PESTICIDE USE PATTERN AND MONITORING OF RESIDUES IN CARDAMOM IN IDUKKI DISTRICT

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DECLARATION

I hereby declare that this thesis entitled **Pesticide use pattern and monitoring of residues in cardamom in Idukki district'** 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 fellowship or other similar title of any other University or Society

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Dedicated to

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LIST OF ABBREVIATIONS

%	Per cent
@	At the rate of
a.i.	Active ingredient
AR	Analytical reagent
BDL	Below detectable level
CRM	Certified reference material
cm	Centimetre(s)
°C	Degree Celsius
et al	And others
Fig.	Figure
g^{-1}	per gram
HAS	Hours After Spraying
HPLC	High performance liquid chromatography
µg	Microgram
ha^{-1}	per hectare
l^{-1}	per litre
kg	Kilogram
LOD	Limit Of Detection
LOQ	Limit Of Quantitation
m	Metre
ml	Millilitre
µL	Microlitre
MSL	Mean sea level
MRL	Maximum Residue Limit
OC	Organochlorines
OP	Organophosphates
ppm	Parts per million
RSD	Relative standard deviation
SD	Standard deviation

SL	Soluble liquid
Sp.	Species
SP	Synthetic pyrethroids
viz.	namely

Introduction

1. INTRODUCTION

Cardamom, *Elettaria cardamomum* L. Maton, of commerce is the matured /ripe fruit processed by artificial drying and curing. It is often referred as the "Queen of Spices" because of its very pleasant aroma, taste *etc* and is used as an exquisite flavoured spice all around the globe. Its reputation as a spice is unmatchable as it is one of the highly priced and most expensive spices after vanilla and saffron. Cardamom as a crop is generally cultivated in the tropical regions of the world and the crop prefers a well drained, deep, good textured soil rich in humus for optimum growth and production. Cultivation of cardamom is mostly concentrated in the ever green forests of Western Ghats in south India. The cardamom growing regions of south India lies within 8 - 30 degree N latitudes and 75-78 degree longitudes. Besides India, it is grown as a commercial crop in Guatemala and on small scale in Tanzania, Sri Lanka, El Salvador, Vietnam, Laos, Thailand, Cambodia, Honduras, and Papua & New Guinea.

According to traditional wisdom of Ayurveda, cardamom has unique therapeutic properties. It stimulates digestion and is a good stimulant for those suffering from flatulence and gas problems, prevents stomach cramps, helps in cleansing the body, improves blood circulation especially to the lungs and prevents spasms or convulsions.

India accounts for the largest area under cardamom at the global level, but the productivity is low compared to other producing countries (Thomas and Kuruvila, 2007). The world production of this spice is around 35000 metric tonnes per annum. According to the recent statistics, Guatemala accounts for the maximum production of cardamom followed by India and Tanzania. In India, cardamom is cultivated in the hilly forests of south India comprising of Kerala, (60%) Karnataka, (32%) and Tamilnadu (8%). One of the major constraints in the production of cardamom is its proneness to infestation by diverse group of insect pests and diseases. At present, these pests are kept under check with the steady use of synthetic pesticides. Considering the number of rounds of pesticide sprays and quantity of pesticides used in cardamom, one can rate cardamom as the highest pesticide consuming rainfed crop in the world and hence reckoned as a pesticide hot spot of the world (Murugan *et al*, 2011). On an average, farmers apply a minimum 27 kg of pesticides in a hectare (ha) of cardamom plantation as against 9 kg of active ingredient in tea plantations. In a desperate bid to save the crop and the highly priced produce, farmers often resort to application of pesticides in every 15 to 18 days in the cardamom plantations resulting in 18 to 25 sprays per year as against the recommended use of seven to eight rounds (Murugan *et al*, 2011).

Unscientific use of dangerously high levels of pesticides on cardamom plantations is hazardous both to human and environment and may result in several social problems from the unethical use of pesticide in the fragile ecosystems of the Cardamom Hill Reserve. The irrational and random application of pesticides for the control of major pests has resulted in the presence of excessively high levels of harvest time residues in cardamom. Studies on monitoring of pesticide residues in cardamom under the All India Network Project on Pesticide Residues had revealed wide spread occurrence of multiple residues of pesticides in majority of the sample which become a matter of threat for export and foreign exchange revenue. Though the insecticides deposited by plant protection operations might be reduced during curing, garbling and storage, it is emphasized to have strict monitoring of pesticide residues in cardamom capsules before being exported. In the light of the above facts, a detailed study entitled "Pesticide use pattern and monitoring of residues in cardamom in Idukki district" has been undertaken in the major cardamom growing zones of Idukki district with the following objectives.

1. To generate data on pesticide use pattern among the farmers in cardamom plantations in Udumbanchola, Vandenmedu and Poopara of Idukki district.
2. To validate Multi Residue Methods (MRM) for pesticide residue analysis in cardamom.

3. To monitor the level of pesticide residues in cardamom
4. To study the effect of curing process on removal of residues.

Review of literature

2. REVIEW OF LITERATURE

Cardamom, the Queen of spices is indigenous to the southern states of India. It is cultivated in Western Ghats in an area of 73,725 ha (2005-06) and one of the important products fetching considerable foreign exchange (Stanley, 2007). Among the cardamom plantations, 60% of the area is occupied by Kerala, 30% by Karnataka and the remaining 10% by Tamil Nadu (Thomas and Kuruvila, 2007). India was the world's largest producer and exporter until it was taken over by Guatemala in the 18th century. One of the major constraints in the production of cardamom is the excessive damage inflicted by pests. At present, these pests are kept under check with the help of synthetic insecticides. With the strict legislations enforced by the EPA, cardamom capsules with pesticide residues have a chance of being rejected by the hitherto importing countries, which in turn would have a major say in foreign revenues (Kumar *et al.*, 2009). Recently, residues of insecticides such as triazophos and profenophos were detected in the consignment exported from India (Thomas and Kuruvila, 2007).

It is in this context, a study was undertaken to find out the pesticide use pattern and the levels of pesticide residues in cardamom. The earlier work done in relation to the above topic is reviewed under the following heads.

2.1 Pests of cardamom

There are 56 different insect and mite species reported as pests of cardamom in India (Kumaresan and George, 1999). Considering the infestation of plant parts they can be placed into three common categories *viz.*, foliage pests, pests on flowering parts and sub terranean parts. Ecological changes, particularly edaphic factors have added new pest problems in cardamom plantation in recent years. Many pests considered minor are assuming alarming proportions. Excessive use of insecticides in cardamom hills was reported to flare up incidence of minor pests like white fly, red spider mite, scale insects, shoot borer etc (Varadarasan, 2003). However, in 2009 Spices Board reported that minor pests infesting cardamom are white fly, shoot fly, scale insects, hairy caterpillar, lacewing bug, red spider mites etc and they may become major pests under conditions of improper use of chemical pesticides. Root grub has emerged as serious pest in exposed, warm and less shaded conditions. Outbreak of whiteflies and locusts in certain pockets is another example of ill effects of changes in microclimate (Nybe and Miniraj, 2007).

Among the different pests of cardamom, thrips is the most persistent and destructive one requiring timely control measures. The extent of damage by thrips in terms of quality and quantity ranges from 30 to 80% (Kumaresan *et al.*, 1988).

2.1.1 Management of cardamom pests

Thrips are the most noxious pest infesting cardamom due to which the capsules obtained will be inferior in quality and quantity and is the critical factor affecting the economy of cardamom cultivation. Spices Board, India, recommended a schedule for its effective control.

Table 1. Chemical methods of pest control in small cardamom (Anon., 2009).

Rainfed	Irrigated
First spray (February first week) quinalphos or phenthoate @ 200 ml or 150 ml 100 l^{-1} of water.	First spray (February first week) quinalphos or phenthoate @ 200 ml or 150 ml 100 l^{-1} of water.
Second spray (March second week) profenophos or monocrotophos @ 200 ml or 150 ml 100 l^{-1} of water.	Second spray (March first week) profenophos @150ml 100 l^{-1} of water.
Thrid spray (April third week) chlorpyriphos or phosalone @ 200 ml in 100 l^{-1} of water	Thrid spray (April first week) chlorpyriphos or phosalone @ 200 ml 100 l^{-1} of water
Fourth spray (May fourth week) acephate (150 g) in 100 l^{-1} of water	Fourth spray (May first week) acephate (200 g) in 100 l^{-1} of water
Fifth spray (July end) quinalphos or phenthoate @ 200 ml or 150 ml 100 l^{-1} of water	Fifth spray (June first week) monocrotophos @ 200 ml 100 l^{-1} of water
Sixth spray (Sept./Oct.) profenophos or monocrotophos @ 200 ml or 150 ml 100 l^{-1} of water	Sixth spray (July end/August) quinalphos or phenthoate @ 200 ml or 150 ml 100 l^{-1} of water
Seventh spray (December) methyl parathion @100ml 100 l^{-1} of water	Seventh spray (September) profenophos @ 150 ml 100 l^{-1} of water
	Eighth spray (early November) monocrotophos @ 200 ml 100 l^{-1} of water
	Ninth spray (December third week) Methyl parathion @100 ml 100 l^{-1} of water

Ambıkadevı 2007 summarısed the chemıcal management of major pests and dıseases of cardamom ın Kerala, the detaıls of whıch are furnıshed under

Table 2 Chemıcal management of major pests and dıseases ın cardamom ın Kerala

Insect pest/dısease	Chemıcal Management
Cardamom thrıps *Scıothrıps cardamom* (Ramk)	Applıcatıon of any of the recommended ınsectıcıdes from January to May at monthly ıntervals Profenophos 50 EC (0 05 %) fenthıon 80 EC (0 075%) monocrotophos 36 EC (0 075 %) dımethoate 30 EC (0 05 %) or hostathıon 40 EC (0 04%) followed by 3 rounds of sprayıng at 45 days ıntervals from August to January wıth bee safe ınsectıcıdes lıke quınalphos 25 EC(0 05 %) or phosalone 35 EC (0 07 %)
Shoot and capsule borer *Conogethes punctıferalıs* (Guenee)	Spray recommended ınsectıcıdes on early larval stages *ıe* 15 20 days after adult emergence ın the field Profenophos50 EC (0 05 %) fenthıon 80 EC (0 075 %) monocrotophos 36 EC (0 075 %) dımethoate 30 EC (0 05 %) or hostathıon 40 EC (0 04 %)
Root grub *Basılepta fulvıcorne* Jacoby	Drench the soıl wıth chlorpyrıphos 20 EC (0 04 %) at 5 7 lıtres/plant after forkıng Apply phorate 10 G at 30 g plant or carbofuran 3 G (100 g/plant durıng September/October after ensurıng adequate moısture ın soıl)
Cardamom whıte fly *Sınghıella cardamomı* Davıd & Subramanıam	Nymphs can be controlled by sprayıng under surface of leaves wıth a mıxture of neem oıl 0 5 %+ wettıng agent 0 5 % or acephate(0 075 %)
Shoot fly *Formosına flavıpes* Mall	Sprayıng dımethoate or quınalphos (0 05 %) or apply carbofuran 3 G (0 5 kg a ı/ha)
Nematodes *Meloıdogyne sp*	Apply carbofuran 3 G 100 g/plant or phorate 10 G 30 g/plant durıng September/October
Lace wıng Bug	Sprayıng of ınsectıcıdes recommended for thrıps

Stephanitis typicus (Dist)	
Azhukal or capsule rot	Spraying of bordeaux mixture 1% or akomin 0 4% and drenching copper oxy chloride (0 2 %) in May/June July/August and also in September according to the severity of the disease
Clump rot or rhizome rot *Pythium vexans* de Bary *Rhizoctonia solani* Kuihn *and Fusarium sp*	Drenching the plant base with copper oxy chloride (0 2 %) 2 3 times starting from June/July depending on the severity of the disease
Chenthal (*Colletotrichum gloeosporoides* (Penz))	Spraying carbendazim 0 2 %/ mancozeb 0 3 %
Leaf blotch *Phaeodactylium alpiniae* (Sawada)	Need based spraying of bordeaux mixture 1 % or mancozeb 0 3 %
Leaf spot *Cercospora zingiberi* Togshi Katsaki	Need based spraying of mancozeb 0 3 % or carbendazim 0 2 %
Capsule brown spot (*Colletotrichum gloeosporoides* (Penz)	Need based application of mancozeb 0 3 % or carbendazim 0 2 %
Leaf blight *Phytophthora meadii* Mc Rac	Need based spraying of bordeaux mixture 1 % or akomin 0 4 %

2 1 2 Pesticides used for the management of cardamom pests

Chozhan and Regupathy (1994) reported that for the effective management of cardamom thrips and shoot and capsule borer high volume spray applications of chlorpyriphos 0 05 % dimethoate 0 05 % fenthion 0 05 % methyl parathion 0 05 % and monocrotophos 0 025 % (a i) were recommended

