact action (Table 2) which resulted in the incorporation of the pesticide into the structural components of cell wall of capsule cover. A study conducted by Teixeira *et al.* (2004) revealed that systemic pesticides such as oxadixyl were preferably found in the pulp of grapes, while contact pesticides such as folpet were detected in the skin but not in the whole grape. They also reported that lipophilicity, mode of action and concentration of the active ingredient are the driving forces in this transfer, but adjuvants in commercial formulation and grape skin constitution may also interfere. Hence the mobility of pesticides in cardamom is difficult to discuss, because other factors like capsule cell wall constitution, concentration of active ingredient, adjuvants in commercial preparation etc rather than pesticides actuation mode, such as the time gap between application and sampling, might have interfered.

Similar trend in removal of pesticide residues as a result of decortication was observed in other insecticides like quinalphos (71.42 - 93.41 %), profenophos (48.19 - 89.09 %), cypermethrin (86.67 - 99.58 %), lambda cyhalothrin (90.25 - 100 %), ethion (86.62 %) and bifenthrin (66.61 %). It may be seen that most of the detected residues remained on the surface of capsule cover and some insecticides like profenophos had penetrated into the seeds. Though negligible levels of quinalphos, profenophos and ethion were also detected in some seed samples even after decortication, their magnitude was much below the prescribed maximum levels (MRL) for these insecticides.

In the case of profenophos, a wide range in percentage removal (48.19-

89.09 %) through decortication in different cardamom samples analyzed gives an impression that as the residues get aged they will penetrate more into seeds, thereby decreasing the efficiency of decortication. The penetration of pesticides into the deeper layers of commodity which is characterized as "ageing of the residue" was also observed by Holland *et al.* (1994) while explaining the low efficiency of the washing of stored products. So an association among each pesticide's mode of action, its preferential localization and ageing of residues could be found.

The presence of pesticide residues in capsule cover of cardamom indicated that decortication process is a very simple and easy way to be adopted to remove pesticide residues from the commodity. Hence this study has opened a new strategy for using pesticide residue free cardamom in the form of seeds for flavouring food. Home makers in Kerala have the practice of flavouring tea, snacks, biriyani and sweet disserts like payasam etc with whole cardamom capsules. Now they have to be educated to change the culinary practice by removing the capsule covers and to use only seeds in their recipes.

5.6 STANDARDISATION OF WASHING WITH SOLUTIONS OF HOUSE HOLD PRODUCTS TO REMOVE INSECTICIDE RESIDUES FROM SELECTED VEGETABLES

Based on the monitoring data, insecticides *viz.*, malathion, methyl parathion, chlorpyriphos, quinalphos, profenophos, ethion, cypermethrin and fenvalerate were selected for standardizing a washing solution using household products in order to remove insecticide residues from capsicum, okra and curry leaf. The different treatments include dipping the sprayed vegetable in solutions of tamarind (2 %), vinegar (2 %), common salt (2 %), butter milk (2 %), turmeric (1 %), luke warm water and water (control) for 15 minutes, followed by washing in tap water. The efficiency of decontaminating solution was expressed in terms of percentage removal of insecticide residues and processing factor. Processing factor less than one indicate reduction of pesticide residues while those greater than one indicate concentration of pesticide residue.

5.6.1 Capsicum

The effect of washing solutions of different household products on removal of pesticide residues in capsicum at five hours after spraying are summarized in Table 27. The result indicated that washing with tamarind (2 %), vinegar (2 %), turmeric (1 %), common salt (2 %) and butter milk (2 %) showed significant effect in reducing both organophosphorus (malathion, methyl parathion, chlorpyriphos, quinalphos, ethion and profenophos) and synthetic pyrethroid (cypermethrin and fenvalerate) pesticide residues when compared to washing in tap water. Zohair (2001) reported that organophosphorus pesticides (pirimiphos-methyl, malathion, and profenophos) were eliminated more effectively by acidic, neutral and alkaline solutions and their removal depended on the kind and concentration of solutions.

Among the different treatment solutions, dipping of capsicum fruits in vinegar (2 %) for 15 min followed by washing in tap water removed fairly good amount of residues of fenvalerate (74.88 %), cypermethrin (57.70 %), malathion (48.46 %), ethion (46.13 %), methyl parathion (42.40 %), profenophos (41.80 %) and chlorpyriphos (35.80 %) whereas washing in water could remove residues only to a tune of 7.19-16.73 per cent. This may be due to the high acidity and/or high redox potential of this solution. The pH and oxidation reduction potential (ORP) of acetic acid was reported as 3.74 and 617 m V, respectively (Klinhom *et al.,* 2008). This is in agreement with that of Satpathy (2011) who reported the significance of pH and oxidation reduction potential of solutions in removing residues. Thus, it could be the reason that, residues degraded at such a low pH (acidic) solution. As this treatment was found effective for majority of insecticides under the present study, vinegar solution (2 %) can be recommended as a good decontaminating agent to remove pesticide residues from capsicum fruits. Zhang and co workers (2007) reported the effectiveness of acetic acid solution (10 %) in removing residues of profenophos, *p, p* DDT, cypermethrin and chlorothalonil from cabbage. Radwan and co workers (2005) showed that washing with acetic acid solution gave high percent removal of profenophos residues in sweet pepper (capsicum).

Dipping capsicum fruits in tamarind solution (2 %) for 15 min followed by washing in tap water stood next in performance, which resulted in 39.93, 37.73, 34.42, 33.46, 30.95, 28.10, 25.92 and 24.84 per cent removal of fenvalerate, cypermethrin, ethion, profenophos, methyl parathion, quinalphos, chlorpyriphos and malathion residues respectively. Kumar (1997) reported the effectiveness of tamarind solution in removing residues of phosphamidon and monocrotophos from bittergourd and cowpea pods.

Dipping in common salt solution (2 %) for 15 min followed by washing in tap water resulted in 54.74, 53.26, 48.00, 42.50, 37.54, 35.86, 35.20 and 33.09 per cent loss of pesticides like fenvalerate, cypermethrin, quinalphos, malathion, ethion, methyl parathion, profenophos and profenophos respectively. Common salt solution (2 %) was found as a better option in the case of quinalphos as it removed about 48.00 per cent residues when compared to simple water wash. Liang and co workers (2012) reported that 63.40, 60.00, 50.00, 31.10 and 66.70 per cent reduction in the residues of trichlorfon, dimethoate, dichlorvos, fenitothion and chlorpyriphos respectively, were observed in cucumber when dipped in 2 % sodium chloride solution for 20 min. These results agree with those obtained by Zohair (2001) who reported that soaking of contaminated potatoes in neutral (NaCl) solution (5 and 10 %) for 10 min resulted in 100 percent removal of pirimiphos methyl residues. The cause and effect of the reduction in 2 % NaCl washing solutions is still not known and needs further investigation.

About 21.44 - 33.28 and 16.52 - 22.71 per cent removal of pesticide residues were observed when treated capsicum fruits were dipped in buttermilk (2 %) and turmeric solution (1 %) respectively, for 15 min followed by washing in tap water.

Percentage removal of pesticides from treated capsicum samples varied and depended on the composition of washing solution. Vinegar (2 %) solution was found to be more effective in reducing all pesticides tested when compared with other treatment solutions. Dipping in luke warm water for 15 minutes followed by washing in tap water did not show significant difference in removing residues from simple water wash (Table 27). Washing in tap water proved the least effective, showing 16.73, 14.65, 13.81, 13.74, 12.94, 12.31, 11.50 and 7.19 per cent reduction in the quinalphos, malathion, chlorpyriphos, methyl parathion, cypermethrin, profenophos, fenvalerate and ethion respectively, which is in agreement with the findings of Walia *et al.* (2010) who reported that reduction of residues of cypermethrin on brinjal after washing treatment with water was minimal.

5.6.2 Okra

The pattern of persistence of pesticide residues at different interval in fortified okra fruits (Table 28) indicated that synthetic pyrethroid insecticides like cypermethrin had lesser dissipation (66.67 %) when compared to other studied insecticides which is evident from their half life (Table 41).

Table 41. Half life of pesticides

Sl No	Pesticide	Half life (days)	Reference
1	Malathion	0.3 - 8.7	(Newhart, 2006)
2	Methyl parathion	8	http://www.fao.org/fileadmin/templates/agphor /documents/Pests_Pesticides/Specs/parathio.pd
3	Chlorpyriphos	3.41 - 7.50	http://npic.orst.edu/factsheets/chlorptech.pdf
4	Quinalphos	2.6	(Mohapatra *et al.*, 2011)
5	Profenophos	1.74 - 1.98	(Radwan *et al.*, 2005)
6	Ethion	3.43	(Varghese, 2011)
7	Cypermethrin	4 - 12	(Cox, 1996)
8	Fenvalerate	8 - 10	http://www.inchem.org/documents/ehc/ehc/ehc 5.htm

The effect of washing solutions of different household products on removal of pesticide residues in okra at different intervals (five hours, 1st, 3rd and 5th day) after spraying are summarized in Table 29 to 32 and the efficiency of decontaminating solution in terms of processing factor is illustrated in Fig. 7. For the ease of discussing the results obtained in the present investigation, the percentage removal of insecticide residues in each treatment solution (based on Table 29 to 32) at different intervals (5h, 1st, 3rd and 5th day after spraying) were combined to work out pooled means and presented in Table 42.

The result indicated that washing process including tamarind (2 %), vinegar (2 %), turmeric (1 %), common salt (2 %) and butter milk (2 %) showed significant effect in reducing both organophosphorus (malathion, methyl parathion, chlorpyriphos, quinalphos, ethion and profenophos) and synthetic pyrethroid (cypermethrin and fenvalerate) pesticide residues from okra fruits when compared to washing in tap water.

Among the different treatment solutions, dipping of okra fruits in tamarind solution (2 %) for 15 min followed by washing in tap water removed fairly good amount of residues of profenophos (70.53 %), quinalphos (64.34 %), malathion (63.95 %), ethion (62.15 %), chlorpyriphos (59.09 %), fenvalerate (54.51 %), cypermethrin (53.11 %) and methyl parathion (47.64 %), whereas washing in water could remove residues only to a tune of 7.19-16.73 % (Table 42). Similar studies conducted by Varghese and Mathew (2013) reported that 2 % tamarind solution was the best decontaminating solution in removing residues of spiromesifen (90.03 %) and propargite (96.69 %) from green chilli fruits

The efficiency of washing with tamarind solution in removing insecticide residues may be due to the high acidity of the solution or the adsorption of pesticide residue to the mucilaginous materials of tamarind. Singh *et al.* (2007) reported that tamarind pulp had significant amount of organic acids, of which tartaric acid (98 %) is the major one having a pH of 2.7. This is in agreement with that of Satpathy (2011) who reported the significance of pH of solutions in removing residues. Along with this Munuswamy *et al.* (2011) reported that the main component of tamarind (pulp and seed) is cellulose and lignin, which are carbonaceous material. A study conducted by Rasheed (2013) pointed a good adsorbtion efficiency (70 - 90 %) of lignocellulosic wastes of plant origin like coffee grounds, melon seeds and orange peels for o-nitrophenol and p-nitrotoluene. Thus, it could be the inferred that, insecticide residues degraded at such a low pH and got adsorbed on to mucilage/lignocelluloses fraction of tamarind. As this treatment was found effective for majority of insecticides under the present study, washing with tamarind solution (2 %) can be recommended

Table 42. Extent of removal of insecticide residues from okra fruits collected at different intervals after spraying*

Insecticides	Mean per cent removal of insecticides (%)						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	47.64	35.10	29.02	47.80	33.15	21.93	13.66
Malathion	63.95	41.24	56.61	55.05	59.49	33.43	30.20
Chlorpyriphos	59.09	49.13	26.12	49.93	18.67	21.32	12.31
Quinalphos	64.34	54.41	41.65	58.95	41.52	35.49	26.71
Profenophos	70.53	54.07	43.53	59.44	45.07	27.37	22.09
Ethion	62.15	49.71	38.36	52.26	42.51	18.90	6.87
Cypermethrin	53.11	52.05	29.55	48.92	28.10	23.74	9.57
Fenvalerate	54.51	57.39	34.92	64.40	26.26	17.76	12.41

*subjected to dipping in different treatment solutions for 15 min.

as a good decontaminating agent to remove pesticide residues from okra fruits. A study conducted by Gopichand *et al.* (1999) revealed that (2 %) tamarind solution proved best in reducing residues at 0th and 5th day.

Dipping okra fruits in vinegar solution (2 %) for 15 min followed by washing in tap water resulted in 57.39, 54.41, 54.07, 52.05, 49.71, 49.13, 41.24 and 35.10 per cent removal of fenvalerate, quinalphos, profenophos, cypermethrin, ethion, chlorpyriphos, malathion and methyl parathion residues respectively (Table 42). Two percent vinegar solution is having pH in the range of 2-3, and it is clear from the results that the acidity of the vinegar solution is having much significance in the removal of insecticide residues as all the studied insecticides gave a fair removal. Study conducted by Wheeler (2002) showed that acidic solutions of 5 and 10 per cent citric and ascorbic acid gave more pesticide dissipation (80 %) than neutral and alkaline solutions.

Dipping of okra fruits in common salt solution (2 %) for 15 min followed by washing in tap water resulted in 64.40, 59.44, 58.95, 55.05, 52.26, 49.93, 48.92 and 47.80 per cent loss of pesticides like fenvalerate, profenophos, quinalphos, malathion, ethion, chlorpyriphos, cypermethrin and methyl parathion respectively (Table 42). Reddy and Rao (2002) reported that dipping of grape berries in 2 % salt solution for 10 min followed by washing with water proved to be an effective decontamination procedure, facilitating removal of 67.52 and 65.00 per cent residues of chlorpyriphos and 51.77 and 50 percent quinalphos residues at one and five days respectively after spraying.

About 18.67 – 59.49 per cent and 26.12 - 56.61 per cent removal of pesticide residues were observed when treated okra fruits were dipped in buttermilk (2 %) and turmeric (1 %) solution respectively, for 15 min followed by washing in tap water (Table 42). Pesticide molecules have higher affinity to attach with organic materials. Adsorption of pesticide residues to turmeric powder, which is an organic carbonaceous material having lesser particle size and higher surface area may be the reason for the efficiency of turmeric as a decontaminating agent. Vijayasree *et al.* (2012) reported turmeric as an effective decontaminating agent in removing chlorantraniliprole residues (79.81 - 87.40 %) from vegetable cowpea at 0th day and 3rd day after spraying.

Tamarind (2 %) solution was found to be more effective in reducing all pesticides tested when compared with other treatment solutions. Dipping of okra fruits in luke warm water for 15 min followed by washing in tap water did not show significant difference in removing residues from simple water wash. Washing in tap water proved the least effective, showing 30.20, 26.71, 22.09, 13.66, 12.41, 12.31, 9.57 and 6.87 per cent reduction in the malathion, quinalphos, profenophos, methyl parathion, fenvalerate, chlorpyriphos, cypermethrin and ethion respectively (Table 42) which was in agreement with the findings of Abou-Arab (1999) and Zhang *et al.* (2007)

5.6.3 Curry leaf

The pattern of persistence of pesticide residues at different interval in fortified okra fruits (Table 33) indicated that synthetic pyrethroid insecticides like cypermethrin (62.96 %) and fenvalerate (69.97 %) had lesser dissipation when compared to other insecticides tested which was evident from their half life (Table 41).

The effect of washing solutions of different household products on removal of pesticide residues in curry leaf at different intervals (five hours, 1st, 3rd and 5th day) after spraying are summarized in Table 24 to 37 and the efficiency of decontaminating solution in terms of processing factor is illustrated in Fig. 8. For the ease of discussing the results obtained in the present investigation, the percentage removal of insecticide residues in each treatment solution (based on Table 34 to 37) at different intervals (5h, 1st, 3rd and 5th day after spraying) were combined to work out pooled means and presented in Table 43.

The result indicated that washing process including tamarind (2 %), vinegar (2 %), turmeric (1 %), common salt (2 %) and butter milk (2 %) showed significant effect in reducing both organophosphorus (malathion, methyl parathion, chlorpyriphos, quinalphos, ethion and profenophos) and synthetic pyrethroid (cypermethrin and fenvalerate) pesticide residues when compared to washing in tap water.

Among the different treatment solutions, dipping of curry leaves in tamarind solution (2 %) for 15 min followed by washing in tap water removed fairly good amount of residues of malathion (89.62 %), profenophos (72.10 %), quinalphos (71.89 %), ethion (71.53 %), cypermethrin (71.34 %), fenvalerate (66.19 %), chlorpyriphos (65.07 %) and methyl parathion (54.60 %) whereas washing in water could remove residues only to a tune of 32.10-70.88 per cent (Table 43). The efficiency of tamarind solution in removing insecticide residues may be due to the high acidity of the solution or the adsorption of pesticide residue to the mucilaginous components of tamarind. As this treatment was found effective for majority of insecticides under the present study, tamarind solution (2 %) can be recommended as a good decontaminating agent to remove pesticide residues from curry leaves.

Dipping of curry leaves in turmeric solution (1 %) for 15 min followed by washing in tap water was also found to be very effective in removing the residues of malathion, profenophos, quinalphos, ethion, cypermethrin, fenvalerate, chlorpyriphos, and methyl parathion to a tune of 84.01, 70.88, 69.98, 69.42, 68.24, 66.08, 62.07 and 50.06 per cent respectively (Table 43). Here also, pesticide molecules might have got adsorbed on particles of turmeric suspension and that may be the reason for the efficiency of turmeric as a good decontaminating agent. Vijayasree and co workers (2012) reported turmeric as a decontaminating agent in removing chlorantraniliprole residues (79.81 - 87.40 %) from vegetable cowpea at 0th day and 3rd day after spraying.

Dipping curry leaves in vinegar solution (2 %) for 15 min followed by washing in tap water resulted in 83.54, 63.41, 62.63, 60.45, 57.84, 57.78, 49.30 and 48.03 per cent removal of malathion, cypermethrin, fenvalerate, profenophos, ethion, quinalphos, chlorpyriphos and methyl parathion residues respectively (Table 43).

Dipping of curry leaves in common salt solution (2 %) for 15 min followed by washing in tap water resulted in 82.47, 65.20, 63.42, 62.11, 59.56, 55.44, 53.23 and 48.92 per cent loss of pesticides like malathion, fenvalerate,

Table 43. Extent of removal of insecticide residues from curry leaf collected at different intervals after spraying*

Insecticides	Mean per cent removal of insecticides (%)						
	2% Tamarind	2% Vinegar	1% Turmeric	2% Common salt	2% Buttermilk	Luke warm water	Water
Methyl parathion	54.60	49.30	50.06	48.92	38.79	40.60	32.10
Malathion	89.62	83.54	84.02	82.47	76.72	77.77	70.88
Chlorpyriphos	65.07	48.03	62.07	53.23	44.94	41.67	38.64
Quinalphos	71.89	57.78	69.98	63.42	55.37	54.10	46.94
Profenophos	72.10	60.45	70.88	65.20	58.71	56.47	45.66
Ethion	71.53	57.84	69.42	59.56	58.27	53.27	43.67
Cypermethrin	71.34	63.41	68.24	55.44	60.80	52.45	45.41
Fenvalerate	66.19	62.63	66.08	62.11	61.94	66.58	40.72

*subjected to immersion in different treatment solutions for 15 min profenophos, quinalphos, ethion, cypermethrin, chlorpyriphos and methyl parathion respectively (Table 43). Abou-Arab (1999) reported that tomatoes contaminated at level of 1 mg kg^{-1} upon washing with 10 % NaCl solution gave 42.90, 46.10, 27.20, 90.80, 82.40 and 91.40 per cent loss in HCB, lindane, p,p-DDT, dimethoate, profenophos and pirimiphos-methyl, respectively.

About 38.79 – 76.72 per cent removal of pesticide residues was observed when treated curry leaves were dipped in buttermilk solution (2 %) for 15 min followed by washing in tap water (Table 43).

Tamarind (2 %) solution was found to be more effective in reducing all pesticides tested when compared with other treatment solutions. Dipping of curry leaves in luke warm water for 15 min followed by washing in tap water did not show much significant difference in removing residues from simple water wash. Washing in tap water proved the least effective, showing 70.88, 46.94, 45.66, 45.41, 43.67, 40.72, 38.64 and 32.10 per cent reduction in malathion, quinalphos, profenophos, cypermethrin, ethion, fenvalerate, chlorpyriphos and methyl parathion (Table 43) respectively which was in agreement with the findings of Awasthi (1993) who reported that washing of mango fruits in water reduced residues of organophosphate pesticides like dimethoate and fenthion to the tune of 66–68 per cent.

From the results, it is presumed that all the decontamination process used in the study were effective in reducing the residues on 5 h after spraying because residues were localised on the surface of the commodity which could be dislodged easily. With the elapse of time, residues penetrated into the commodity and resulting in lesser extent of removal on subsequent days. The present results are in consistent with the findings of Duhan *et al.*, 2010.

Comparing the three vegetables, curry leaf was found to be more amenable to decontamination by solutions of household products followed by okra and capsicum.

In this study, the residue reduction of residues was not attributed to solubility of pesticides in water. Malathion which had higher solubility than quinalphos (143 *vs* 17.8 mg/l), showed lower degree of reduction (Table 2). This is consistent with the earlier studies which showed that the reduction of pesticides on fruits and vegetables were not directly correlated with water solubility of pesticides (Youssef *et al.*, 1995; Izumi, 1999).

Eventhough the lipophilicity of synthetic pyrethroids were high when compared to organophosphates it is clear from the present study that the effects of different treatment solutions on the removal of synthetic pyrethroid pesticide were greater when compared to organophosphates. This result is not in agreement with that of Bonnechere and co workers (2012) who reported that low removal is observed in the case of pesticides having high lipophilicity which is indicated by their high log octanol water partitioning coefficient value.

One important conclusion of this study is that the rinsability of a pesticide is dependent on many factors (treatment solution and physicochemical properties of both the pesticide and the crop skin, among others), being not always correlated with the water solubility and/or the K_{ow} of the pesticide.

The present study on "Monitoring and decontamination of pesticide residues in agricultural commodities" portray the extent of contamination of pesticide residues in agricultural commodities and the efficiency of different decontamination techniques in removing the residues from these commodities. Data on monitoring of pesticide residues in agricultural commodity revealed that none of the rice flour, atta, maida, raw rice and parboiled rice samples showed the presence of pesticide residues. However, monitoring studies in cardamom, cumin seed and curry leaf have established the overdependence and abuse of pesticides by growers. The high extent of pesticide residues in these commodities calls for improved techniques for the management of residues at production, post harvest and marketing especially of vegetables. Further, effectiveness of those pesticides which are not having label claim as on date should be studied and steps for label expansion may be taken up. Risk assessment to human health showed that chronic dietary risks of lambda cyhalothrin and ethion in cardamom, profenophos in cumin seed, chlorpyriphos, profenophos and ethion in curry leaf are of concern. Therefore, monitoring of pesticide residues in agricultural commodities is required on a regular basis to ensure food safety to consumers.