6 Acetone HPLC grade

7 Sodium sulphate AR grade (anhydrous)

8 Primary Secondary Amine (PSA)

11 Florisil AR grade

Equipments

1 Electronic weighing balance

2 Vortex shaker

3 Turbovap LV

4 Laboratory centrifuge

5 Mechanical shaker

6 Rotary vacuum flash evaporator

7 Hot air oven

8 Gas Chromatograph (Shimadzu GC 2010 A)

All the glassware were first washed with clean tap water then with 1% labolme again washed thoroughly with tap water distilled water followed by rinsing with acetone These were kept at room temperature for drying Fully dried glassware were kept in a hot air oven at 50^0C Syringes were thoroughly rinsed with acetone followed by hexane Solvents used in the study were all glass distilled Sodium sulphate was prewashed with acetone dried at room temperature and then activated in an oven at 110 ^{0}C for three hours Analytical standard mixtures of commonly used pesticides in cardamom were prepared from the Certified Reference Materials (CRM) procured from Sigma Aldrich Cardamom was fortified at five different levels (0 01 0 05 0 10 0 50 1 µg g) Extraction and clean up methods were performed by using different solvent and reagent systems

Among the granular pestıcıdes phorate at 2 5g a ı/clump gave effectıve control of thrıps (Eapen 1994) Profenophos 0 05 per cent (Renuka 2001) lambda cyhalothrın 15 ppm (Kumar *et al* 2002) and dıafenthıuron (Stanley 2007) were recommended for the control of thrıps Evaluatıon of certaın newer ınsectıcıdes such as profenophos thıamethoxam and dıafenthıuron ındıcated that profenophos at 0 05% could effectıvely reduce thrıps as well as shoot and capsule borer ınfestatıon thereby recordıng the hıghest yıeld ın cardamom In another study Rajabasker *et al* (2000) reported that dıafenthıuron was effectıve agaınst shoot and capsule borer and thrıps Dıafenthıuron a new molecule that specıfically ınterferes on mıtochondrıal ATP ase of ınsects could reduce thrıps ınfestatıon sıgnıficantly (Josephrajkumar *et al* 2007) Nambıar and coworkers (1975) recommended the use of dımethoate and phosphamıdon 0 05 per cent on cardamom ın Kerala for the management of shoot and capsule borer Sprayıng acephate 0 075 per cent ethıon 0 1 per cent and trıazophos 0 05 per cent were found equally effectıve agaınst the nymphs of whıtefly (Kumaresan and Gopakumar 1993 Josephrajkumar *et al* 2007) Applıcatıon of phorate 10 G or carbofuran 3 G were done for the management of root grubs or root knot nematode subject to the condıtıon that enough soıl mo sture ıs avaılable at the tıme of applıcatıon Under poor soıl moısture condıtıon chlorpyrıphos 20EC @ 0 04% (2 to 5 lıtres per clump) may be drenched ın soıl around and ınsıde the clump for root grub management (Anon 2009)

Shetty (2000) reported that on an average farmers use 27 kg of pestıcıdes ın a hectare (ha) of cardamom plantatıon In another study Shetty *et al* (2008) reported that as far as Kerala ıs concerned 50 % of the total pestıcıde consumptıon goes to cardamom and small cardamom requıres 12 ınsectıcıde and sıx fungıcıde sprays per year Consıderıng the number of rounds of pestıcıde sprays and quantıty of pestıcıdes used ın Indıan cardamom hılls one can rate cardamom as the h ghest pestıcıde consumıng raınfed crop ın the world (Murugan *et al* 2011)

Usha(2007) reported that there has been an ıncrease ın the pestıcıde consumptıon ın cardamom durıng the last ten years and the results of a survey showed an unscıentıfic and non judıcıous use of pestıcıdes by farmers ın Kattappana block of Idukkı dıstrıct She also reported that small cardamom consumes more than 100 kg (ha year) of phorate ın Kerala The other pestıcıdes used are quınalphos monocrotophos chlorpynphos fenthıon methyl parathıon endosulfan and emısan Fenthıon endosulfan emısan and phosphamıdon are some chemıcals ın use ın cardamom plantatıons whıch are not recommended Murugan and co workers (2011) reported that around 650 tonnes of pestıcıdes actıve ıngredıents are applıed for the control of pests and dıseases ın cardamom ın 2009 and cardamom needs at least 15 18 rounds of pestıcıde sprays per year The crop ıs prone to ınfestatıon by varıous ınsect pests whıch deterıorate the qualıty of the produce and thıs necessıtates frequent applıcatıon of pestıcıdes even at 15 20 days ınterval towards the base of the plant (Paul *et al* 2012)

The Central Insectıcıdes Board advıses quınalphos monocrotophos and phenthoate for the management of cardamom thrıps and dıafenthıuron agaınst cardamom thrıps and capsule borer (www cıbrc nıc ın/major uses/ınsectıcıdes)

2 2 Pestıcıde resıdues ın cardamom

In a monıtorıng study carrıed out by Chozhan and Regupathy (1989) 130 cardamom samples were analyzed for findıng out the resıdues of organophosphorus ınsectıcıdes the number of samples whıch contaıned resıdues of quınalphos monocrotophos and fenthıon above maxımum resıdue lımıt were 12 25 and one respectıvely Resıdues of more than one ınsectıcıde were detected ın some samples The level of resıdues varıed from 0 008 0 72 ppm ın the case of qunalphos 0 001 0 54 ppm ın the case of fenthıon and 0 004 0 98 ppm ın the case of monocrotophos A study conducted by Mathew and co workers(1998) showed that resıdues of quınalphos were present ın fresh and drıed cardamom capsules

Spıce samples ıncludıng cardamom monıtored durıng 1980 89 ın Indıa ındıcated 75 100 per cent contamınatıon wıth DDT and HCH (Kathpal and Kumarı 1993) Sınghal (2000) reported that ₹1000 crore worth agrıcultural exports are rejected due the presence of hıgh level of pestıcıde resıdues Studıes conducted under the All Indıa Network Project on Pestıcıde Resıdues ındıcated the presence of resıdues of ınsectıcıdes ın varyıng levels Endosulfan quınalphos and monocrotophos were the common pestıcıdes whıch exceeded the Maxımum Resıdue Lımıt (Anon 2001)

Shetty (2006) reported that residues of seven pesticides were detected in cardamom samples collected from the cardamom hill reserve and the highly toxic pesticides like triazophos quinalphos and endosulfan were obtained at a higher level in these samples In cardamom ecosystem the number of pesticide sprays was as high as 20 per season in Kerala and Tamil Nadu

Monitoring of pesticide residues in cardamom under the DAC funded project on monitoring of pesticide residues at national level revealed the occurrence of residues of dichlorvos in samples collected from Coimbatore region Similarly samples collected from Idukki and Thiruvananthapuram districts showed the residues of quinalphos to the tune of 0 06 to 0 395mg kg ^{1} (www fssai gov in /portals/0/pdf)

During 2012 out of the 597 spice samples analysed 37 18 percentage samples were detected with pesticide residues and 15 91 % samples contained multiple residues of pesticides Number of samples containing pesticide residues above PFA/Codex MRL were 52 whereas 372 were without PFA/Codex MRL (Anon 2012) According to the data generated by Pest cide Res due Research and Analytical Laboratory (PRRAL) KAU Vellayani Centre 90 30% of the different food commodities (>4000 samples tested over 6 years) were found to be totally free of pesticide residues and only 9 69% of the samples showed the residues out of this 9 69 % only 3 92 % had pesticide residues above maximum residue limit (MRL) fixed by FSSAI Commodity wise data showed that among the spices monitored for pesticide residues cardamom (79 2%) had detectable levels of pesticide residues (Mathew *et al* 2012) The residues of pesticides deposited during plant protection operations are a major concern of today through out the world Pesticide residues in spices had affected our exports in the past few years (Bhardwaj *et al* 2011)

2 3 Health hazards to non target organisms

The accumulation of organochlorine pesticides in the body fat of mammals causes potential hazards (Jensen 1983) A study done in the Nilgiris district of Tamil Nadu by Muralidharan and Murugavel (1998) reveals that water sediments six species of fishes birds like little grey heron Pond heron Little egret are contaminated with pesticides like DDT and its metabolites like DDD and DDE isomers of HCH and alpha and beta endosulfan A wide range of non target organ sms including human beings and domestic animals are exposed to these pesticides which lead to adverse health effects While spraying the most common problem felt by labourers is vomiting sensation Continuous spraying of any chemical for three hours resulted in head ache Other symptoms include itching and burning allergy diseases fever etc (Usha 2007)

2 4 Validation of Multi Residue Methods (MRM) for pesticide residue analysis in cardamom

A multi residue method for the estimation of six organophosphorous insecticides commonly used in cardamom crop was optimized by Chozhan and Regupathy in 1994 and found that under isothermal analysis using 5% SE 30 column the order of peak emergence was methyl parathion monocrotophos chlorpyriphos dimethoate quinalphos and fenthion

A method for the simultaneous estimation of eight insecticides representing organochlorines organophosphates and synthetic pyrethroids was standardized and validated in which the percentage recoveries ranged from 73 to 88 in the case of organochlorines 81 to 119 for organophosphates and 80 103 for synthetic pyrethroids (George *et al* 2007)

2 5 Effect of processing on removal of residues

Unit operat ons normally involved in processing of food crops reduce or remove res dues of insecticides and other pestic des that are present in them Operations such as washing peeling blanching and cooking play a role in reduction of residues (Elkins 1989) Sun drying of raisins decreased the dimethoate residues (1 02 µg g) by 81% while oven drying preceded by wash ng led to 72% decline in residues (Cabras *et al* 1998) Drying of grapes led to 64 2 71 9% losses of methamidophos possibly due to evaporation of the pesticide during the process (Athanasopoulos *et al* 2005) In a study conducted by Mathew *et al* (1998) it was proved that the residues of quinalphos fenthion methyl parathion and monocrotophos in cardamom showed degradation from the initial levels of 0 46 1 04 2 81 and 3 43 µg g to 0 01 0 01 0 01 and 0 007 µg g respectively on the 28th day after spraying and their waiting periods were fixed as 4 74

9 45 15 and 21 8 days respectively Removal of residues of quinalphos and monocrotophos to the tune of 30 to 50 per cent due to curing process in cardamom was reported by Mathew *et a l* (1998) Similarly the residues of mancozeb could be reduced to 62 per cent by washing the capsules (Mathew *et al* 1999) Curing of green pods resulted in degradation of diafenthiuron residue to the tune of 50 7 to 52 4 per cent in cardamom (Rajabaskar *et al* 2008) Some part of the pesticides might have dissipated during the processing (Tiwari *et al* 2008) Study conducted by Pathan *et al* (2009) revealed that initial deposits of dicofol (18 5 EC) ethion (50 EC) and cypermethrin (25 EC) in fresh chilli were 0 72 0 40 and 0 02 mg kg^{1} where as in sundried chilli powder the residue levels were 4 03 1 41 and 0 15 mg kg^{1} and the processing factors computed were 5 59 3 52 and 7 5 respectively It could be inferred that the increase in concentration of pesticides in dry chillies was due to reduction in total weight

Materials and Methods

3 MATERIALS AND METHODS

The present study entitled Pesticide use pattern and monitoring of residues in cardamom in Idukki District aims to develop a database on pesticide use pattern in cardamom plantations of Idukki district validation of multiresidue methods (MRM) for estimation of pesticide residues in cardamom monitoring of pesticide residues in cardamom and to study the effect of curing process on removal of residues from cardamom capsules All the experiments connected with the study were conducted in different locations of Idukki district *viz* Udumbanchola Vandanmedu and Poopara The samples for the estimation of pesticide residues collected from these locations were brought to the Pesticide Residue Research and Analytical Laboratory (PRRAL) AINP on Pesticide Residue College of Agriculture Vellayam for further analysis and estimation

3 1 Development of database on pesticide use pattern in cardamom plantations of Idukki district

A detailed survey was conducted to study the consumption and use pattern of pesticides in the major cardamom growing zones of Idukki district during 2010 11 A purposive survey was carried out among farmers with the help of a suitable questionnaire (Appendix II) Three cardamom growing zones based on productivity in decreasing level *viz* Vandenmedu (A zone) Udumbanchola (B zone) and Poopara (C zone) were identified From each location ten farmers/planters were selected randomly making a total sample size of 30 Each of them was interviewed separately and informations pertinent to pesticides used socio economic status source of pesticides source of technical information major pests quantity rate time frequency and method of application of pesticides equipments used for application of pesticides pesticide handling practices storage safety precautions followed etc were recorded

3 2 Validation of Multi Residue Methods (MRM) for pesticide residue analysis in cardamom

Multi Residue Methods (MRM) for cardamom were validated using the validated protocol

The following glassware reagents and equipments were used for the study

Laboratory glasswares

1 Centrifuge tubes 15 mL and 50 mL

2 Micropipette 1mL and 5 mL

3 Turbovap tubes 20 mL and 30 mL

4 Test tubes 5mL

5 Microsyringe 10 µL and 500 µL

6 Separatory funnel 500 mL and 1 L

7 Sintered chromatographic glass column 2 2 cm x 60 cm

8 Round bottom vacuum flask 500 mL

9 Conical flask 250 mL

10 Beaker 100 250 500 mL

11 Funnel 75 mm

12 Graduated test tubes 10 mL and 20 mL

Chemical reagents

1 Acetonitrile AR grade

2 Acetonitrile HPLC grade

3 Magnesium sulphate (hydrated) AR grade

4 Sodium chloride AR grade

5 n Hexane HPLC grade

3 2 1 Preparation of standard insecticide mixtures

Certified reference material of different pesticides used in the present study having purity ranging from 95 1 to 99 99 per cent were purchased from M/s Sigma Aldrich A weighed amount of analytical grade material was dissolved in minimum of distilled acetone and diluted with n hexane toluene (1 1) to obtain a stock solution Aliquots of stock solution of individual pesticide were drawn in a separate volumetric flask so as to get a final mixture of twenty two pesticides at concentration level of 50 mg L Final volume was made up with n hexane and lower concentrations were prepared by serial dilution A working standard of 5 μg $g^{1}$of the mixture was prepared and stored in refrigerator for further use Then 5 μg g^{1} mixture is serially diluted to 01 0 50 0 1 0 05 and 0 01 μg g and were injected in Gas Liquid Chromatograph (ECD) and a calibration curves were prepared by plotting concentration vs peak area