In a developing country like India there is a great need to regulate the use of pesticides where the extensive use of pesticides is causing serious health and alarming environmental problems. So, great significance has to be given to standardize simple cost effective strategies to eliminate harmful pesticides which could be practiced by home makers. The present study emphasize the importance of different decontamination techniques to minimize the risk of pesticides on health. Results from the present study revealed that dipping in 2% tamarind for 15 minutes was the best treatment to eliminate residues of malathion, methyl parathion, chlorpyriphos, quinalphos, profenophos, ethion cypermethrin and fenvalerate from okra and curry leaf whereas dipping in 2% vinegar solution was the best for decontaminating capsicum. Problem of residues of malathion, methyl parathion, chlorpyriphos, quinalphos, cypermethrin and fenvalerate in rice and wheat could be managed easily by four washing followed by cooking. In the case of cardamom, decortications of capsule cover before use is the best remedy for removing pesticide residue. Since the efficiency of decontamination techniques depends on many factors like physicochemical properties of both the pesticide and the commodity, age of the residue etc it is proposed to take up detailed investigation on standardization and popularization of decontamination techniques (home remedies) for each and every agricultural commodity.

Summary

6. SUMMARY

The use of pesticides in commercial agriculture has led to an increase in farm productivity, so that farmers can produce a wide variety of agricultural commodities at a reasonably low cost. The disadvantage of pesticide use is that residues remain on food commodities where they contribute to the total dietary intake of pesticides. The main exposure to pesticides for humans is via food (especially by fruit and vegetables), contributing upto five times more than other routes, such as air and drinking water. It is well known that processing food can affect the level of pesticide residues. Typical operations employed in processing food crops such as washing, peeling, blanching, cooking etc play a role in the reduction of residues. To estimate the potential pesticide exposure from contaminated food, it is important to estimate the level of exposure at the point of consumption after processing. Hence an extensive study was carried out during 2011-2013 to monitor the pesticide residues in agricultural commodities like rice, wheat, rice flour, wheat flour, cardamom, cumin seed, capsicum, okra and curry leaf which were already identified as highly contaminated and to study the effect of different decontamination techniques on removal of pesticide residues.

The results are summarized below:

- For monitoring of pesticide residues in various agricultural commodities, multi residue methods for rice, wheat, rice flour, wheat flour (atta and maida), cardamom, cumin seed, capsicum, okra and curry leaf were developed and validated. Five important validation parameters *viz.*, Limit of Detection, Limit of Quantification, Linearity, Recovery and Repeatability were established for 21 pesticides. The mean recovery of all the 21 pesticides under study were in the range 70-110 per cent and the repeatability of the recovery results, as indicated by the relative standard deviations, RSD < 20 % confirmed that the method is sufficiently reliable for pesticide residue analysis in different agricultural commodities. The estimation of residues were performed using Gas Chromatograph (GC) equipped with ECD (Electron Capture Detector)

- Data on monitoring of pesticide residues in agricultural commodity revealed that out of the 72 samples analysed, 33 samples showed the presence of various pesticides, whereas 39 samples were free of residues. None of the rice flour, atta, maida, raw rice and parboiled rice samples showed the presence of pesticide residues. However, all the cardamom, cumin seed and curry leaf samples showed presence of multiple pesticide residues at varying levels. Basmathi rice (5 samples), wheat (5 samples), capsicum (3 samples) and okra (2 samples) showed the presence of pesticide residues. The pesticides detected included malathion, chlorpyriphos, fenvalerate, methyl parathion, cypermethrin, quinalphos, profenophos, bifenthrin, lambda cyhalothrin, ethion, alpha endosulphan, triazophos, fenpropathrin and cyfluthrin.
- Comparing organophosphate, organochlorine and synthetic pyrethroid groups, insecticides belonging to organophosphate group was most frequently detected. Chlorpyriphos (20 samples) was the most frequently detected insecticide followed by profenophos (19 samples), cypermethrin (12 samples) and quinalphos (10 samples).
- All the cardamom, cumin seed and curry leaf samples showed multiple pesticide residues at varying levels. All the cardamom samples analyzed during the study period contained residues above MRL fixed by FSSAI and all the detected insecticides except quinalphos were not at all registered for use in cardamom by Directorate of Plant protection, Govt. of India. The pesticides detected in curry leaf and cumin seed also were not registered for use in these commodities. A level as high as 25.63 mg kg^{-1} of profenophos was detected in curry leaf.

- Among the three different commodities *viz.*, cereals, vegetables and spices, highest pesticide residue accumulation was observed in spices.
- An overall analysis of the data showed that out of 33 samples detected with pesticides, 22 samples showed presence of multiple pesticides and most of these were not having label claim/approval for use in India by CIB&RC in that specific commodity.
- Monitoring data revealed the presence of banned pesticides like methyl parathion, profenophos and endosulphan in basmathi rice, cardamom, cumin seed, curry leaf, capsicum and okra samples tested which were banned for sale and use in Kerala state.
- None of the detected pesticides in commodities monitored during the study period resulted in an intake of >50 per cent of ARfD value which indicated that their consumption doesnot cause acute health risk. Among the different agricultural commodity like cardamom, cumin seed and curry leaf, highest detected level of pesticides *viz.*, (lambda cyhalothrin and ethion in cardamom, profenophos in cumin seed and chlorpyriphos, profenophos and ethion in curry leaf exceeded 4 per cent of ADI value, which was considered as a margin indicating chronic health risk. Among the different pesticides studied, profenophos was present in levels >85.00 % of the ADI which represented a high level of chronic health risk to consumers.
- Studies conducted to assess the effect of washing, soaking and cooking on removal of insecticide residues in rice revealed that out of the different processing techniques evaluated, four washings in tap water for two minutes along with rubbing of grains followed by cooking removed maximum amount of residues (88.36 - 98.63 %). Extent of removal of residues as a result of other processing techniques were: two washings in tap water for two minutes along with rubbing of grains (38.01 - 81.93 %), four washings in tap

water for two minutes along with rubbing of grains (44.94 - 84.27 %), soaking (17.22 - 34.56 %), soaking followed by two washings in tap water for two minutes along with rubbing of grains (57.30 - 86.80 %), soaking followed by four washings in tap water for two minutes along with rubbing of grains (62.46 - 89.26 %), cooking (78.81 - 92.59 %), two washings in tap water for two minutes along with rubbing of grains followed by cooking (84.74 - 98.37 %).

- Studies conducted to assess the effect of washing, sun drying and milling on removal of insecticide residues in wheat revealed that out of different processing techniques studied, four washings in tap water for two min along with rubbing of grains removed maximum amount of residues (51.09 - 75.67 %) in wheat. Extent of removal of residues as a result of other processing techniques were: two washings in tap water for two minutes along with rubbing of grains (30.86 - 56.87 %), sun drying (19.15 - 34.10 %), two washings in tap water for two minutes along with rubbing of grains followed by sun drying and milling (10.15 - 51.63 %) and four washings in tap water for two minutes along with rubbing of grains followed by sun drying and milling (20.19 - 60.81 %).
- The present study revealed that the removal of pesticide residue is not correlated with its water solubility.
- There was no significant difference in the concentration of pesticides belonging to organophosphates and synthetic pyrethroids in rice grains and wheat grains, when analyzed at five hours and two weeks after insecticide application.
- An overall reduction in the efficiency of different processing techniques in rice and wheat grains was observed at two weeks after spraying due to the ageing of residues.

- The present study revealed that wheat grains are less amenable to removal of pesticide residues when compared to rice grains through different processing techniques.
- Study conducted to assess the effect of decortication on removal of pesticide residues in cardamom yielded very useful information that decortication process had significant effect on the removal of pesticide residues as majority of the residues were present only in capsule cover. Extent of removal of residues as a result of decortication were: chlorpyriphos (73.65 - 86.81 %), quinalphos (71.42 - 94.11 %), profenophos (48.19 - 89.09 %), cypermethrin (86.67 - 99.62 %), lambda cyhalothrin (89.65 - 100 %), ethion (86.62 %) and bifenthrin (66.61 %).
- Most of the detected residues remained on the surface of cardamom capsule cover and some insecticides like profenophos had penetrated into the seed.
- Studies conducted to standardize a washing solution of house hold product to remove insecticide residues from selected vegetables revealed that dipping in 2 % tamarind solution for 15 min followed by washing in tap water was the best treatment to eliminate residues from okra (37.28 - 80.37 %) and curry leaf (38.70 - 98.05 %) whereas dipping in 2 % vinegar solution for 15 min followed by washing in tap water was the best for decontaminating capsicum (31.18 - 74.88 %).
- The present investigations revealed that efficiency of decontaminating treatments depended on the chemistry of pesticide molecule, age of the pesticide residue and the surface character of the commodity.

To conclude, high extent of pesticide residues in agricultural commodities calls for improved management of residues at production, post harvest and marketing of food commodities especially of vegetables. Further, effectiveness of those pesticides which are not having label claim as on date should be studied and steps for label expansion may be taken up. Moreover, great significance has to be given to standardize simple cost effective strategies to eliminate harmful pesticides which could be practiced by home makers. Hence it is proposed to take up detailed investigation on standardization and popularization of decontamination techniques (home remedies) for each and every agricultural commodity.

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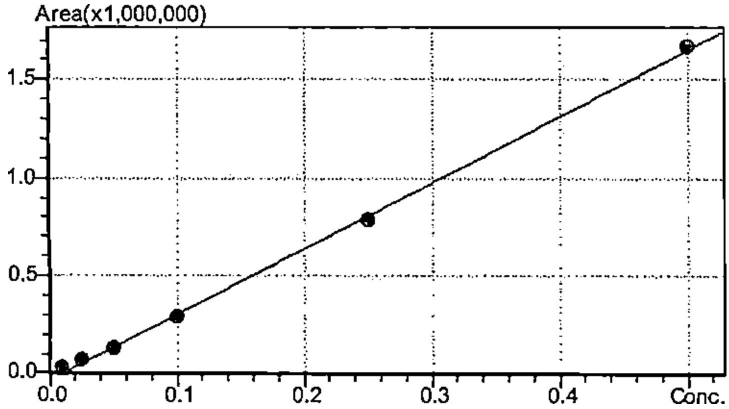
Appendices

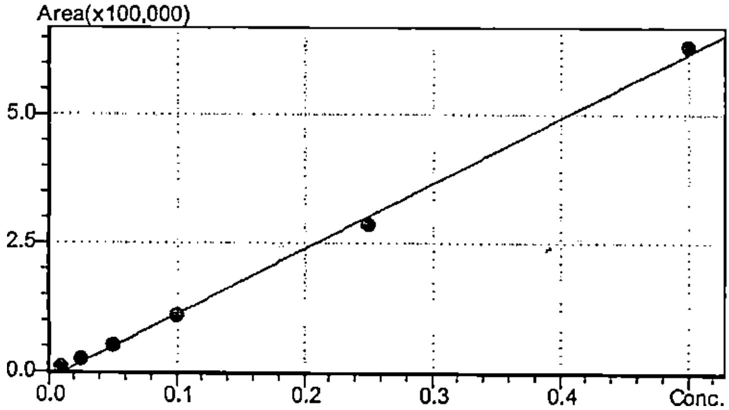
Appendix I

Calibration curve of insecticides



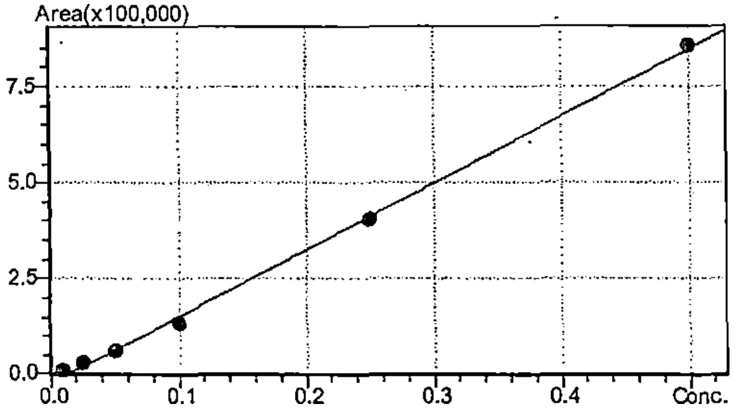
Y = aX + b, a = 3365421, b = -32612.27, R^2 = 0.9992471, R = 0.9996235, RF % RSD: 17.47959

Calibration curve of alpha HCH



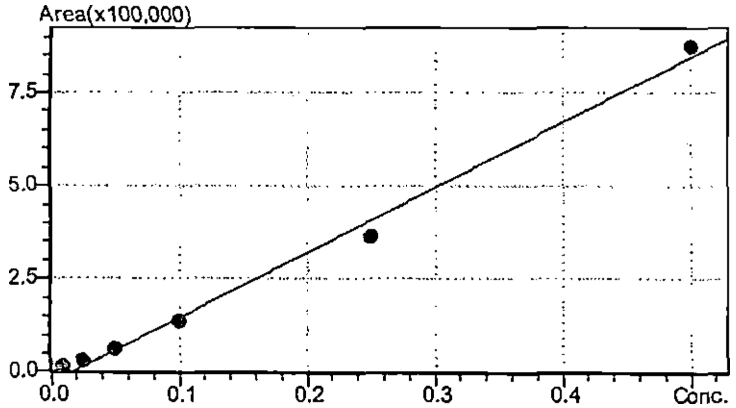
Y = aX + b, a = 1264180, b = -12095.66, R^2 = 0.9977349, R = 0.9988668, RF % RSD: 10.89383

Calibration curve of beta HCH



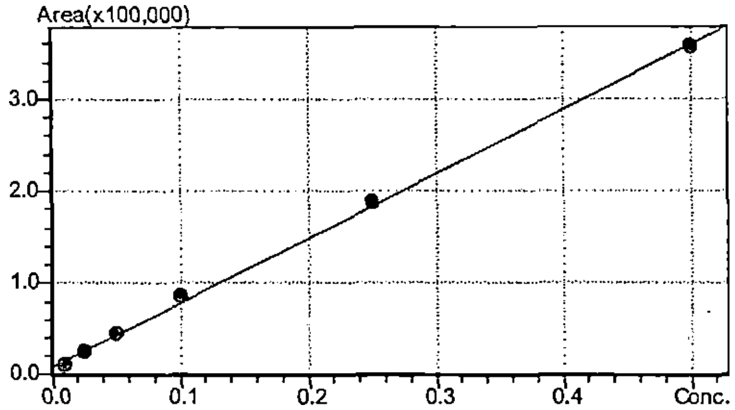
Y = aX + b, a = 1734479, b = -21455.29, R^2 = 0.9987275, R = 0.9993635, RF % RSD: 19.47959

Calibration curve of lindane



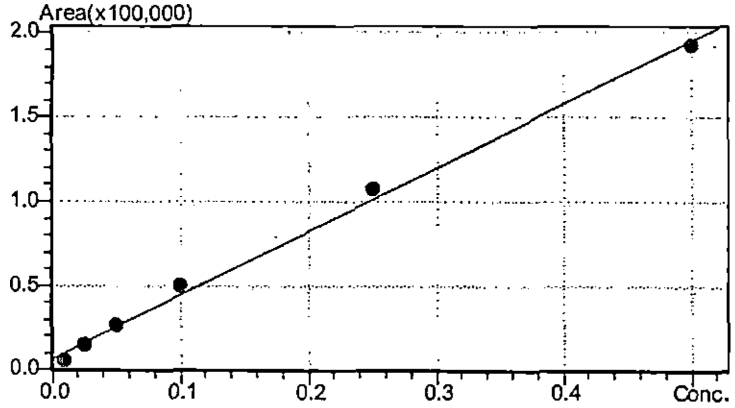
Y = aX + b, a = 1747555, b = -27257.66, R^2 = 0.9935319, R = 0.9967607, RF % RSD: 16.03338

Calibration curve of delta HCH



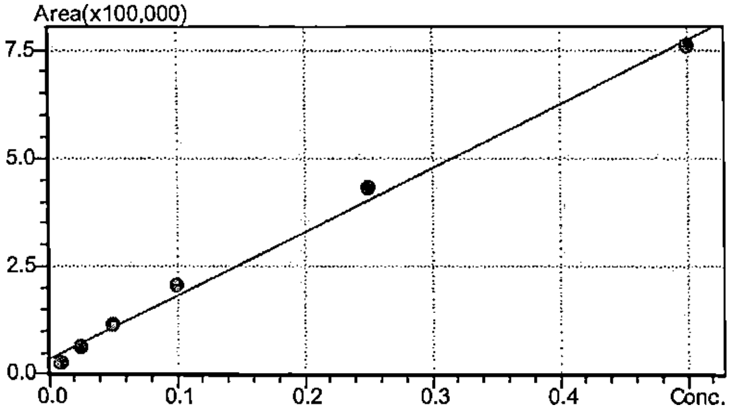
Y = aX + b, a = 699939.0, b = 9033.433, R^2 = 0.9989621, R = 0.9994809, RF % RSD: 14.06790

Calibration curve of methyl parathion



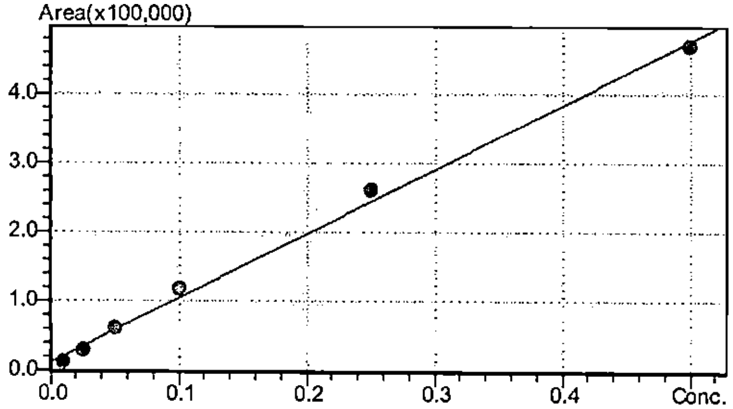
Y = aX + b, a = 377549.4, b = 6956.436, R^2 = 0.9961806, R = 0.9980885, RF % RSD: 10.47969

Calibration curve of malathion



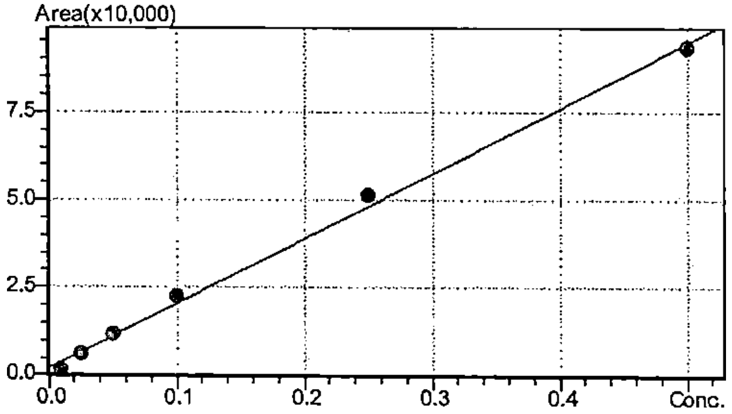
Y = aX + b, a = 1474100, b = 35879.11, R^2 = 0.9944649, R = 0.9972286, RF % RSD: 19.42083

Calibration curve of chlorpyriphos



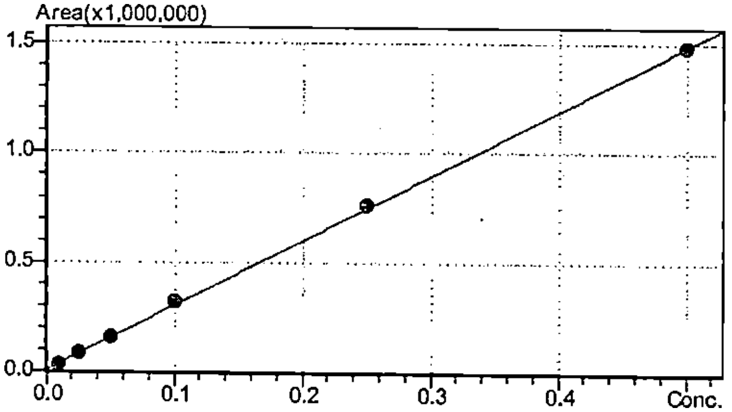
Y = aX + b, a = 928540.2, b = 13799.63, R^2 = 0.9963780, R = 0.9981873, RF % RSD: 10.02646

Calibration curve of phorate



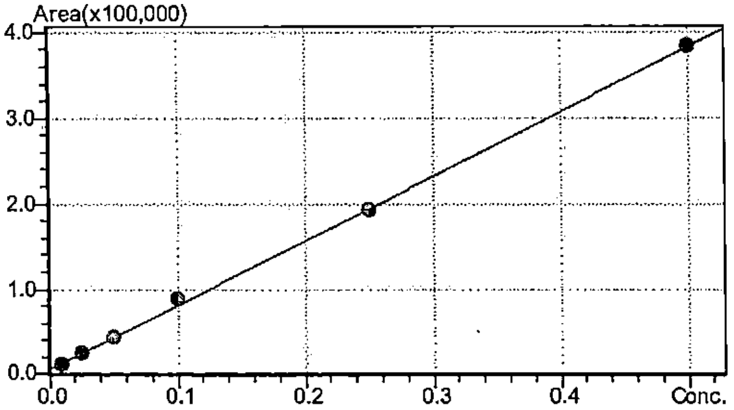
Y = aX + b, a = 184942.5, b = 2066.472, R^2 = 0.9968498, R = 0.9984237, RF % RSD: 12.88356

Calibration curve of quinalphos



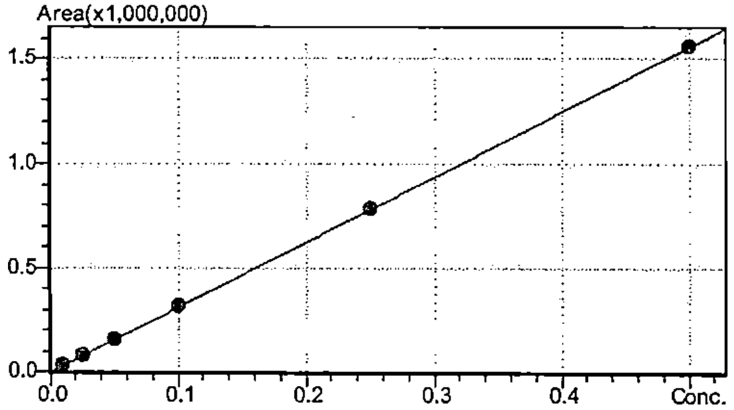
Y = aX + b, a = 2947930, b = 12521.38, R^2 = 0.9997281, R = 0.9998641, RF % RSD: 3.684671