Standardization of GC condition

Gas Chromatograph equipped with ^{63} Ni electron capture detector (ECD) fitted with DB 1 column (dimethyl polysiloxane 30m X 0 25mm 0 5μm film thickness) was used for analysis Ultra High Purity (99 999 %) nitrogen was used as carrier gas with flow rate 0 79ml min^{1} linear velocity 39 90 cm S^{1} The temperature at injection port and detector port were kept at 250^{0}C and 300°C respectively and the total run time was fixed as 70 minutes An oven temperature programme was developed to get proper separation of all pesticides used in the analysis

Determination of Limit of Detection (LOD)

Working standards of 1 μg g^{1} 0 5 μg g 0 1 μg g^{1} 0 05 μg $g^{1}$and 0 01 μg g were prepared Two micro litres of each standard was injected under set standard GC conditions Each standard was injected in three replications The limit of detection of instrument for each pesticide was calculated based on the lowest quantity of pesticide standard that can be identified under standard GC conditions Lowest concentration for which a response of >3 times the noise peak obtained was considered as LOD of the particular compound The linearity

Table 3 List of Certified Reference Materials (CRM) used in the preparation of insecticide mixture

Pesticide group	Certified Reference Material
Organochlorines	Alpha HCH
	Beta HCH
	Lindane
	Delta HCH
	Alpha endosulfan
	pp DDE
	Beta endosulfan
	p p DDD
	p p DDT
	Endosulfan sulphate
Organophosphates	Methyl parathion
	Malathion
	Chlorpyriphos
	Quinalphos
	Phorate
	Profenophos
	Ethion
Synthetic pyrethroids	Fenpropathrin
	Lambda cyhalothrin
	Cyfluthrin
	Cypermethrin
	Fenvalerate

Vandanmedu and Poopara owned 1 2 acres In Poopara, Udumbanchola and Vandanmedu 40 20 and 10 per cent owned 2 5 acres respectively However 20 per cent farmers in Udumbanchola 10 per cent each in Vandanmedu and Poopara had plantations having more than 5 acres In Vandanmedu 30 per cent of farmers owned plantations of size more than 10 acres while in Poopara only 10 per cent had an area more than 10 acres On the other hand none of the growers in Udumbanchola possessed more than 10 acres Considering the educational status of the farmers 30 per cent each were below matriculation m Udumbanchola and Vandanmedu whereas 60 per cent were below matriculation m Poopara In Udumbanchola Vandanmedu and Poopara 40 30 and 20 per cent had an educational status of matriculation However 10 per cent each of farmers in these three areas were pre degree holders though 20 10 and 10 per cent farmers were graduates in Vandanmedu Udumbanchola and Poopara respect vely In Udumbanchola and Vandanmedu 10 per cent each was post graduates whereas none of the farmers in Poopara was post graduate Regarding the extent of irrigation in Udumbanchola and Vandanmedu the number of respondents giving irrigation to their crop were 90 and 80 per cent respectively whereas 90 per cent of the respondents in Poopara grow cardamom as rainfed crop

4 1 2 Major pests and their management strategies

Data on major pests and their management strategies (Table 6) indicate that shoot borer and thrips were the major pests in cardamom in these areas In all these three locations 90 per cent of farmers reported shoot borer as the most serious pest and only 10 per cent of the farmers reported thrips as the major pest None of the farmers reported root grub and white fly as major pests Data on the pest management strategies followed indicate that 10 per cent each from Udumbanchola and Poopara adopted integrated pest management strategies While cent per cent of the farmers in Vandanmedu and 90 per cent each of farmers in Udumbanchola and Poopara follow prophylactic application of pesticides None of the farmers resort to botanicals or biocontrol measures for management of the pests in cardamom

Table 4 Punty and date of expıry of CRM Standards used ın fortıficatıon study

Sl no	Name of Pestıcıde	Punty (%)	Date of Expıry
1	Phorate	96 0	07/01/2013
2	Alpha HCH	99 8	16/03 2015
3	Beta HCH	99 2	28/07/2016
4	Lındane	99 8	07/02/2014
5	Delta HCH	99 5	16/03/2015
6	Methyl parathıon	99 8	21/11/2012
7	Malathıon	97 2	26/11 2015
8	Chlorpyrıphos	99 9	01/03/2014
9	Quınalphos	99 2	15/07 2013
10	Alpha endosulfan	99 6	24/08/2012
11	Profenophos	98 2	13/02/2015
12	p p DDE	99 9	03/04 2014
13	Beta endosulfan	99 8	12/06/2015
14	p p DDD	99 2	07/08 2013
15	Ethıon	97 8	09/06/2014
16	Endosulfan sulphate	98 8	07/08/2013
17	p p DDT	99 5	06/06/2013
18	Fenpropathrın	98 7	20/03/2011
19	Lambda cyhalothrın	97 4	07/02/2014
20	Beta cyfluthrın	99 8	24/05/2014
21	Cypermethrın	95 1	16/07/2014
22	Trıazophos	96 5	24/04/2014
23	Imıdaclopnd	99 9	22/04/2014

response line (calibrat on curve) was plotted with quantity of pesticide at X axis and peak area count at Y axis

3 2 2 Fortification of cardamom with standard insecticide mixture

Five gram each of coarsely ground cardamom samples were taken in 50 mL centrifuge tubes and were spiked separately with 0 01 mL 0 05 mL 0 1 mL 0 5 mL 1mL each of 5 µg g^{1} working standard mixture to get 0 01 0 05 0 10 0 50 and 1 µg g^{1} levels respectively

3 2 3 Recovery experiment

A recovery experiment was conducted for the standardization of the extraction and clean up procedures The experiment was conducted by adding a known quantity of insecticide mixture to cardamom samples and different solvent systems were used for the extraction of the added insecticides from cardamom HPLC grade solvents were used for the extraction and clean up procedures

3 2 3 1 Method I (CDFA method)

In this method a 10 g of fortified cardamom samples were extracted twice with 50 and 40 mL HPLC grade acetonitrile These samples were partitioned with hexane and finally concentrated to dryness and made up to 5 mL using n hexane

3 2 3 2 Method II (QuEChERS method)

QuEChERS method was also adopted for extraction of spiked pesticides from ground cardamom samples In this method five gram ground cardamom sample was taken in 50 mL centrifuge tube and was fortified with the standard insecticide mixture (Table 3) To this 4g magnesium sulphate 1g sodium chloride and 1 5 g sodium citrate were added and homogenized for 1min at a speed of 14000 rpm Twenty ml of acetomtrile was added and shaken for 5 min in a Vortex and centrifuged at 4000 rpm for 4 m n Fifteen mL of the supernatant was transferred to a 50 ml centrifuge containing 1 5 g activated magnesium sulphate (hydrated) and 0 10 g PSA (Primary Secondary Amine) to carry out the dispersive solid phase extraction clean up process These tubes were shaken well and kept in vortex for 1min Two ml of the supernatant was evaporated to dryness and reconstituted to 2mL with n hexane for analysis in Gas Chromatograph

3 2 3 3 Method III (Modified QuEChERS method)

In this method extraction and clean up of residues of cardamom was tried adopting QuEChERS with slight modifications For this purpose 5 g ground cardamom was taken in a 50 mL centrifuge tube and spiked with the standard insecticide mixture These cardamom samples were spiked with 0 01 mL 0 05 mL 0 1 mL 0 5 mL and 1 mL of 5 µg g ^{1} standard insecticide solution to get 0 01 µg g ^{1} 0 05 µg g ^{1} 0 10 µg g ^{1} 0 50 µg g and 1 µg g ^{1} levels respectively To this 4 g activated magnesium sulphate (hydrated) and 1 g activated 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 minute in a vortex and centrifuged at 3 500 rpm for 2 minutes A dispersive solid phase extraction clean up process was carried out by transferring the supernatant (6 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 3 500 rpm for 2minutes Three mL of the cleaned supernatant extract was evaporated to dryness using turbovap The dry residue was reconstituted to 1 mL with a mixture of n hexane acetone (7 3 v/v basis) and analyzed m Gas Chromatograph

3 2 3 4 Estimation

The cleaned extracts were analyzed on a Gas Liquid Chromatograph equipped with Ni 63 Electron Capture Detector (ECD) fitted with capillary column (J&W DB 5) of 30 m×0 25 mm i d × 0 25 µm 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 300^0C respectively The column temperature was programmed at 160 °C to 270 °C at the rate of 5° C per minute (8 min hold) The volume of sample injected was 2 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 39 90 cm sec ^{1}

3 2 3 5 Residue quantification

Residue – Concentration of peak obtained from chromatogram X Dilution factor

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

3 3 Monitoring of pesticide residues in cardamom

Cardamom samples were monitored for the presence of pesticide residues Ten samples were collected from each of the above mentioned cardamom growing zones *viz* Vandenmedu Udumbanchola and Poopara at monthly intervals for a period of six months (August 2011 January 2012) A total of 60 samples were collected from each location at the rate of 10 samples/month and a total of 180 samples were analysed for the presence of pesticide residues The residues were estimated as per the procedure standardised and validated for cardamom vide 3 2 3 3 3 2 3 4 and 3 2 3 5

3 4 Effect of curing process on removal of residues

The experiment was conducted at the seventh block of Cardamom Research Station Pampadumpara Idukki district The experimental field was selected in an area with no recent history of pesticide usage Six pesticides commonly used in cardamom plantations were selected for studying the effect of curing process on removal of pesticide residues in cardamom The pesticides selected include organophosphates like quinalphos chlorpyriphos and triazophos synthetic pyrethroids like lambda cyhalothrin and cypermethrin and a neonicotinoid imidacloprid

Number of insecticides used in the study 6

Number of replications 4

3 4 1 Preparation of insecticide solutions

Spray fluids of each pesticide was prepared by dissolving desired quantity of respective pesticide formulation in water Spray solution of 0 025% quinalphos was prepared by dissolving 1 mL of Ekalux 25EC in 1L of water Similarly spray fluid of 0 025% chlorpyriphos was prepared by dissolving 1 25 mL of Radar 20EC in 1L water Likewise the spray fluids of 0 025% triazophos 0 0025% lambda cyhalothrin 0 0025% cypermethrin and 0 006% imidacloprid were prepared by dissolving 1 mL Hostathion 40EC 0 5mL Reeva 5EC and 0 5 mL Lacer 10EC and 0 4 mL of Confidor 200SL in 1L water Each of the prepared spray solutions were sprayed in cardamom plants at the rate of 2L/clump in four replications

3 4 2 Sampling

Cardamom samples were taken at zero day (2 hours after spraying) first day (24 hours after spraying) third day (72 hours after spraying) and fifth (120 hours after spraying) days after treatment of insecticide Mature bold uniformly shaped cardamom capsules were selected and about 100 g of the sample was drawn from each replicate and transferred separately to polythene carry bags and labelled The samples were partially processed and was stored in a deep freezer at sub zero temperature (18 ^{0}C) in CRS Pampadumpara These were brought to the PRRAL College of Agriculture Vellayani for further processing and estimation of residues The remaining samples were weighed separately labelled and kept for curing in the curing house of CRS Pampadumpara at 50 60^{0}C for 18 24 hours Similarly samples were drawn at 24 48 and 72 hours after spraying and fresh samples were extracted and the remaining portion was kept for curing

3 4 3 Residue estimation in fresh cardamom samples

3 4 3 1 Extraction

12 5 g of pesticide treated cardamom samples drawn in four replicates were ground well and 25 mL of analytical grade acetonitrile was added To this 5g heat treated sodium chloride was added and mixed well with the help of a vortex

and centrifuged at 3500 rpm for four minutes Transferred eight mL of the supernatant to 50 mL centrifuge tube to which three g sodium sulphate was added Again centrifuged at 3500 rpm for four minutes Transferred six mL of the extract to a 15 mL centrifuge tube along with 0 6 g magnesium sulphate and 0 1 g PSA Evaporated four mL of the extract to dryness and reconstitute to one mL with n hexane

3 4 3 2 Residue Estimation

The pesticide residue was estimated and quantified as explained in 3 2 3 4 and 3 2 3 5

3 4 4 Residue estimation in processed cardamom capsules

The cured cardamom samples were extracted cleaned up and estimated as per the procedure 3 2 3 3 3 2 3 4 and 3 2 3 5

3 4 5 Estimation of processing factor

Processing factor was worked out for each treatment using the formula, (Pathan *et al* 2009)

$$\text{Processing factor} = \frac{\text{Residue in cured samples}}{\text{Residue in fresh samples}}$$

3 5 2 Percentage removal of residues

Percentage removal from cured cardamom samples were worked out using the formula

$$\frac{\text{Mean residues before curing} - \text{Mean residues in cured sample on fresh weight basis}}{\text{Mean residues before curing}} \times 100$$

Results

4 RESULTS

One of the major constraints in the production of cardamom often referred to as the Queen of Spices is the excessive ravages caused by pests and d seases Unscientific use of dangerously high levels of pesticides on cardamom plantations to combat these pests and diseases is hazardous to environment and human health and may result in several problems in the fragile ecosystems of the Cardamom Hill Reserve Excessive use of pesticides has resulted in high levels of harvest time residues of pesticides in cardamom which is being rejected by the hitherto importing countries which in turn would have a major say in foreign exchange revenues

In this context an investigation was carried out to study the pesticide use pattern pesticide consumption in cardamom plantations of Idukki district to monitor the level of pesticide residues in cardamom to validate multiresidue method for estimation of residues and to study the effect of curing on the removal of residues from cardamom the results of which are furnished hereunder

4 1 Development of database on pesticide use pattern in cardamom plantations of Idukki district

Results of survey on socioeconomic status incidence of major pests their management strategies pesticide consumption and use pattern among the farmers from three major cardamom growing zones *viz* Udumbanchola Vandanmedu and Poopara are presented below

4 1 1 Data on socioeconomic status of farmers

Data on the average size of the holdings presented in Table 5 from the three major cardamom growing zones *viz* Udumbanchola, Vandanmedu and Poopara indicated that 30 per cent farmers in Vandanmedu and 20 per cent each in Udumbanchola and Poopara owned plantations below one acre However 40 per cent of farmers in Udumbanchola had 1 2 acres while 20 per cent each of farmers in

4 1 3 Pesticide use pattern

Pesticide use pattern in the three different cardamom growing zones were studied in detail during the survey The survey revealed that 32 pesticides were used by the farmers for pest control in the region of which insecticides fungicides and herbicides were 25 6 and 6 respectively Among the insecticides lion share was occupied by organophosphorous insecticides especially quinalphos (96 66%) Cent per cent each of the farmers from Udumbamchola and Poopara 90% farmers from Vandanmedu had used quinalphos for pest control This was followed by chlorpyriphos (76 66%) which was used by 80 per cent farmers each from Udumbanchola and Vandanmedu and 70 per cent from Poopara Percentage of farmers using other organophosphorous insecticides were phorate acephate triazophos (53 33% each) methyl parathion, malathion (50% each) monocrotophos (46 66%) ethion (43 33%) phosolone(6 66%) and phenthoate (3 33%) Endosulfan (26 66%) was the only organochlorine molecule used by the farmers Mostly used synthetic pyrethroid was cypermethrin (70%) followed by lambda cyhalothrin (66 66%) fenvalerate (43 33%) deltamethrin (33 33%) fenpropathrin (26 66%) and bifenthrin (10%) Fipronil (33 33%) was the most widely used new generation insecticide followed by imidacloprid (13 33%) flubendiamide (6 66%) indoxacarb novaluron and chlorantraniliprole (3 33% each) In the case of fungicides cent per cent of farmers used bordeaux mixture followed by copper oxy chloride (96 66%) carbendazim and mancozeb (70 % each) propineb (30%) and iprovalicarb (16 66%) Only 6 66 per cent of the farmers used 2 4 D as herbicide for weed control

4 1 4 Information on pesticide use in cardamom

The data on the information on pesticide use in cardamom is presented in Table 8

4 1 4 1 Source of technical information

In Udumbanchola, ten per cent of farmers collected technical information from agriculture officers while none of the farmers in Vandanmedu and Poopara contacted agricultural officers for any technical advice The farmers of Poopara (50%) Vandanmedu (40%) and Udumbanchola (30%) collected technical information from pesticide dealers However none of the farmers from these locations contacted company representatives and media for information In Udumbanchola, 10 per cent of farmers collected information from other progressive farmers while 50 60 and 50 per cent of farmers had taken their own decisions for selection and application of pesticides in Udumbanchola Vandanmedu and Poopara respectively

4 1 4 2 Type of sprayer used

The percentage of farmers utilizing power sprayer for pesticide application were 80 70 and 60 in Udumbanchola, Vandanmedu and Poopara respectively whereas 20 20 and 30 per cent of farmers in Udumbanchola, Vandanmedu and Poopara respectively used motorized sprayer for pesticide application Only 10 per cent each of farmers used rocker sprayer in Vandanmedu and Poopara

4 1 4 3 Frequency of pesticide application

Regarding the frequency of pesticide application 20 30 and 20 per cent of farmers in Udumbanchola Vandanmedu and Poopara respectively applied pesticides at fortnightly intervals while 60 50 and 60 per cent of the farmers applied pesticides at 30 days interval whereas 20 per cent each applied pesticides at 40 days interval in Udumbanchola, Vandanmedu and Poopara respectively

Table 5 Socioeconomic status of the farmers in the study region

Particulars	Percentage of farmers		
	Udumbanchola	Vandanmedu	Poopara
Holding size			
Below 1 acre	20 00	30 00	20 00
1 2 acres	40 00	20 00	20 00
2 5 acres	20 00	10 00	40 00
More than 5 acres	20 00	10 00	10 00
More than 10 acres	0	30 00	10 00
Educational status			
Below matriculation	30 00	30 00	60 00
Matriculation	40 00	30 00	20 00
Pre degree	10 00	10 00	10 00
Graduation	10 00	20 00	10 00
Post graduation	10 00	10 00	0
Extent of irrigation			
Irrigated	90 00	80 00	10 00
Rainfed	10 00	20 00	90 00

Table 6 Major pests and management strategies followed in the study region

	Percentage of farmers		
	Udumbanchola	Vandanmedu	Poopara
Major pests			
Shoot borer	90 00	90 00	90 00
Root grub	0 00	0 00	0 00
White fly	0 00	0 00	0 00
Thrips	10 00	10 00	10 00
Pest management strategies			
IPM	10 00	0	10 00
Prophylactic application of pesticides	90 00	100 00	90 00
Biological control measures	0 00	0 00	0 00
Use of botanicals	0 00	0 00	0 00

Table 7 Pestıcıdes commonly used ın the cardamom plantatıons ın the study regıon

Pest c des used	Pe centage of farmers us ng pest c de			
	Udumbancho a	Vandanmedu	Poopara	Total
I Insectıcıdes				
Organophosphates				
Qu nalphos	100 00	90 00	100 00	96 66
Chlorpyrıphos	80 00	80 00	70 00	76 66
Phorate	50 00	50 000	60 00	53 33
Trıazophos	50 00	50 00	60 00	53 33
Acephate	50 00	50 00	60 00	53 33
Methyl parath on	60 00	50 00	40 00	50 00
Malath on	50 00	50 00	50 00	50 00
Monoc otophos	40 00	50 00	50 00	46 66
Eth on	40 00	40 00	50 00	43 33
Phosolone	0 00	0 00	20 00	6 66
Phen hoate	0 00	0 00	10 00	3 33
Organochlorınes				
Endosulfan	30 00	20 00	30 00	26 66
Synthetıc pyrethroıds				
Cyperme hrın	70 00	70 00	70 00	70 00
Lamda cyhalothrın	70 00	70 00	60 00	66 66
Fenvalerate	40 00	50 00	40 00	43 33
Deltame hrın	40 00	30 00	30 00	33 33
Fenpropathrın	30 00	20 00	30 00	26 66
B fenthrın	20 00	10 00	0 00	10 00
Carbamates				
Carbofuran	50 00	30 00	20 00	33 33
New molecules				
F pron l	30 00	30 00	40 00	33 33
Im dac oprıd	10 00	20 00	10 00	13 33
Flubend am de	10 00	0 00	10 00	6 66
Indoxacarb	10 00	0 00	0 00	3 33
Novaluron	0 00	10 00	0 00	3 33
Chlorant an prole	0 00	10 00	0 00	3 33
II Fungıcıdes				
Bordeaux m x u e	100 00	100 00	100 00	100 00
Copper oxy chlorıde	90 00	100 00	90 00	96 66
Carbendazım	80 00	70 00	60 00	70 00
Mancozeb	70 00	60 00	80 00	70 00
Prop neb	30 00	20 00	40 00	30 00
Ip oval carb	20 00	10 00	20 00	16 66
III Herbıcıde				
2 4 D	10 00	10 00	0 00	6 66

Table 8 Information on pesticide use in the cardamom plantations in the study region

Particulars	Percentage of farmers		
	Udumbanchola	Vandanmedu	Poopara
Source of technical information			
Agriculture officers	10 00	0	0
Pesticide retailers/dealers	30 00	40 00	50 00
Company representatives	0	0	0
Other progressive farmers	10 00	0	0
Own decisions	50 00	60 00	50 00
Media	0	0	0
Type of sprayer used			
Power sprayer	80 00	70 00	60 00
Motorized sprayer	20 00	20 00	30 00
Rocker sprayer	0	10 00	10 00
Frequency of pesticide application			
Fortnightly interval	20 00	30 00	20 00
30 days interval	60 00	50 00	60 00
40 days interval	20 00	20 00	20 00
Awareness regarding the adverse health effects of pesticides			
Well aware	30 00	20 00	10 00
Aware of some adverse effects	60 00	60 00	50 00
Totally ignorant	10 00	20 00	40 00
Adoption of safety measures while spraying			
Gloves	30 00	20 00	0
Mask	10 00	20 00	20 00
Boots	0	0	0
None	60 00	60 00	80 00
Reason for non adoption of safety measures			
Lack of awareness	10 00	20 00	60 00
Inconvenience	80 00	70 00	30 00
Additional cost	10 00	10 00	10 00
Adverse health hazards experienced			
Dizziness and headache	80 00	70 00	30 00
Dermal disease	10 00	20 00	60 00
Stomach pain and general weakness	10 00	10 00	10 00
Disposal of pesticide containers			
Dumping in the field	0	20 00	2
Putting in drainage channels	0	0	0
Burning	80 00	8	7
Burying deep in soil	20 00	0	1

4 1 4 4 Awareness regarding the adverse health effects of pesticides

The percentage of farmers in Udumbanchola (30) Vandanmedu (20) and Poopara (10) were well aware on the adverse health effect of pesticides However 60 60 and 50 per cent of farmers in these three locations were aware of adverse effects of pesticides to certain extent whereas 10 20 and 40 per cent of farmers were totally ignorant about the health effects of pesticides in these three locations

4 1 4 5 Adoption of safety measures while spraying

Regarding the adoption of safety measures while spraying 30 and 20 per cent of farmers in Udumbanchola and Vandanmedu used gloves whereas 10 20 and 20 per cent of farmers m Udumbanchola Vandanmedu and Poopara respectively used masks However none of the safety measures was adopted by 60 60 and 80 per cent of farmers in these three areas while spraying No farmers in these areas wore boots as safety measure during the application of pesticides

4 1 4 6 Reason for non adoption of safety measures

The percentage of farmers (10 20 and 60) expressed their inconvenience as the reason for non adoption of safety measures in Udumbanchola, Vandanmedu and Poopara respectively while 10 20 and 60 per cent of farmers did not use safety measures due to their lack of awareness Additional cost was considered as the reason for non adoption of safety measures by 10 per cent each of farmers in these three locations

4 1 4 7 Adverse health hazards experienced

In Udumbanchola Vandanmedu and Poopara, 80 70 and 30 per cent of farmers respectively experienced dizziness and headache as the adverse health hazard during pesticide application while 10 20 and 60 per cent suffered from dermal diseases in these three locations Ten per cent each of the farmers reported stomach pain and general weakness as the adverse health hazard

4 1 4 8 Disposal of pesticide containers

Data on the the method of disposal of pesticide containers revealed that 20 per cent each of farmers in Vandanmedu and Poopara dumped the empty pesticide containers in field while 80 per cent each of farmers in Udumbanchola, Vandanmedu and 70 per cent of farmers in Poopara burned the empty containers In Udumbanchola (20 %) and Poopara (10 %) buried the pesticide containers deep in soil None of the farmers put the empty containers in drainage channels

4 2 Validation of Multi Residue Methods (MRM) for pesticide residue analysis in cardamom

Development of a multiresidue method satisfying the requirements of specificity/selectivity precision reproducibility accuracy linearity limit of detection and limit of quantitation for the estimation of multiple residues in cardamom is essentially required for monitoring pesticide residues in cardamom Results of the preliminary method validation studies of three different multi residue methods *viz* CDFA method QuEChERS method and modified QuEChERS method are presented in Tables 9 15

4 2 1 Method I (CDFA method)

The mean percentage recovery of pesticides at different levels of fortification using CDFA method is presented in Table 9 The accepted recovery range is 70 120 % Only three pesticide compounds *viz* delta HCH (75 21 %) alpha endosulfan (89 22 %) and ethion (119 26 %) showed satisfactory recovery Except for delta HCH and alpha Endosulfan all other organochlorine insecticides *viz* alpha HCH (66 23 %) beta HCH (60 94 %) lindane (59 28 %) *p p* DDE (29 58 %) beta endosulfan (49 59 %) *p p* DDD (63 78 %) endosulfan sulphate (52 45 %) *p p* DDT (48 23 %) gave unsatisfactory recovery per cent However organophosphate insecticides like phorate (35 22 %) methyl parathion (63 82 %) malathion (50 23 %) chlorpyriphos (129 21 %) quinalphos (56 21 %) profenophos (30 29 %) showed unsatisfactory recovery except ethion with a mean per cent recovery of 119 26 In the case of synthetic pyrethroids all were beyond the satisfactory recovery range The mean recovery percentage of fenpropathrin lambda cyhalothrin cyfluthrin beta,