Calibration curve of alpha endosulphan



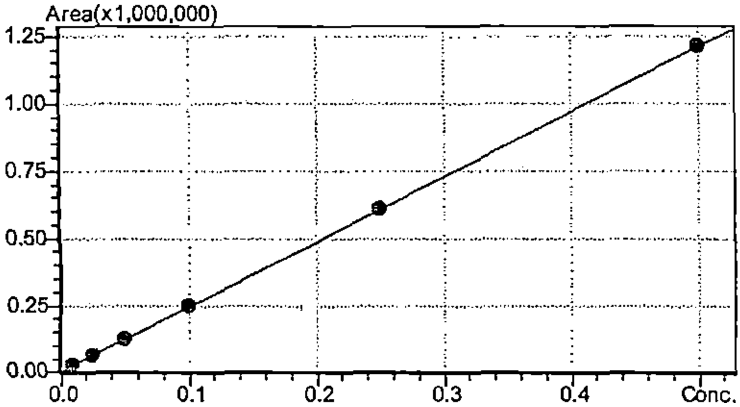
Y = aX + b, a = 753785.7, b = 5938.056, R^2 = 0.9994090, R = 0.9997044, RF % RSD: 11.42993

Calibration curve of profenophos



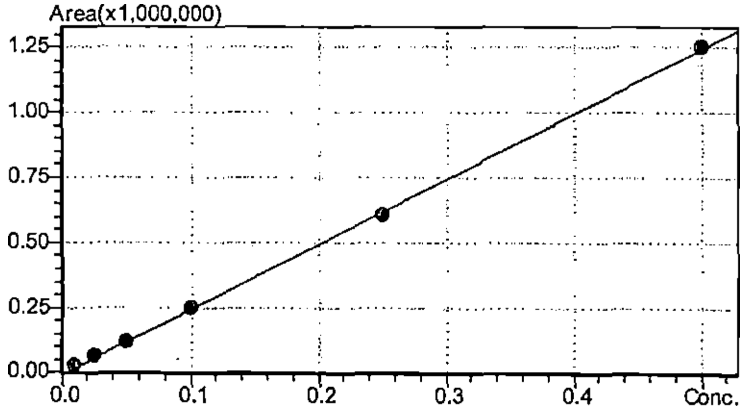
Y = aX + b, a = 3114278, b = 2393.268, R^2 = 0.9999779, R = 0.9999889, RF % RSD: 1.273305

Calibration curve of p,p DDE



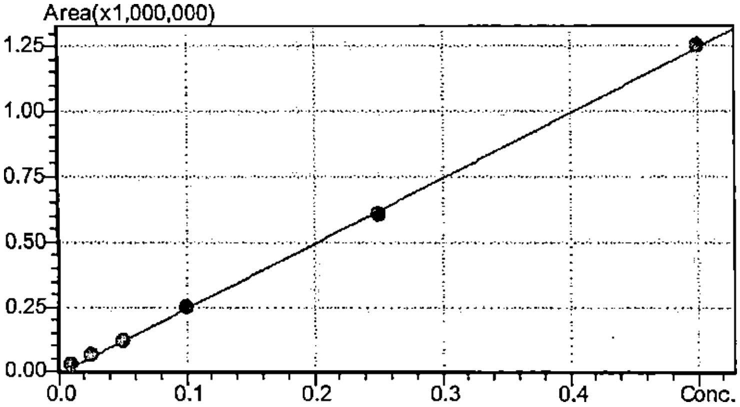
Y = aX + b, a = 2415977, b = 3156.296, R^2 = 0.9999547, R = 0.9999774, RF % RSD: 2.298275

Calibration curve of beta endosulphan



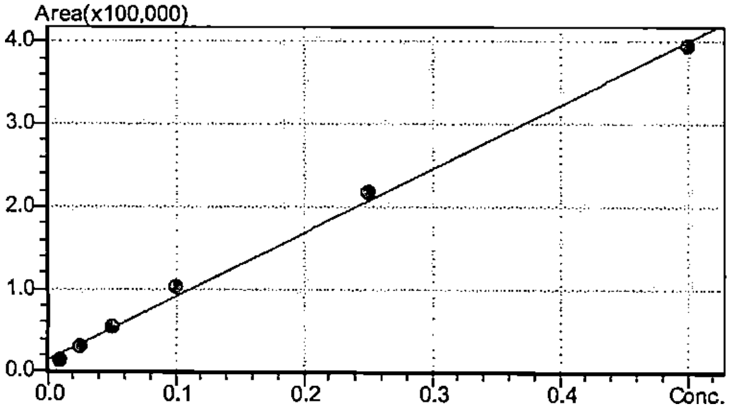
Y = aX + b, a = 2503354, b = -5983.589, R^2 = 0.9997944, R = 0.9998972, RF % RSD: 3.570772

Calibration curve of p,p DDD



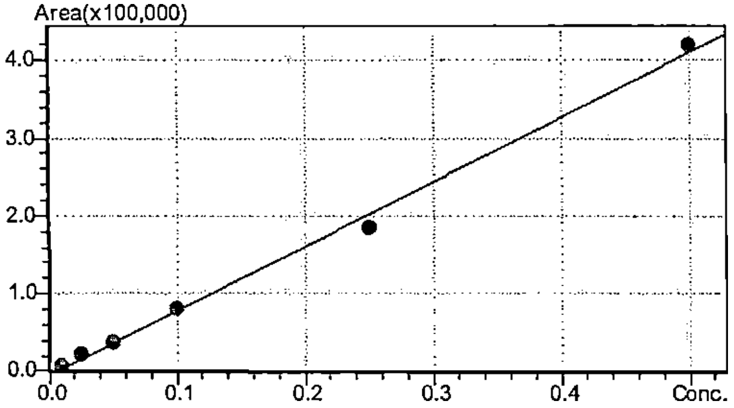
Y = aX + b, a = 2415977, b = 3156.296, R^2 = 0.9999547, R = 0.9999774, RF % RSD: 2.298275

Calibration curve of p p DDT



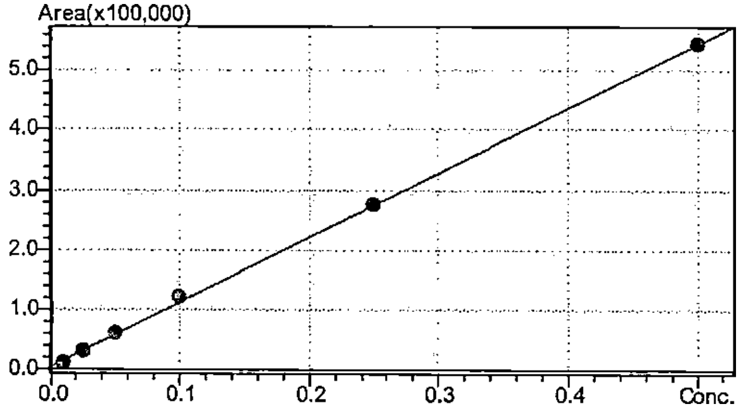
Y = aX + b, a = 771196.5, b = 14470.0, R^2 = 0.9964303, R = 0.9982136, RF % RSD: 15.56415

Calibration curve of ethion



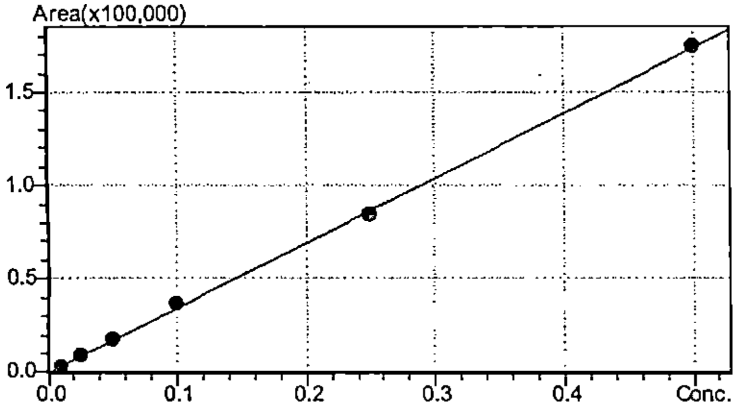
Y = aX + b, a = 828807.8, b = -4589.273, R^2 = 0.9968699, R = 0.9984337, RF % RSD: 7.557541

Calibration curve of fenpropathrin



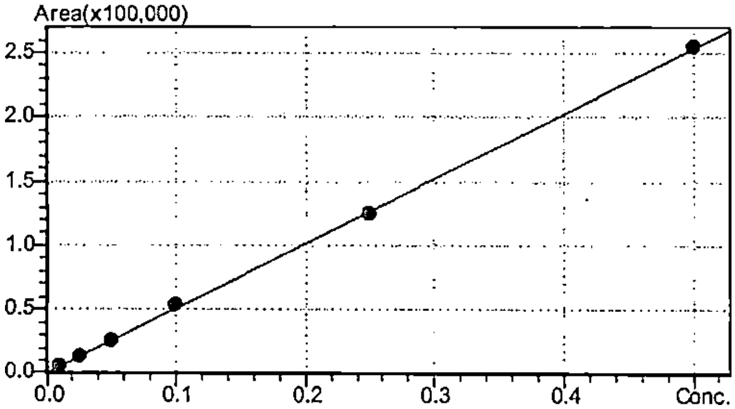
Y = aX + b, a = 1075027, b = 7000.612, R^2 = 0.9996640, R = 0.9998320, RF % RSD: 7.756205

Calibration curve of lambda cyhalothrin



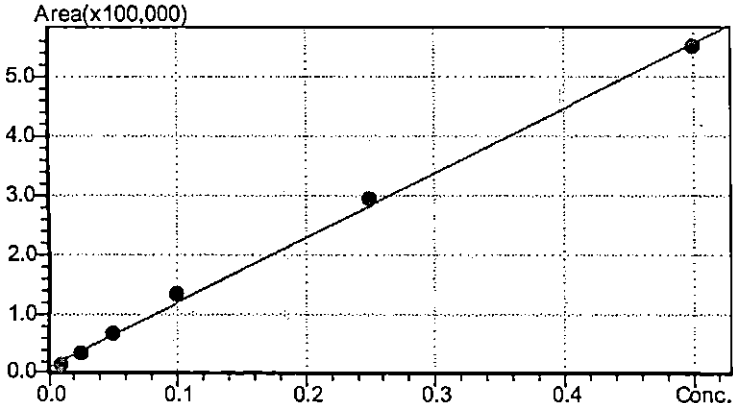
Y = aX + b, a = 346962.5, b = -13.44267, R^2 = 0.9996808, R = 0.9998404, RF % RSD: 6.870387