Table 9 Percentage recoveries of pest c des at d fferent leve s of fort f cat on us ng CDFA Method

Pest c des	°₀ Recovery (1μg g)	% Recovery (0 5 μg g)	°₀ Recovery (0 1 μg g)	°₀ Recovery (0 05 μg g)	% Recovery (0 01 μg g)
Phora e	35 22	77 56	49 55		
A pha HCH	66.23	100.26			
Beta HCH	60 94	9 1			
Lindane	59.28	22 65	40 30		
Delta HCH	75.2	34 55	29 14		
Methy parath on	63 82	21 33		35 05	
Malath on	50.23	48 77			
Ch orpyriphos	29 2	56 87		26 15	
Quinalpho	56.21	49 21			
A pha endo ulfan	89.22	34.22			
P ofenophos	30.29	49 87	41 24		
p p DDE	29 58	56 38			
Beta endo ulfan	49 59	44 38			
p p DDD	63 78	34 25			
Eth on	9 26	29 54			
Endosulfan su pha e	52 45	49 25			
p p DDT	48.23	39 10	30.2		
Fenpropathrin	56.21	51 89			
Lambda cyha othrin	63 99	59 84		29 45	
Cyfluthrin	56 23	31.2			
Cypc methrin	49 1	59 28			
Fen a ra e	33 64	93 82			

cypermethrin and fenvalerate were 56 21 63 99 56 23 49 11 and 33 64 respectively At 0 50 µg g level alpha HCH (100 26 %) beta HCH (119 11 %) and fenvalerate (93 82 %) and phorate (77 56 %) showed satisfactory recovery values Mean recovery percentage of other compounds spiked at 0 50 µg g level is as follows lindane (22 65) delta HCH (34 55) methyl parathion (121 33) malathion (48 77) chlorpyriphos (56 87) qumalphos (49 21) alpha endosulfan (34 22) profenophos (49 87) p p DDD (56 38) beta endosulfan (44 38) p p DDD (34 25) ethion (29 54) endosulfan sulphate (49 25) and p p DDT (39 10) fenpropathrin (51 89) lambda cyhalothrin (59 84) cyfluthrin beta (131 21) cypermethrin (59 28) and fenvalerate (93 82) At 0 1 µg g level out of the 22 compounds spiked only five compounds were detected with mean recovery percentages of phorate (49 55) lindane (40 30) delta HCH (29 14) profenophos (41 24) and *p p* DDT (30 21) At 0 05 µg g^{1} level of fortification pesticides detected were limited to methyl parathion chlorpyriphos and lambda cyhalothrin with mean recovery percentages 135 05 26 15 and 29 45 respectively At the lowest level *ie* 0 01 µg g none of these compounds was detected

Considering the low recovery percentage obtained even at the higher levels of fortification wide variation in the recoveries and very low recovery of some compounds the method was found unsuitable for the mult residue estimation of pesticides from cardamom In addition several compounds were not at all recovered at the lowest level Hence this method was not adopted for the residue estimation from cardamom

4 2 2 Method II (QuEChERS method)

The QuEChERS method us ng acetonitrile as the extractant was tried at five different levels The percentage recovery obtained when cardamom samples fortified at five different levels (0 01 0 05 0 10 0 50 and 1 µg g^{1}) were presented in Table 10

The mean recovery percentage at 1 µg g level varied from 60 56 for p p DDT to 112 84 for chlorpyriphos All the compounds showed satisfactory recovery values except phorate (61 37%) and p p DDT (60 56%) The mean per cent recovery among the organochlorine pesticides in the descending order was delta HCH (93 44) > Lindane (89 58) > beta endosulfan (85 99) > alpha endosulfan (85 48) > alpha HCH (85 32) > p p DDD (82 04) > endosulfan sulphate (81 36) > beta HCH (79 12) > p p DDD (78 58) > p p DDT (60 56) whereas the mean recovery per cent of organophosphate pesticides were chlorpyriphos (112 84) quinalphos (91 25) ethion (89 22) methyl parathion (82 15) profenophos (80 11) malathion (79 55) and phorate (61 37) Mean recovery of synthetic pyrethroids were lambda cyhalothrin (93 33 %) fenpropathrin (87 39 %) cypermethrin (86 08 %) fenvalerate (84 69 %) and cyfluthrin beta (80 59 %) At 0 5 µg g^{1} level of fortification mean recovery percentage varied from 44 85 to 121 84 The descending order of the mean recovery percentage is as follows lambda cyhalothrin (121 84) > fenpropathrin (119 27) > endosulfan sulphate (114 19) > chlorpyriphos (89 25) > qumalphos (80 09) > alpha HCH (79 35) > ethion (78 28) > delta HCH (78 25) > alpha endosulfan (76 81) > beta HCH (76 25) > beta endosulfan (75 09) > methyl parathion (74 58) > cypermethrin (72 71) > fenvalerate (70 02) > malathion (65 28) > p p DDD (62 81) > cyfluthrin beta (62 80) > profenophos (60 07) > p p DDD (59 85) > lindane(59 25) > phorate (49 35) > p p DDT (44 85) Compounds which gave satisfactory recovery values were alpha HCH beta HCH delta HCH methyl parathion chlorpyriphos quinalphos alpha endosulfan beta endosulfan ethion endosulfan sulphate fenpropathrin cypermethrin and fenvalerate At both levels *ie* 1 µg g and 0 5 µg g^{1} *p p* DDT showed the lowest recovery percentage

The mean recovery percentage at 0 1 µg g level varied from 19 28 (phorate) to 83 28 (chlorpyriphos) The mean per cent recovery among the pesticides in the descending order was chlorpyriphos (83 28) > quinalphos (81 69) > endosulfan sulphate (78 54) > lambda cyhalothrin (71 34) > methyl parathion (69 28) >

cyfluthrin beta (68 30) > malathion (62 58) > alpha endosulfan (61 20) > ethion (58 31) > beta endosulfan (56 81) > cypermethrin (55 44) > fenpropathrin (54 25) > p p DDD (50 25) > fenvalerate (49 62) > p p DDD (49 05) > beta HCH (45 18) > delta HCH (41 85) > profenophos (41 55) > alpha HCH (33 98) > lindane(29 58) > p p DDT (21 55) > phorate (19 28) At this level number of pesticides with satisfactory recovery values were limited to four *ie* chlorpyriphos quinalphos endosulfan sulphate and lambda cyhalothrin The mean per cent recovery values at 0 05 μg g were 13 51 29 65 40 25 20 11 19 18 38 12 42 09 61 20 59 41 44 03 27 58 30 25 24 61 30 04 43 60 52 40 9 52 47 02 52 35 49 21 28 19 and 22 51 for phorate alpha HCH beta HCH lindane delta HCH methyl parathion malathion chlorpyriphos quinalphos alpha endosulfan profenophos p p DDD beta endosulfan p p DDD ethion endosulfan sulphate p p DDT fenpropathrin lambda cyhalothrin cyfluthrin beta cypermethrin and fenvalerate respectively Mean recovery was the lowest for p p DDT (9 52%) At 1 0 5 0 1 and 0 05 μg g^{1} levels phorate and p p DDT showed lower recovery values whereas compounds like chlorpyriphos quinalphos lambda cyhalothrin gave higher as well as more or less stable recovery values At 0 01 μg g^{1} out of the 22 compounds spiked only nine compounds were detected with mean recovery percentages of beta HCH (35 12) malathion (19 25) chlorpyriphos (21 52) quinalphos (23 59) alpha endosulfan (14 35) fenpropathrin (30 25) lambda cyhalothrin (31 09) cyfluthrin beta (12 09) cypermethrin (19 91)

The method eventhough is found to be effective in extracting all the compounds the percentage recovery of several of the compounds were very low especially at the lower levels of fortification In this method satisfactory recovery percentage was obtained for all the compounds except p p DDT and Phorate with lower recovery percentages The recovery declined at the lower levels of fortification 0 05 μg g^{1} and 0 01 μg g^{1} A wide variation was evident in the recovery percentages at the same level of fortification This method was not effective in offering a ethion respectively At 0 05µg g and 0 01µg g 1 all the synthetic pyrethroids gave good recovery with RSD < 20 The per cent recovery values at 0 05µg g were 82 50 94 95 86 67 95 94 and 82 82 for fenpropathrin lambda cyhalothrin cyfluthrin beta, cypermethrin and fenvalerate respectively The descending order of their mean recoveries at 0 01µg g 1 was fenpropathrin (106 86 %) > cyfluthrin beta (102 17 %) > lambda cyhalothrin (101 13 %) > fenvalerate (99 67 %) > cypermethrin (93 50 %)

A satisfactory recovery was obtained for almost all the compounds fortified The reasonable good recovery even at the lowest level of fortification coupled with minimal variation and acceptable RSD values together with the easiness are added advantages of this method All these clearly demonstrate the superiority of the method over the other two methods validated Method validation was accomplished with good linearity and satisfactory recoveries (69 70 – 110%) were obtained with 22 pesticides at 1 0 5 0 1 0 05 and 0 01 µg g 1 levels of fortification The developed method could be employed as a simple reliable and cost effective method for the routine detection and analysis of pesticides in cardamom samples

4 2 4 Calibration curve/ Linearity studies

The response of the instrument in the detection of the compounds under study was assessed by injecting graded concentrations of the individual pesticides and plotting the response vs concentration to assess the linearity parameter From the R^2 value the linear fit of the instrument response vs concentration curve was evaluated A calibration curve was prepared by the analysis of each of the pesticide at five different concentrations prepared from Certified Reference Materials (0 01 µg g 0 05 µg g 0 10 µg g 1 0 50 µg g and 1 µg g) (Fig 1 28) The calibration curves were best fitted to a linear curve with good linearity

The chromatograms of the standard mixture fortified at 0 01 µg g 0 05 µg g 0 10 µg g 0 50 µg g and 1 µg g 1 were kept as Appendix I

Table 10 Percen age recoveries of pest c des at d fferent levels of fort f cat on us ng QuEChERS me hod

Pe tic des	Reco ery (1µg g)	Recovery (0 5 µg g)	Reco ery (0 1 µg g)	Reco ery (0 05 µg g)	Reco ery (0 0 µg g)
Phorate	6 37	49 35	9 28	3 51	
A pha HCH	85 32	79 35	33 98	29 65	
Beta HCH	79 2	76 25	45 8	40 25	35 2
Lindane	89 58	59 25	29 58	20	
Delta HCH	93 44	78 25	41 85	9 18	
Methy parath on	82 5	74 58	69 28	38 2	
Malath on	79 55	65 28	62 58	42 09	19 25
Ch orpyriphos	112 84	89 25	83 28	61 20	21 52
Quinalphos	91 25	80 09	8 69	59 41	23 59
Alpha endosulfan	85 48	76 8	6 20	44 03	14 35
P ofenophos	80 1	60 07	4 55	27 58	
p p DDE	82 04	59 85	50 25	30 25	
Beta endosulfan	85 99	75 09	56 81	24 61	
p p DDD	78 58	62 8	49 05	30 04	
Eth on	89 22	78 28	58 31	43 60	
Endo ulfan sulphate	8 36	114 9	78 54	52 40	
p p DDT	60 56	44 85	2 55	9 52	
Fenp opathrin	87 39	19 27	54 25	47 02	30 25
Lambda cyhalothrin	93 33	21 84	7 34	52 35	3 09
Cyfluthrin	80 59	62 80	68 30	49 21	2 09
Cype methrin	86 08	72 71	55 44	28 9	19 91
Fen a era e	84 69	0 02	49 62	22 5	

satısfactory recovery of all the compounds fortıfied Hence thıs was not adopted for multıresıdue extractıon of pestıcıdes from cardamom

4 2 3 Method III (Modıfied QuEChERS method)

The percentage recovery of each compound at dıfferent levels of fortıficat on by thıs method ıs presented ın Tables 11 to 15

At 1 µg g all the compounds regıstered satısfactory recovery values rangıng from 83 46 to 106 65 (Table 11) In thıs method p p DDT showed good recovery percentage of 106 65wıth RSD of 5 1 Mean recovery per cent values among OC compounds ranged from 88 00 (alpha HCH) to 106 65 (p p DDT) The mean per cent recovery ın the descendıng order among organochlorıne compounds were p p DDT(106 65 RSD 5 1)> endosulfan sulphate (105 89 RSD 4 9) > delta HCH (101 54 RSD 6 9) > alpha endosulfan (100 87 RSD 4 8) > beta endosulfan (98 43 RSD 5 5) > p p DDD (93 90 RSD 6 8) > beta HCH (93 23 RSD 6 5) > p p DDD (91 98 RSD 4 9) > lındane (90 48 RSD 6 9) > alpha HCH (88 00 RSD 8 1) Thıs method gave satısfactory recovery among OP compounds also wıth a range of 83 46 (quınalphos) to 104 21 (chlorpyrıphos) The descend ng order of mean per cent recoverıes among OP compounds was as follows chlorpyrıphos (104 2 RSD 5 7) > methyl parathıon (98 80 RSD 5 9) > ethıon (92 44 RSD 3 3) > phorate (89 07 RSD 6 0) > profenophos (88 66 RSD 7 5) > malathıon (85 75 RSD 5 1) > quınalphos (83 46 RSD 5 7) Among synthet c pyrethro ds cypermethrın gave maxımum recovery of 104 60 wıth RSD 5 0 Fenpropathrın lambda cyhalothrın cyfluthrın and fenvalerate gave 92 95% (RSD 6 7) 103 82% (RSD 7 0) 102 30% (RSD 7 8) and 98 10% (RSD 7 8) recoverıes respectıvely