Calibration curve of cyfluthrin 1



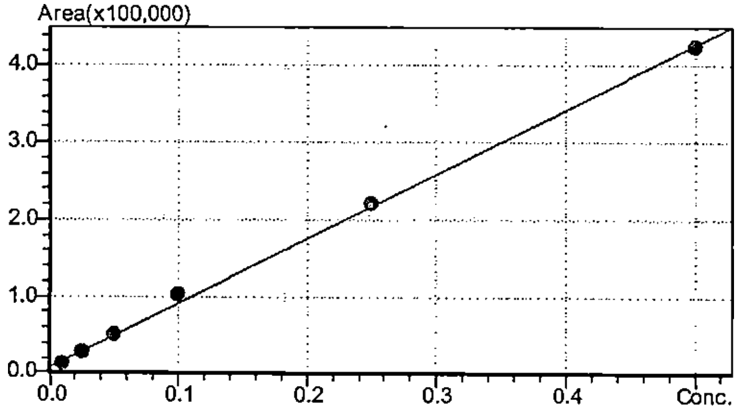
Y = aX + b, a = 505790.3, b = 675.9611, R^2 = 0.9996668, R = 0.9998334, RF % RSD: 5.190227

Calibration curve of cyfluthrin 2



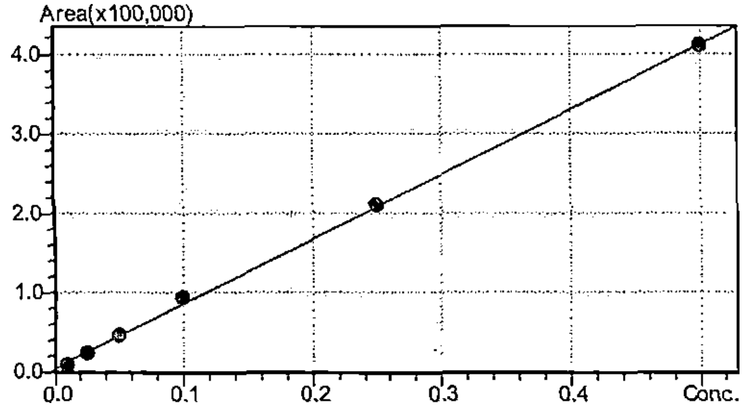
Y = aX + b, a = 1092878, b = 10636.59, R^2 = 0.9981976, R = 0.9990984, RF % RSD: 7.136593

Calibration curve of cypermethrin 1



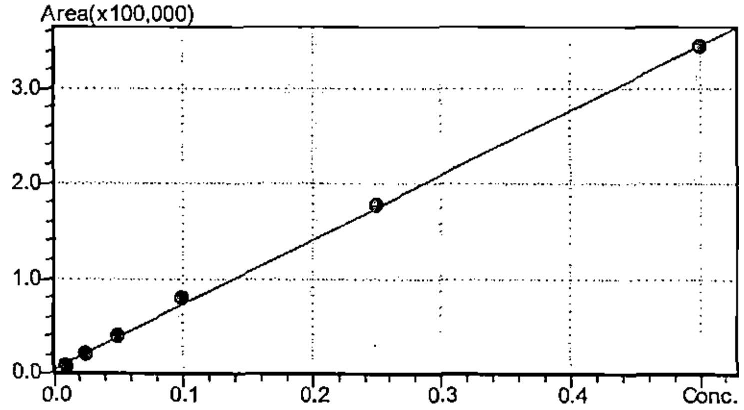
Y = aX + b, a = 836512.0, b = 8441.522, R^2 = 0.9988647, R = 0.9994322, RF % RSD: 9.965763

Calibration curve of cypermethrin 2



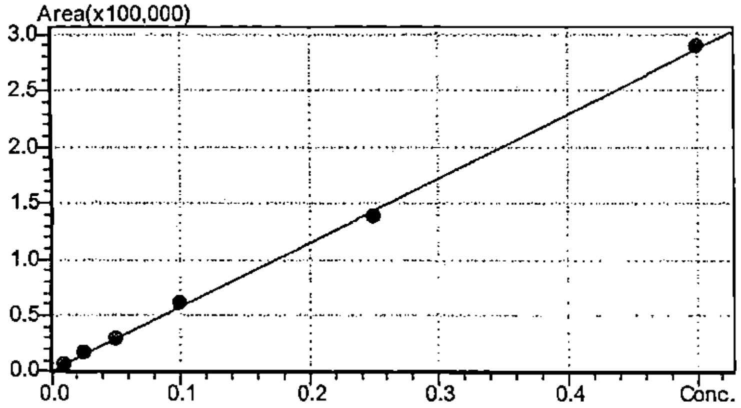
Y = aX + b, a = 809094.8, b = 6178.699, R^2 = 0.9992762, R = 0.9996380, RF % RSD: 10.02365

Calibration curve of cypermethrin 3



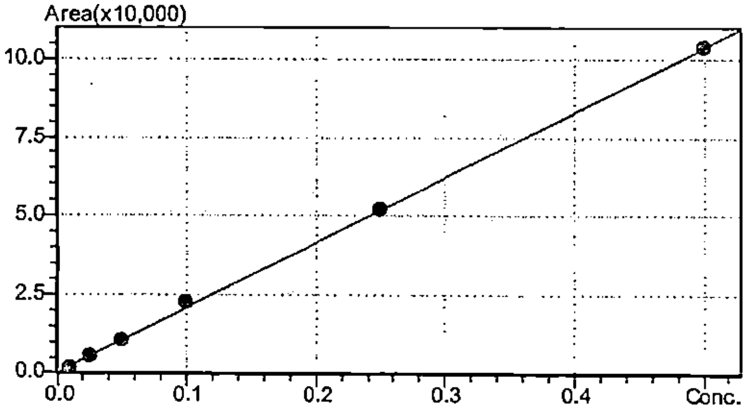
Y = aX + b, a = 679343.2, b = 4766.353, R^2 = 0.9994127, R = 0.9997063, RF % RSD: 10.18386

Calibration curve of cypermethrin 4



Y = aX + b, a = 571458.8, b = 847.7588, R^2 = 0.9991913, R = 0.9995956, RF % RSD: 7.524464

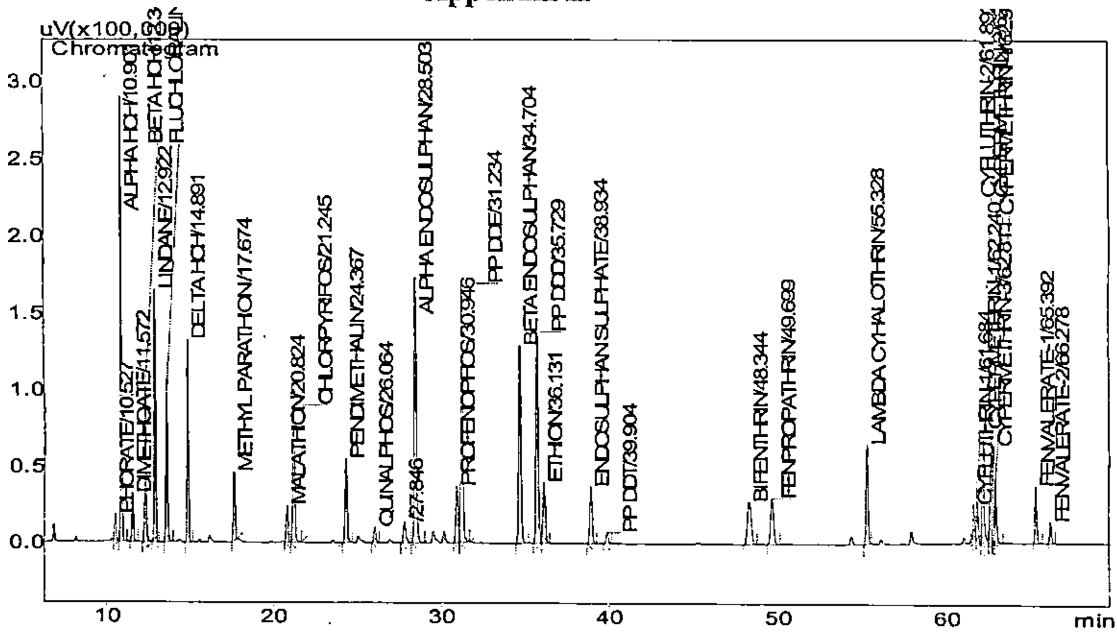
Calibration curve of fenvalerate 1



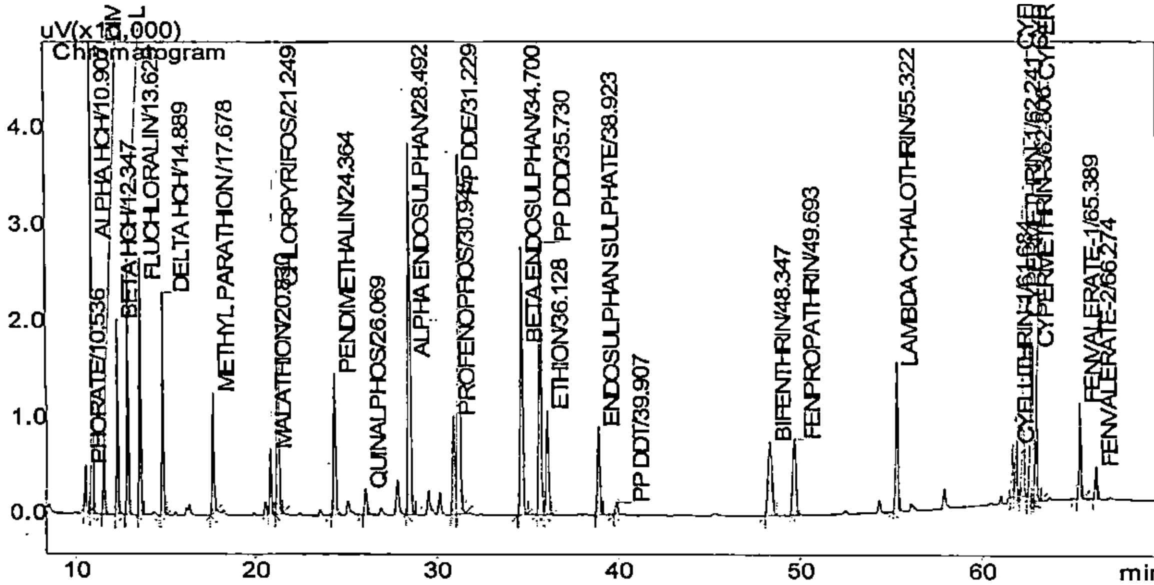
Y = aX + b, a = 206761.7, b = 308.6956, R^2 = 0.9997707, R = 0.9998854, RF % RSD: 6.015727

Calibration curve of fenvalerate 2

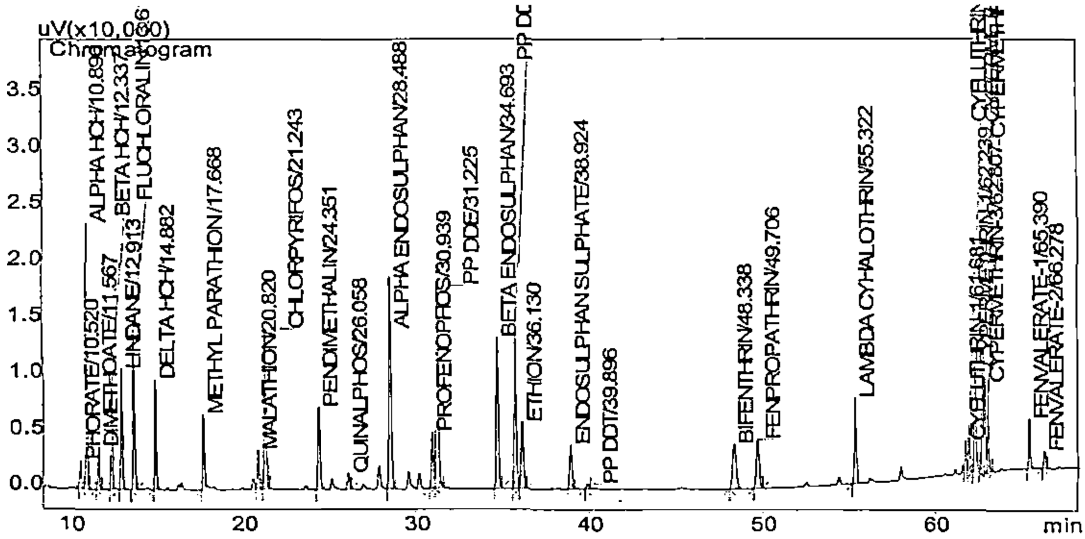
Appendix II



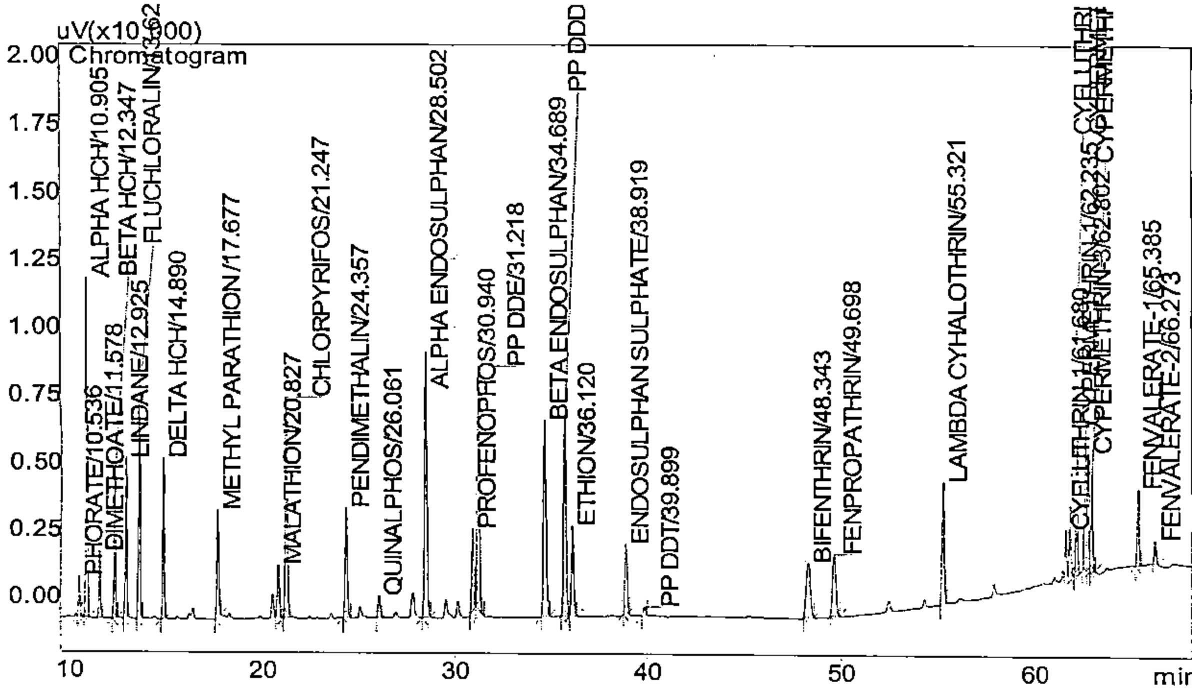
Name	Ret. Time	Conc.	Units	Area
PHORATE	10.527	0.43811	ppm	106175
ALPHA HCH	10.901	0.50406	ppm	1663753
DIMETHOATE	11.572	0.45813	ppm	205199
BETA HCH	12.347	0.49647	ppm	615528
LINDANE	12.922	0.56454	ppm	957723
FLUCHLORALIN	13.623	0.48831	ppm	662854
DELTA HCH	14.891	0.47106	ppm	795949
METHYL PARATHION	17.674	0.43897	ppm	316285
MALATHION	20.824	0.45807	ppm	179901
CHLORPYRIFOS	21.245	0.48259	ppm	747261
PENDIMETHALIN	24.367	0.48961	ppm	468425
QUINALPHOS	26.064	0.48317	ppm	91426
ALPHA ENDOSULPHAN	28.503	0.49728	ppm	1478460
PROFENOPHOS	30.946	0.44316	ppm	339988
PP DDE	31.234	0.49218	ppm	1535173
BETA ENDOSULPHAN	34.704	0.49170	ppm	1191083
PP DDD	35.729	0.48706	ppm	1213303
ETHION	36.131	0.47459	ppm	380474
ENDOSULPHAN SULPHATE	38.934	0.43940	ppm	359587
PP DDT	39.904	0.67212	ppm	69806
BIFENTHRIN	48.344	0.48710	ppm	432914
FENPROPATHRIN	49.699	0.48150	ppm	383244
LAMBDA CYHALOTHRIN	55.328	0.47114	ppm	513489
CYFLUTHRIN-1	61.684	0.37217	ppm	129115
CYFLUTHRIN-2	61.892	0.41141	ppm	208764
CYPERMETHRIN-1	62.240	0.46195	ppm	515490
CYPERMETHRIN-2	62.669	0.46032	ppm	393504
CYPERMETHRIN-3	62.811	0.46688	ppm	383925
CYPERMETHRIN-4	62.999	0.46421	ppm	320123
FENVALERATE-1	65.392	0.45484	ppm	260771
FENVALERATE-2	66.278	0.47460	ppm	98438



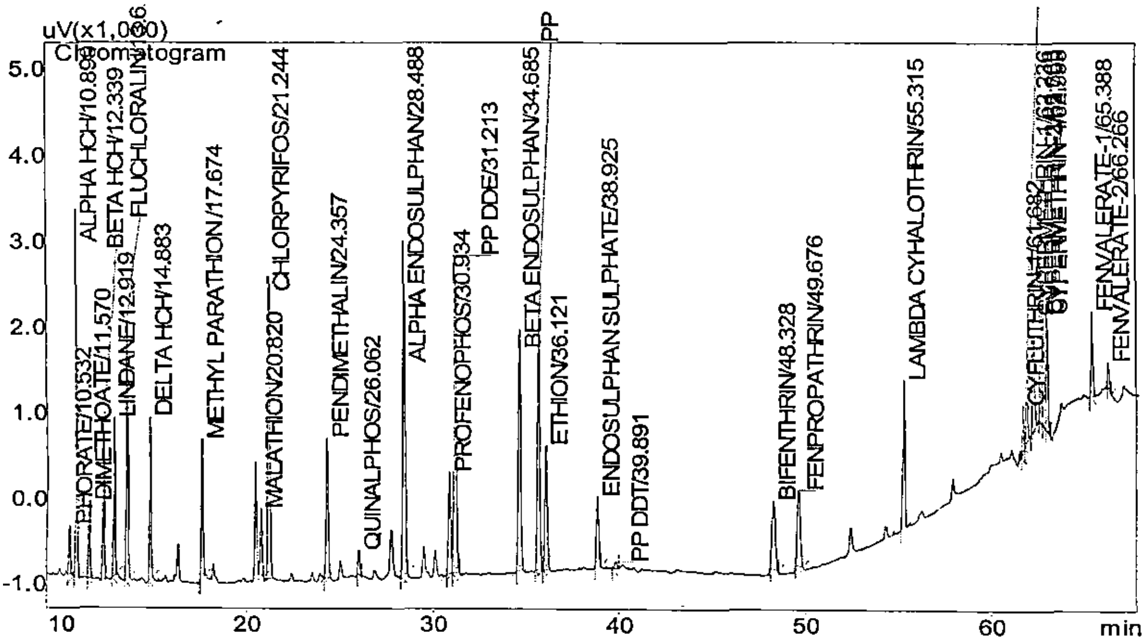
Name	Ret. Time	Conc.	Units	Area
PHORATE	10.536	0.10421	ppm	28302
ALPHA HCH	10.907	0.09594	ppm	290281
DIMETHOATE	11.575	0.10729	ppm	48713
BETA HCH	12.347	0.09896	ppm	113013
LINDANE	12.928	0.09387	ppm	141355
FLUCHLORALIN	13.629	0.11319	ppm	171723
DELTA HCH	14.889	0.09506	ppm	138860
METHYL PARATHION	17.678	0.11092	ppm	86671
MALATHION	20.830	0.10860	ppm	47957
CHLORPYRIFOS	21.249	0.11643	ppm	207514
PENDIMETHALIN	24.364	0.11209	ppm	117879
QUINALPHOS	26.069	0.11067	ppm	22534
ALPHA ENDOSULPHAN	28.492	0.10426	ppm	319869
PROFENOPHOS	30.945	0.11275	ppm	90927
PP DDE	31.229	0.10198	ppm	319990
BETA ENDOSULPHAN	34.700	0.10365	ppm	253574
PP DDD	35.730	0.10199	ppm	249346
ETHION	36.128	0.11401	ppm	102394
ENDOSULPHAN SULPHATE	38.923	0.10668	ppm	83831
PP DDT	39.907	0.09589	ppm	8998
BIFENTHRIN	48.347	0.11404	ppm	111894
FENPROPATHRIN	49.693	0.11475	ppm	101551
LAMBDA CYHALOTHRIN	55.322	0.10715	ppm	122192
CYFLUTHRIN-1	61.684	0.08694	ppm	30152
CYFLUTHRIN-2	61.891	0.09794	ppm	50212
CYPERMETHRIN-1	62.241	0.10945	ppm	130247
CYPERMETHRIN-2	62.671	0.11077	ppm	101102
CYPERMETHRIN-3	62.806	0.10972	ppm	94956
CYPERMETHRIN-4	62.998	0.10925	ppm	78987
FENVALERATE-1	65.389	0.10802	ppm	62579
FENVALERATE-2	66.274	0.10598	ppm	22222