The mean recovery percentages at 0 5 µg g ranged from 80 64 to 106 92 The mean recovery percentages of the organochlorınes ın the descendıng order were beta endosulfan (106 92) > beta HCH (105 89) > delta HCH (105 00) > lındane (101 86) > alpha HCH (100 10) > endosulfan sulphate (99 70) > p p DDD (99 63) > alpha endosulfan (98 31) > p p DDD (93 55) > p p DDT (80 64) Among organophosphates the mean recovery percentages ranged from 83 65 to 107 34 The mean per cent recovery of phorate methyl parathıon malathıon chlorpyrıphos quınalphos profenophos and ethıon were 90 53 107 34 83 65 104 05 85 41 98 28 and 97 33 wıth RSD <20 All the synthetıc pyrethroıds gave satısfactory recovery values and RSD <20 The recovery values were 101 54 92 91 101 20 100 63 and 99 12 percentages for fenpropathrın lambda cyhalothrın cyfluthrın beta, cypermethrın and fenvalerate

At 0 1µg g level of fortıficatıon the mean recovery values ranged between 81 5 to 110 It gave satısfactory recovery for organochlorınes organophosphates and synthetıc pyrethroıds wıth RSD < 20 The mean recovery of the fortıfied compounds ıs as follows phorate 103 89 alpha HCH 106 beta HCH 106 27 lındane 90 87 delta HCH 87 72 methyl parathıon 104 6 malathıon 108 2 chlorpyrıphos 103 9 quınalphos 99 35 alpha endosulfan 103 6 profenophos 109 2 p p DDD 86 75 beta endosulfan 108 8 p p DDD 99 27 ethıon 110 endosulfan sulphate 104 8 p p DDT 81 5 fenpropathrın 91 69 lambda cyhalothrın 101 5 cyfluthrın beta 87 28 cypermethrın 104 37 and fenvalerate 89 7

At 0 05 µg g[1] organochlorıne compouds gave recovery of 84 72 % 95 89 % 77 65 % 93 05 % 87 35 % 94 18 % 80 43 % 69 76 % 83 15 % 95 87 % for alpha HCH beta HCH Lındane delta HCH alpha endosulfan p p DDD beta endosulfan p p DDD endosulfan sulphate and p p DDT respectıvely The correspondıng values at 0 01 µg g were 104 87 90 23 88 17 99 87 104 8 100 40 109 4 85 07 107 23 and 109 36 respectıvely All compounds gave RSD < 20 At 0 05µg g all the organophosphate compounds gave satısfactory recovery wıth a maxımum of 97 53 and a mınımum of 83 62 They gave more or less stable values at all the levels The descendıng order of theır mean per cent recovery were quınalphos (97 53) > ethıon (95 73) > malathıon (93 13) > phorate (90 20) > chlorpyrıphos (90 00) > profenophos (88 41) > methyl parathıon (83 62) At 0 01µg g[1] the mean recovery percentages were 91 87 90 67 108 73 84 43 99 30 102 20 and 92 97 for phorate methyl parathıon malathıon chlorpyrıphos quınalphos profenophos and

Table 11 Pe centage recoveries of pest c des at 1 µg g us ng mod f ed QuEChERS method

Compound name	Recovery (%)				STDEV	RSD
	R1	R2	R3	Mean		
Phorate	84 52	87 74	94 96	89 07	5 3	6 0
Alpha HCH	86 17	81 95	95 89	88 00	7 2	8 1
Beta HCH	90 71	88 85	100 12	93 23	6 0	6 5
L ndane	88 11	85 79	97 53	90 48	6 2	6 9
Delta HCH	105 55	93 39	105 68	101 54	7 1	6 9
Me hyl parath on	94 03	97 10	105 28	98 80	5 8	5 9
Malath on	82 50	86 87	87 89	85 75	2 9	5 1
Chlorpyr phos	98 24	104 24	110 16	104 21	6 0	5 7
Qu nalphos	81 26	86 75	82 37	83 46	2 9	3 5
Alpha endosulfan	100 26	96 35	106 00	100 87	4 9	4 8
Profenophos	81 01	92 96	92 02	88 66	6 6	7 5
p p DDE	93 09	86 99	95 86	91 98	4 5	4 9
Beta endosu fan	96 98	93 94	104 37	98 43	5 4	5 5
p p DDD	89 97	90 51	101 23	93 90	6 3	6 8
Eth on	89 51	92 19	95 63	92 44	3 1	3 3
Endosulfan sulphate	108 10	99 99	109 57	105 89	5 2	4 9
p p DDT	109 14	119 48	91 93	106 65	6 5	5 1
Fenpropathrin	95 16	85 91	97 78	92 95	6 2	6 7
Lambda cyha othrin	105 90	95 72	109 84	103 82	7 3	7 0
Cyflu hr n	104 10	93 60	109 20	102 30	8 0	7 8
Cypermethrin	104 25	99 60	109 95	104 60	5 2	5 0
Fenvalerate	106 80	92 70	94 80	98 10	7 6	7 8

Table 12 Percentage recoveries of pest c des at 0 5µg g us ng mod f ed QuEChERS method

Compound name	Recovery (%)				STDEV	RSD
	R1	R2	R3	Mean		
Phorate	89 03	85 24	97 32	90 53	8 95	9 88
Alpha HCH	97 09	97 58	105 64	100 10	8 93	8 92
Beta HCH	105 71	108 30	103 68	105 89	8 90	7 91
L ndane	99 69	97 94	107 96	101 86	8 21	8 06
Delta HCH	104 65	102 42	107 93	105 00	8 12	7 73
Methyl parathıon	105 14	109 46	107 43	107 34	8 14	7 35
Malath on	84 09	83 40	83 46	83 65	7 59	9 07
Chlorpyr phos	104 93	106 17	101 05	104 05	7 04	6 77
Qu nalphos	85 65	87 30	83 27	85 41	7 02	8 22
Alpha endosu fan	98 88	98 98	97 07	98 31	6 47	6 59
Profenophos	96 72	99 32	98 81	98 28	6 74	6 86
p p DDE	92 84	88 81	99 00	93 55	7 04	7 52
Beta endosulfan	108 98	103 23	108 55	106 92	7 14	6 68
p p DDD	102 08	97 76	99 05	99 63	6 77	6 79
Eth on	94 54	97 26	100 18	97 33	7 09	7 28
Endosulfan sulphate	99 86	97 84	101 38	99 70	7 54	7 57
p p DDT	80 31	79 29	82 34	80 64	8 03	9 96
Fenpropathrın	100 40	97 85	106 37	101 54	4 16	4 10
Lambda cyhalothrın	93 53	95 69	89 51	92 91	4 07	4 38
Cyfluthrın	100 65	101 57	101 37	101 20	2 20	2 18
Cype methr n	99 66	98 92	103 32	100 63	2 64	2 62
Fenvale ate	102 74	97 86	96 75	99 12	3 18	3 21

Table 13 Percentage recoveries of pest c des at 0 1µg g us ng mod f ed QuEChERS method

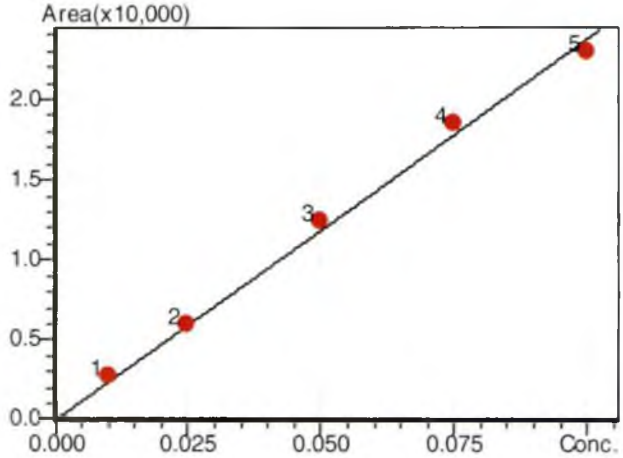
Compound name	Recovery (%)				STDEV	RSD
	R1	R2	R3	Mean		
Pho ate	102 04	107 78	101 85	103 89	8 52	7 63
Alpha HCH	100 64	111 615	105 645	106	5 50	5 19
Beta HCH	106 33	104 63	107 85	106 27	4 48	3 97
L ndane	86 205	88 215	98 175	90 87	6 41	7 05
Delta HCH	81	87 975	94 185	87 72	6 60	7 52
Methyl para h on	106 59	102 38	105 02	104 6	4 31	3 87
Malath on	110 34	109 625	104 88	108 2	7 37	6 57
Chlorpyriphos	101 57	105 84	104 19	103 9	2 16	2 08
Qu na phos	84 36	115 905	97 77	99 35	15 83	15 94
Alpha endosulfan	102 13	103 43	105 245	103 6	1 57	1 38
Profenophos	104 37	105 705	117 555	109 2	7 26	6 65
p p DDE	80 31	85 965	93 975	86 75	6 87	7 91
Beta endosulfan	108 56	108 6	108 095	108 8	0 89	1 03
p p DDD	87 855	98 58	111 375	99 27	11 78	11 86
Eth on	103 17	109 605	117 36	110	7 11	6 46
Endosulfan sulphate	110 28	92 94	111 225	104 8	10 29	9 82
p p DDT	80 475	82 23	81 795	81 5	0 91	1 12
Fenp opathrin	90 915	95 52	88 62	91 69	3 51	3 83
Lambda cyhalothrin	96 51	108 72	99 36	101 5	6 39	6 29
Cyfluthrin	89 475	89 85	82 5	87 28	4 14	4 74
Cyperme hrin	101	106 62	105 5	104 37	4 44	4 00
Fenvale ate	93 9	88 95	86 25	89 7	3 88	4 33

Table 14 Percentage recove es of pest c des at 0 05µg g us ng mod f ed QuEChERS method

Compound name	Recovery (%)				STDEV	RSD
	R1	R2	R3	Mean		
Phorate	82 04	85 12	103 44	90 20	8 71	9 66
Alpha HCH	80 9	86 52	86 74	84 72	8 66	10 22
Beta HCH	104 3	91 52	91 84	95 89	8 64	9 01
L ndane	71 24	80 3	81 42	77 65	8 56	11 03
Delta HCH	88 24	100 34	90 58	93 05	8 21	8 82
Methyl parath on	80 08	82	88 78	83 62	8 28	9 90
Mala h on	93 08	95 64	90 66	93 13	8 39	9 01
Ch orpyriphos	80 08	95 72	94 2	90 00	8 57	9 53
Qu nalphos	99 9	94 88	97 82	97 53	8 66	8 88
Alpha endosulfan	83 5	88 46	90 08	87 35	8 56	9 80
Profenophos	84 2	94 62	86 42	88 41	8 88	10 05
p p DDE	90 28	94 4	97 86	94 18	9 18	9 75
Beta endosulfan	80 5	80 28	80 5	80 43	9 32	11 59
p p DDD	64 54	71 14	73 6	69 76	9 58	13 73
Eth on	90 46	97 64	99 08	95 73	7 46	7 80
Endosulfan sulphate	81 86	83 54	84 04	83 15	7 47	8 98
p p DDT	84 42	104 62	98 58	95 87	7 66	7 99
Fenpropathrin	80 36	80 92	86 22	82 50	6 82	8 26
Lambda cyhalothr n	89 1	98 5	97 26	94 95	6 68	7 04
Cyflu h n	81 62	89 58	88 8	86 67	6 56	7 57
Cypermethrin	94 7	100 33	92 79	95 94	7 63	7 95
Fenvalera e	83 78	81 72	82 96	82 82	1 04	1 25

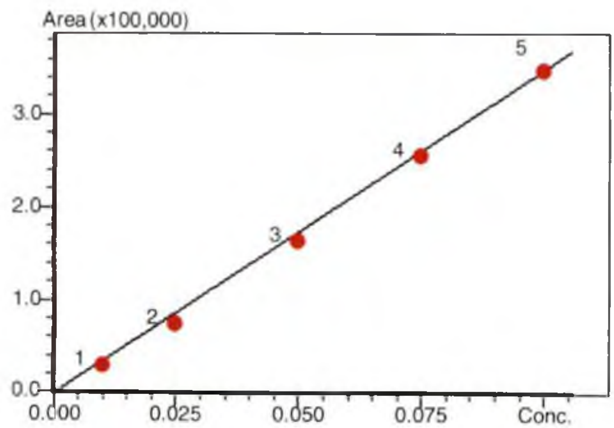
Tab e 15 Pe centage recove es of pest c des at 0 01µg g us ng mod f ed QuEChERS me hod

Compound name	Recovery (°)				STDEV	RSD
	R1	R2	R3	Mean		
Phora e	89 2	86 7	99 7	91 87	11 20	12 19
A pha HCH	108 4	101 7	104 5	104 87	11 25	10 73
Be a HCH	86 2	99	85 5	90 23	11 26	12 47
L ndane	87 4	91 6	85 5	88 17	11 02	12 50
Delta HCH	100 9	93 5	105 2	99 87	10 71	10 73
Methyl parath on	96 6	82 2	93 2	90 67	10 96	12 09
Mala h on	108 7	108 2	109 3	108 73	10 83	9 96
Chlorpyr phos	85 8	82 6	84 9	84 43	11 06	13 09
Qu nalphos	101 6	99 1	97 2	99 30	10 37	10 45
Alpha endosu fan	110 1	114 1	109 2	111 13	10 71	9 64
P ofenophos	106	100 1	100 5	102 20	10 88	10 65
p p DDE	92 4	99	109 8	100 40	11 35	11 30
Beta endosulfan	119 7	118 2	110 3	116 07	11 67	10 06
p p DDD	88 4	81 5	85 3	85 07	11 29	13 27
Eth on	88 5	96 4	94	92 97	10 20	10 98
Endosulfan sulphate	106	110 4	115 3	110 57	9 97	9 02
p p DDT	112 5	112 5	116 1	113 70	10 38	9 13
Fenp opath n	110 7	118 3	111 6	113 53	10 29	9 06
Lambda cyhalothr n	87 6	95 8	120	101 13	9 29	9 18
Cyfluthrın	105	95	106 5	102 17	6 75	6 61
Cypermethr n	94	91 5	95	93 50	6 70	7 16
Fenvalera e	110	95	94	99 67	8 96	8 99



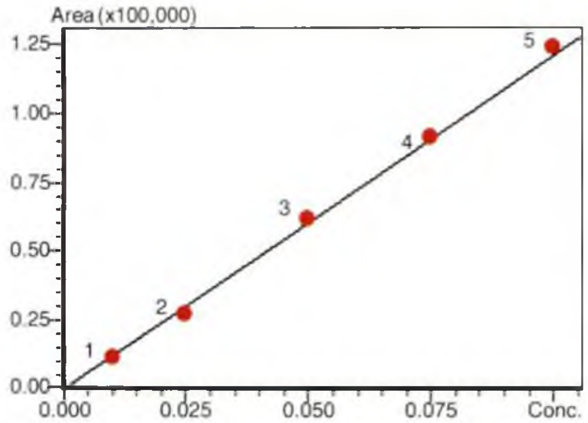
Y = aX + b, a = 237938.4, b = 0.0, R^2 = 0.9966269, R = 0.9983120, RF %RSD : 6.640195

Fig 1. Calibration curve of phorate



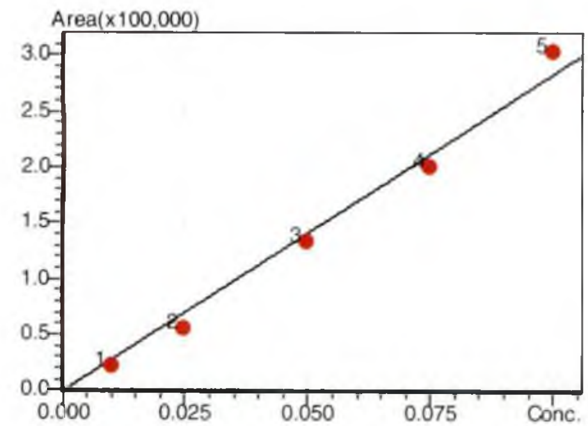
Y = aX + b, a = 3488021, b = 0.0, R^2 = 0.9963751, R = 0.9981859,RF %RSD : 9.384339

Fig 2. Calibration curve of alpha HCH



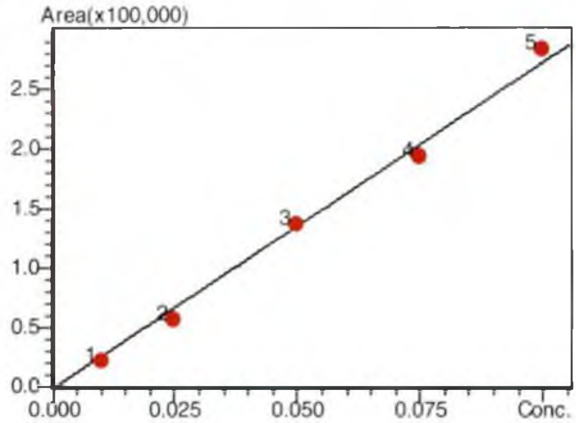
Y = aX + b, a = 1211169, b = 0.0, R^2 = 0.9958695, R = 0.9979326, RF %RSD : 6.861821

Fig 3. Calibration curve of beta HCH



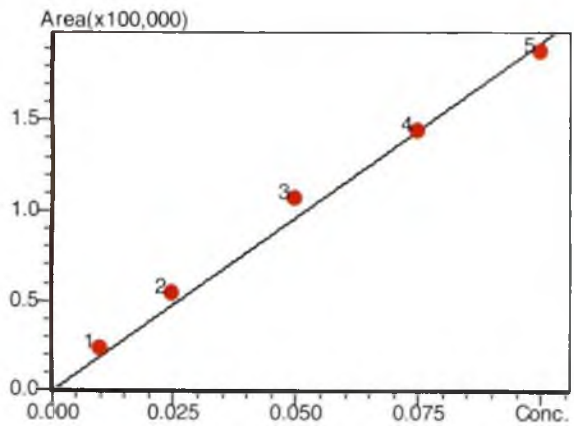
Y = aX + b, a = 2833408, b = 0.0, R^2 = 0.9919301, R = 0.9959569, RF %RSD : 12.66300

Fig 4. Calibration curve of lindane



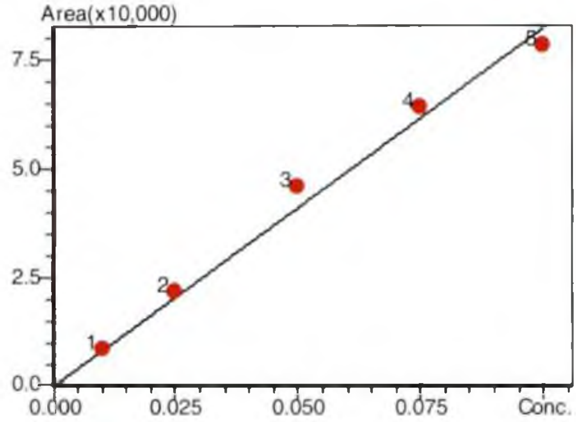
Y = aX + b, a = 2730522, b = 0.0, R^2 = 0.9950199, R = 0.9975068, RF %RSD : 9.808968

Fig 5. Calibration curve of delta HCH



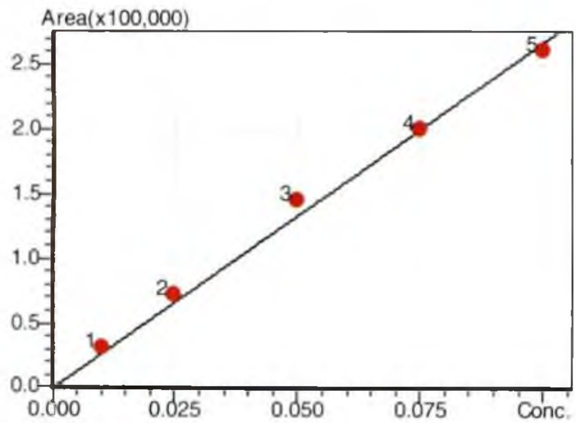
Y = aX + b, a = 1930008, b = 0.0, R^2 = 0.9960837, R = 0.9980399, RF %RSD : 8.814859

Fig 6. Calibration curve of merhyl parathion



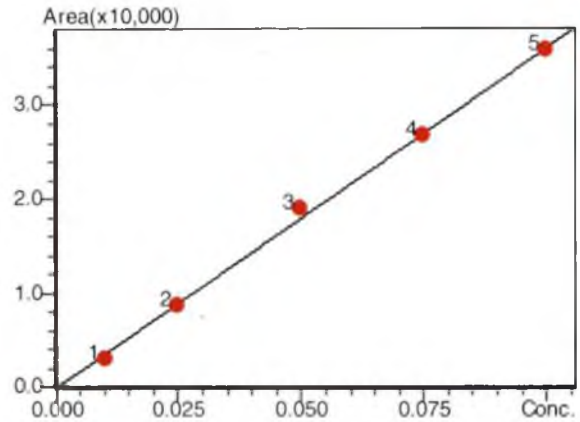
Y = aX + b, a = 821301.1, b = 0.0, R^2 = 0.9885086, R = 0.9942377, RF %RSD : 6.571496

Fig 7. Calibration curve of malathion



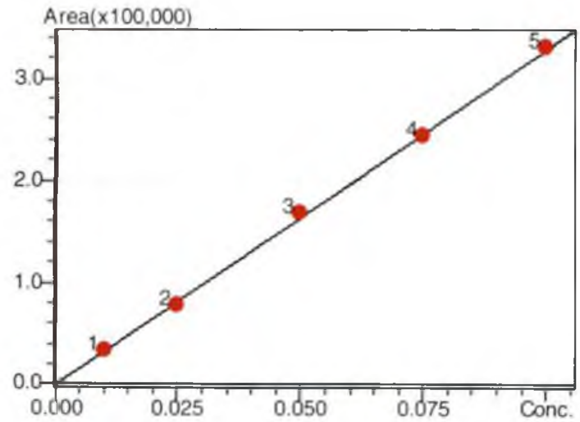
Y = aX + b, a = 2668573, b = 0.0, R^2 = 0.9972010, R = 0.9985995, RF %RSD : 6.658856

Fig 8. Calibration curve of chlorpyriphos



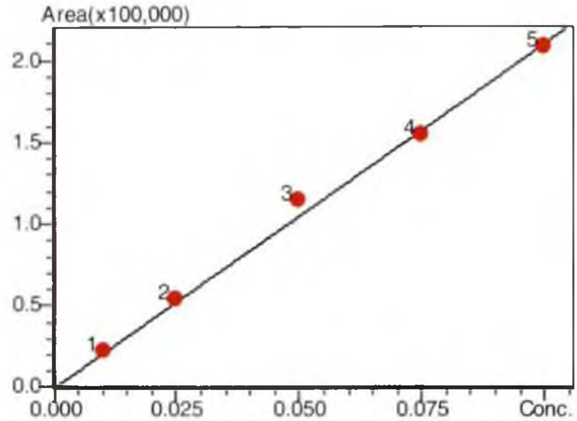
Y = aX + b, a = 360235.9, b = 0.0, R^2 = 0.9980724, R = 0.9990357, RF %RSD : 5.535834

Fig 9. Calibration curve of quinalphos



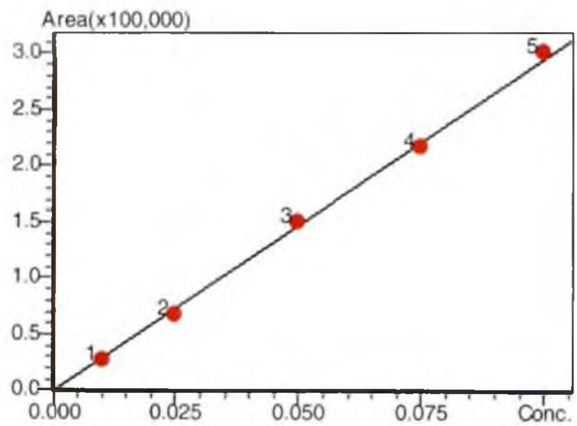
Y = aX + b, a = 3279532, b = 0.0, R^2 = 0.9994551, R = 0.9997275, RF %RSD : 2.464618

Fig 10. Calibration curve of alpha endosulfan



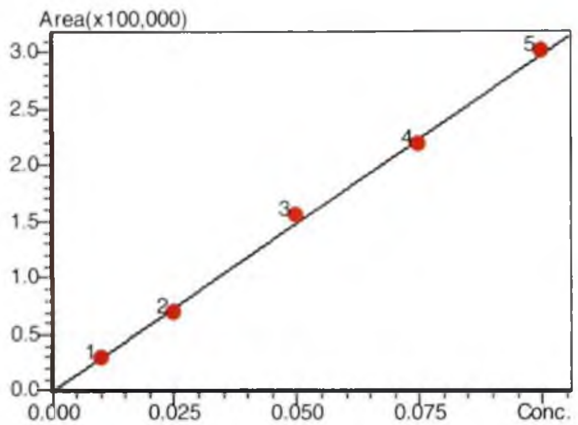
Y = aX + b, a = 2101603, b = 0.0, R^2 = 0.9965021, R = 0.9982495, RF %RSD : 4.684324

Fig 11. Calibration curve of profenophos



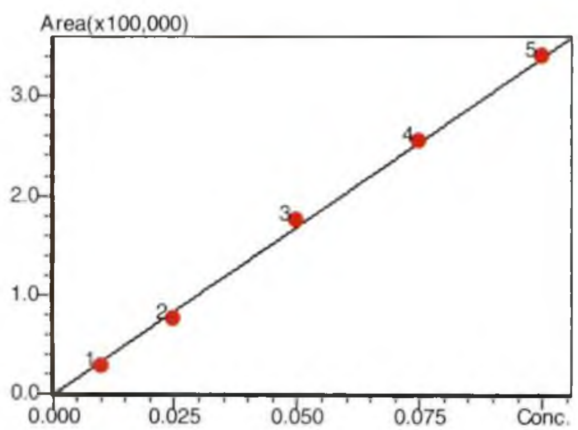
Y = aX + b, a = 2953736, b = 0.0, R^2 = 0.9988061, R = 0.9994029, RF %RSD : 4.770539