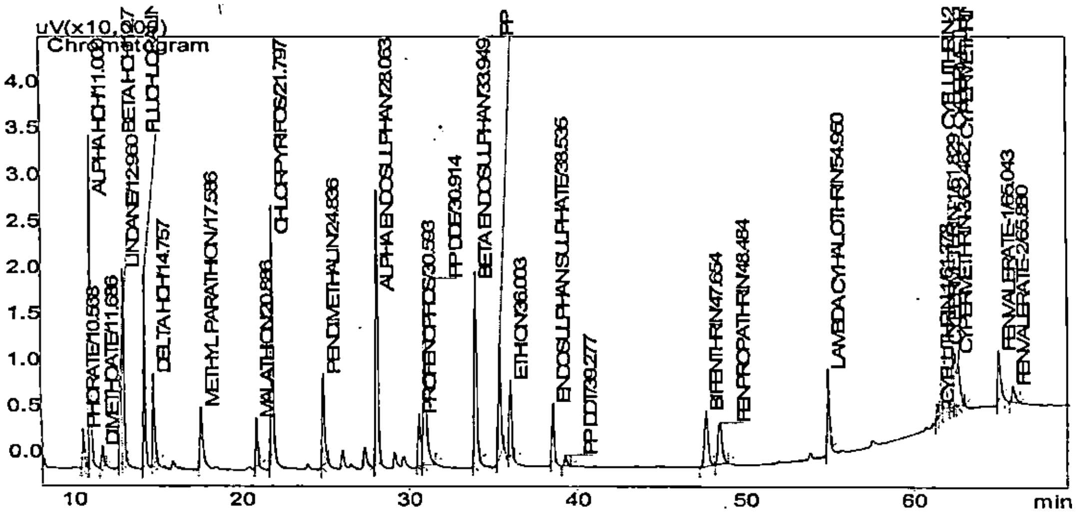
Name	Ret. Time	Conc.	Units	Area
PHORATE	10.520	0.04652	ppm	14847
ALPHA HCH	10.896	0.04779	ppm	128214
DIMETHOATE	11.567	0.04804	ppm	22284
BETA HCH	12.337	0.04987	ppm	50945
LINDANE	12.913	0.04783	ppm	61499
FLUCHLORALIN	13.613	0.05182	ppm	91367
DELTA HCH	14.882	0.04937	ppm	59027
METHYL PARATHION	17.668	0.05045	ppm	44349
MALATHION	20.820	0.04768	ppm	24959
CHLORPYRIFOS	21.243	0.05200	ppm	112530
PENDIMETHALIN	24.351	0.05112	ppm	61263
QUINALPHOS	26.058	0.05037	ppm	11382
ALPHA ENDOSULPHAN	28.488	0.04965	ppm	158895
PROFENOPHOS	30.939	0.04928	ppm	43086
PP DDE	31.225	0.04928	ppm	155860
BETA ENDOSULPHAN	34.693	0.04970	ppm	123223
PP DDD	35.727	0.04860	ppm	115680
ETHION	36.130	0.05076	ppm	53614
ENDOSULPHAN SULPHATE	38.924	0.04996	ppm	36818
PP DDT	39.896	0.04710	ppm	3849
BIFENTHRIN	48.338	0.05114	ppm	57769
FENPROPATHRIN	49.706	0.05103	ppm	52607
LAMBDA CYHALOTHRIN	55.322	0.04969	ppm	60416
CYFLUTHRIN-1	61.681	0.04114	ppm	14262
CYFLUTHRIN-2	61.883	0.04502	ppm	23445
CYPERMETHRIN-1	62.239	0.05027	ppm	65574
CYPERMETHRIN-2	62.665	0.05151	ppm	51526
CYPERMETHRIN-3	62.807	0.05103	ppm	47464
CYPERMETHRIN-4	62.996	0.05108	ppm	39466
FENVALERATE-1	65.390	0.04864	ppm	28645
FENVALERATE-2	66.278	0.04822	ppm	10280



Name	Ret. Time	Conc.	Units	Area
PHORATE	10.536	0.01694	ppm	7947
ALPHA HCH	10.905	0.02866	ppm	63829
DIMETHOATE	11.578	0.02850	ppm	13571
BETA HCH	12.347	0.03153	ppm	27758
LINDANE	12.925	0.03082	ppm	31995
FLUCHLORALIN	13.628	0.01857	ppm	47832
DELTA HCH	14.890	0.03517	ppm	34210
METHYL PARATHION	17.677	0.02474	ppm	26350
MALATHION	20.827	0.01834	ppm	13880
CHLORPYRIFOS	21.247	0.01808	ppm	62536
PENDIMETHALIN	24.357	0.01860	ppm	31067
QUINALPHOS	26.061	0.02045	ppm	5848
ALPHA ENDOSULPHAN	28.502	0.02377	ppm	82580
PROFENOPHOS	30.940	0.02268	ppm	23031
PP DDE	31.218	0.02320	ppm	74653
BETA ENDOSULPHAN	34.689	0.02572	ppm	65297
PP DDD	35.726	0.02803	ppm	64194
ETHION	36.120	0.01997	ppm	29869
ENDOSULPHAN SULPHATE	38.919	0.03257	ppm	22403
PP DDT	39.899	0.03378	ppm	2443
BIFENTHRIN	48.343	0.01785	ppm	29126
FENPROPATHRIN	49.698	0.01806	ppm	27285
LAMBDA CYHALOTHRIN	55.321	0.02499	ppm	33863
CYFLUTHRIN-1	61.680	0.02450	ppm	8486
CYFLUTHRIN-2	61.884	0.02653	ppm	14096
CYPERMETHRIN-1	62.235	0.01993	ppm	32414
CYPERMETHRIN-2	62.663	0.02344	ppm	28046
CYPERMETHRIN-3	62.802	0.02333	ppm	25053
CYPERMETHRIN-4	62.993	0.02420	ppm	21208
FENVALERATE-1	65.385	0.02947	ppm	17690
FENVALERATE-2	66.273	0.02571	ppm	5625



Name	Ret. Time	Conc.	Units	Area
PHORATE	10.532	0.00404	ppm	3056
ALPHA HCH	10.899	0.01652	ppm	22987
DIMETHOATE	11.570	0.00932	ppm	5018
BETA HCH	12.339	0.01685	ppm	9207
LINDANE	12.919	0.01819	ppm	10095
FLUCHLORALIN	13.620	0.00369	ppm	18690
DELTA HCH	14.883	0.02206	ppm	11301
METHYL PARATHION	17.674	0.00175	ppm	10258
MALATHION	20.820	0.00466	ppm	5199
CHLORPYRIFOS	21.244	0.00654	ppm	26244
PENDIMETHALIN	24.357	0.00205	ppm	11896
QUINALPHOS	26.062	0.00135	ppm	1817
ALPHA ENDOSULPHAN	28.488	0.00677	ppm	32486
PROFENOPHOS	30.934	0.00494	ppm	9664
PP DDE	31.213	0.00959	ppm	32269
BETA ENDOSULPHAN	34.685	0.00894	ppm	24745
PP DDD	35.722	0.01184	ppm	23660
ETHION	36.121	0.00317	ppm	12024
ENDOSULPHAN SULPHATE	38.925	0.01436	ppm	7314
PP DDT	39.891	0.01773	ppm	750
BIFENTHRIN	48.328	0.00402	ppm	10301
FENPROPATHRIN	49.676	0.00403	ppm	10319
LAMBDA CYHALOTHRIN	55.315	0.00572	ppm	13151
CYFLUTHRIN-1	61.682	0.00836	ppm	2889
CYFLUTHRIN-2	61.885	0.00889	ppm	5172
CYPERMETHRIN-1	62.236	0.00249	ppm	13360
CYPERMETHRIN-2	62.660	0.00341	ppm	11297
CYPERMETHRIN-3	62.799	0.00598	ppm	11015
CYPERMETHRIN-4	62.993	0.00658	ppm	9236
FENVALERATE-1	65.388	0.00948	ppm	6267
FENVALERATE-2	66.266	0.00784	ppm	1929



Name	Ret. Time	Conc	Units	Area
PHORATE	10.568	0.07474	ppm	31594
ALPHA HCH	11.000	0.07411	ppm	231178
DIMETHOATE	11.686	0.07546	ppm	20245
BETA HCH	12.778	0.07251	ppm	72109
LINDANE	12.960	0.07211	ppm	149734
FLUCHLORALIN	14.224	0.07426	ppm	147077
DELTA HCH	14.757	0.07165	ppm	80490
METHYL PARATHION	17.586	0.07658	ppm	61098
MALATHION	20.886	0.07454	ppm	40537
CHLORPYRIFOS	21.797	0.07481	ppm	259427
PENDIMETHALIN	24.836	0.07517	ppm	94969
ALPHA ENDOSULPHAN	28.063	0.07335	ppm	259878
PROFENOPHOS	30.593	0.08146	ppm	56921
PP DDE	30.914	0.08453	ppm	238921
BETA ENDOSULPHAN	33.949	0.07274	ppm	201032
PP DDD	35.355	0.07078	ppm	122589
ETHION	36.003	0.07313	ppm	81492
ENDOSULPHAN SULPHATE	38.535	0.07249	ppm	58927
PP DDT	39.277	0.07856	ppm	11783
BIFENTHRIN	47.654	0.09960	ppm	93371
FENPROPATHRIN	48.484	0.00000	ppm	76660
LAMBDA CYHALOTHRIN	54.950	0.07246	ppm	76108
CYFLUTHRIN-1	61.378	0.11501	ppm	11276
CYFLUTHRIN-2	61.564	0.07601	ppm	16745
CYPERMETHRIN-1	61.829	0.07352	ppm	62091
CYPERMETHRIN-2	62.245	0.09523	ppm	40367
CYPERMETHRIN-3	62.462	0.07981	ppm	48040
CYPERMETHRIN-4	62.636	0.09007	ppm	56175
FENVALERATE-1	65.043	0.06821	ppm	50752
FENVALERATE-2	65.880	0.00000	ppm	21918

MONITORING AND DECONTAMINATION OF PESTICIDE RESIDUES IN AGRICULTURAL COMMODITIES

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Abstract of the
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MASTER OF SCIENCE IN AGRICULTURE

Faculty of Agriculture

Kerala Agricultural University, Thrissur.

DEPARTMENT OF AGRICULTURAL ENTOMOLOGY
COLLEGE OF AGRICULTURE,
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2013

ABSTRACT

The present investigation on "Monitoring and decontamination of pesticide residues in agricultural commodities" was conducted at the Department of Entomology, College of Agriculture, Vellayani during 2011 - 2013. The objectives were to monitor the pesticide residues in agricultural commodities like rice, wheat, rice flour, wheat flour (atta and maida), cardamom, cumin seed, capsicum, okra and curry leaf and to standardize techniques for decontamination.

Multi Residue Methods (MRM) for pesticide residue analysis in rice flour, wheat flour (atta and maida), rice, wheat, cardamom, cumin seed, capsicum, okra and curry leaf were validated by conducting recovery studies. Five important validation parameters *viz.,* limit of detection, linearity, limit of quantification, recovery and repeatability were established.

Data on monitoring of pesticide residues in agricultural commodity revealed that none of the rice flour, atta, maida, raw rice and parboiled rice samples showed the presence of pesticide residues. However, all the cardamom, cumin seed and curry leaf samples showed presence of multiple pesticide residues at varying levels. Basmathi rice (5 samples), wheat (5 samples), capsicum (3 samples) and okra (2 samples) showed the presence of pesticide residues.

Based on the monitoring data, six insecticides *viz.,* malathion, methyl parathion, chlorpyriphos, quinalphos, cypermethrin and fenvalerate were selected for assessing the effect of washing, soaking and cooking on the removal of insecticide residues in rice and washing, drying and milling on the removal of insecticide residues in wheat at five hours and two weeks after insecticide spraying. Out of different processing techniques studied, four washings in tap water for two minutes along with rubbing of grains followed by cooking removed maximum amount of residues (88.36 - 98.63 %) and four washings in tap water for two minutes along with rubbing of grains removed maximum amount of residues (51.09 - 75.67 %) in wheat.

In order to assess the effect of decortication on removal of insecticide residues, cardamom samples with presence of more than one insecticide were subjected to decortication. It may be seen that most of the detected residues remained on the surface of capsule cover and highly systemic insecticides like profenophos had penetrated into the seed.

In order to standardize a decontaminating solution of household product an experiment was conducted with seven treatments and three replications. Among the decontamination methods adopted to reduce the insecticide residues in vegetables, dipping in 2 % tamarind for 15 minutes was the best treatment to eliminate residues from okra (37.28 - 80.37 %) and curry leaf (38.70 - 98.05 %) whereas dipping in 2 % vinegar solution was the best for decontaminating capsicum (31.18 - 74.88 %). It may be concluded that the efficiency of decontaminating treatments depend on the chemistry of pesticide molecule, age of the pesticide residue and the surface character of the commodity.