Fig 12. Calibration curve of pp DDE



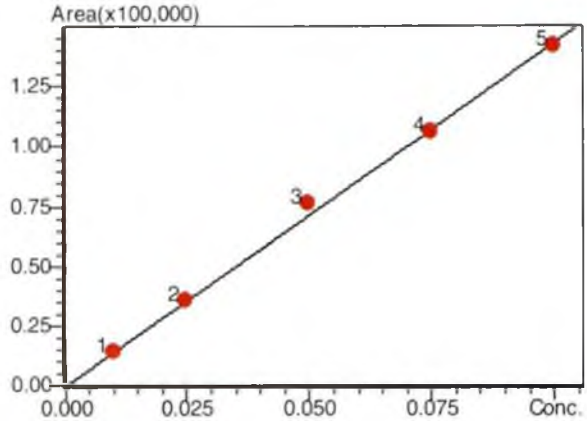
Y = aX + b, a = 2978493, b = 0.0, R^2 = 0.9979864, R = 0.9989927, RF %RSD : 4.319246

Fig 13. Calibration curve of beta endosulfan



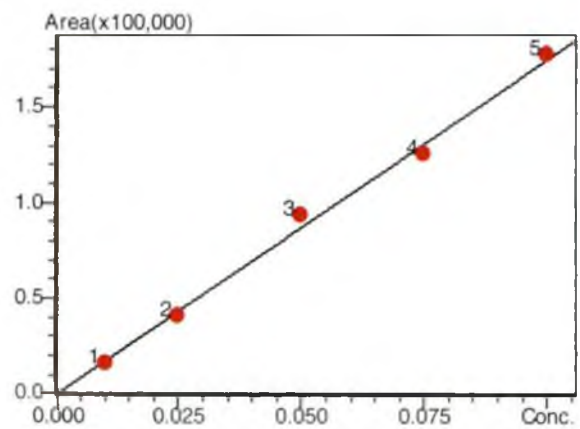
Y = aX + b, a = 3392574, b = 0.0, R^2 = 0.9984620, R = 0.9992307, RF %RSD : 7.549603

Fig 14. Calibration curve of pp DDD



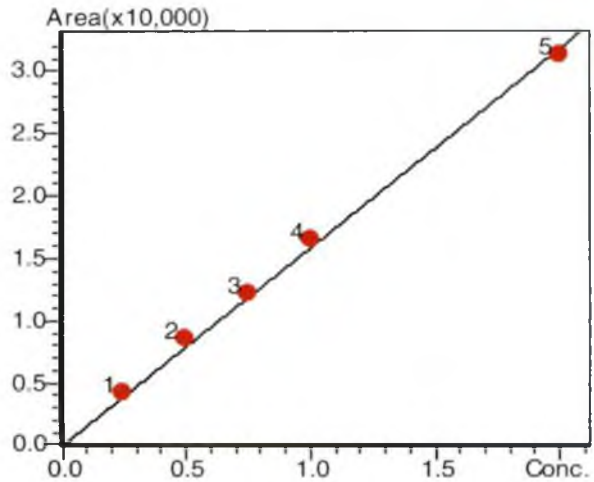
Y = aX + b, a = 1431726, b = 0.0, R^2 = 0.9975293, R = 0.9987639, RF %RSD : 3.52850

Fig 15. Calibration curve of ethion



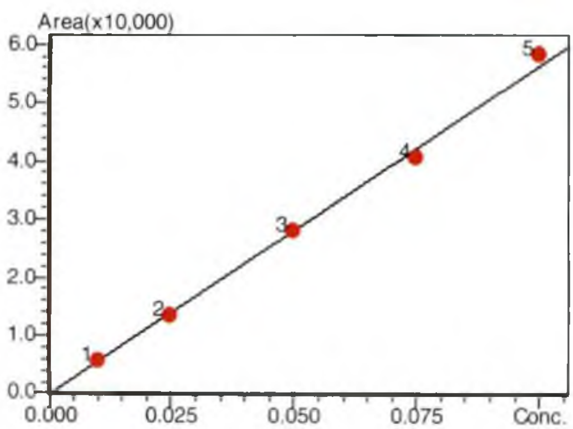
Y = aX + b, a = 1746423, b = 0.0, R^2 = 0.9952204, R = 0.9976073, RF %RSD : 6.095141

Fig 16. Calibration curve of endosulfan sulphate



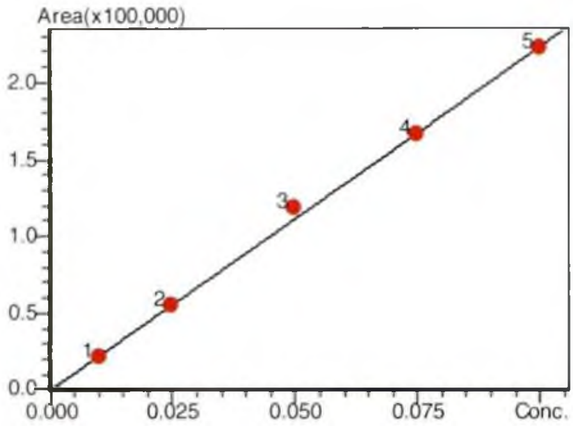
Y = aX + b, a = 15933.04, b = 0.0, R^2 = 0.9991051, R = 0.9995525, RF %RSD : 5.932167

Fig 17. Calibration curve of triazophos



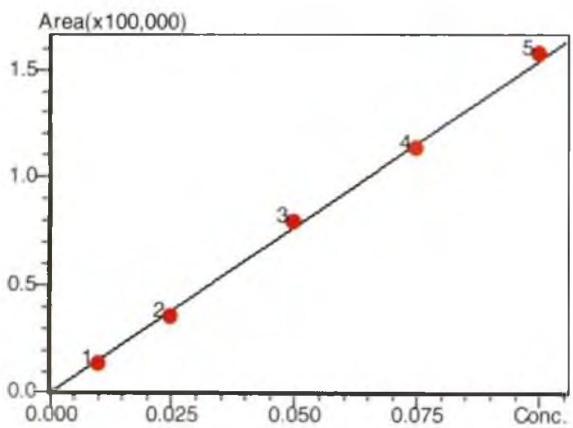
Y = aX + b, a = 564533.2, b = 0.0, R^2 = 0.9973721, R = 0.9986852, RF %RSD : 4.456146

Fig 18. Calibration curve of pp DDT



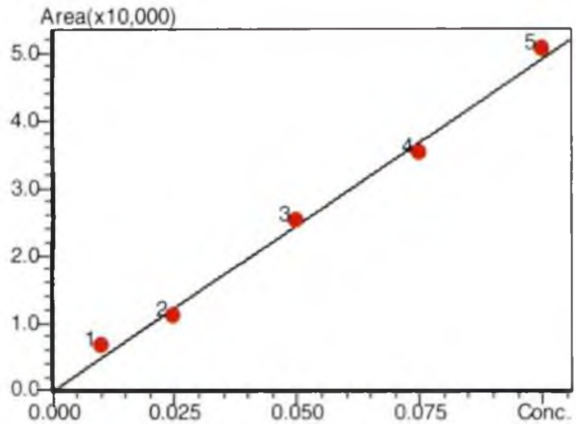
Y = aX + b, a = 2231658, b = 0.0, R^2 = 0.9977643, R = 0.9988815, RF %RSD : 3.872328

Fig 19. Calibration curve of bifenthrin



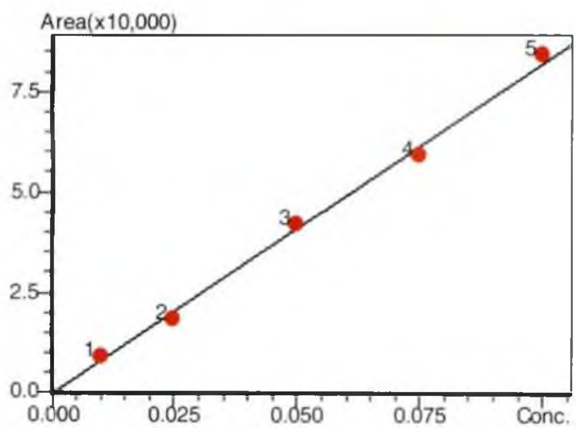
Y = aX + b, a = 1545433, b = 0.0, R^2 = 0.9983160, R = 0.9991577, RF %RSD : 5.950177

Fig 20. Calibration curve of lambda cyhalothrin



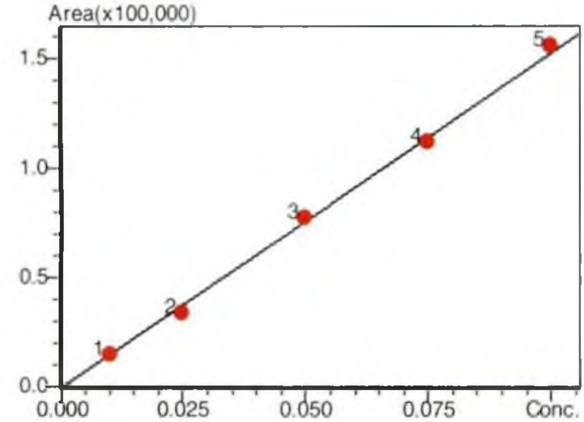
Y = aX + b, a = 491165.8, b = 0.0, R^2 = 0.9929914, R = 0.9964896, RF %RSD : 13.19284

Fig 21. Calibration curve of cyfluthrin-1



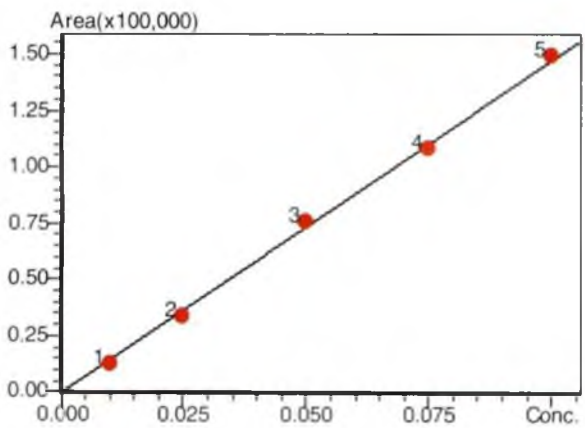
Y = aX + b, a = 820830.9, b = 0.0, R^2 = 0.9959535, R = 0.9979747, RF %RSD : 7.474020

Fig 22. Calibration curve of cyfluthrin -2



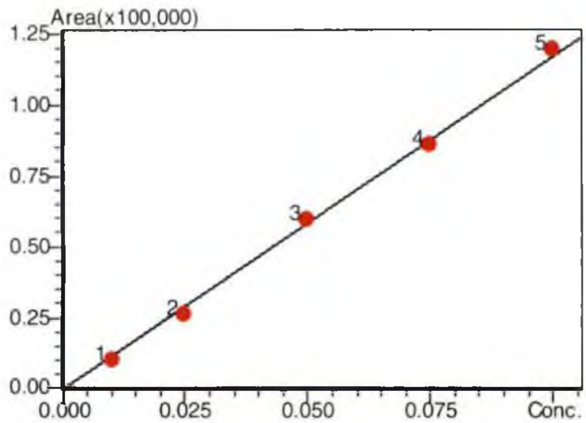
Y = aX + b, a = 1528061, b = 0.0, R^2 = 0.9982274, R = 0.9991133, RF %RSD : 5.007005

Fig 23. Calibration curve of cypermethrin -1



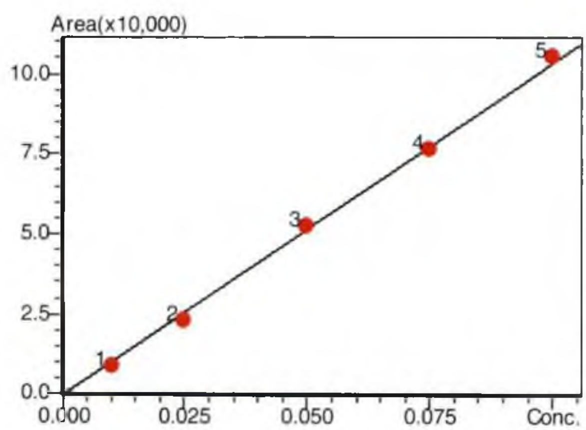
Y = aX + b, a = 1474896, b = 0.0, R^2 = 0.9987258, R = 0.9993627, RF %RSD : 6.539734

Fig 24. Calibration curve of cypermethrin-2



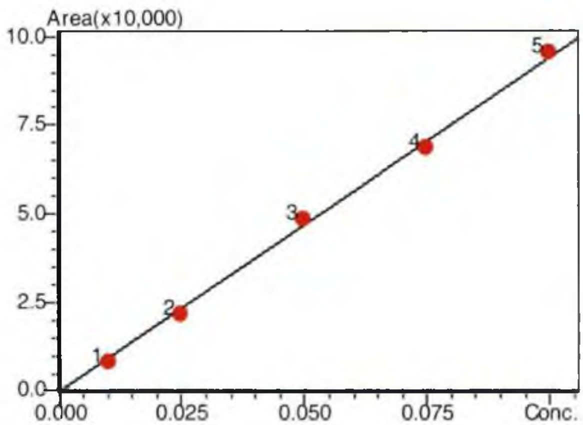
Y = aX + b, a = 1170821, b = 0.0, R^2 = 0.9987072, R = 0.9993534, RF %RSD : 6.312931

Fig 25. Calibration curve of cypermethrin-3



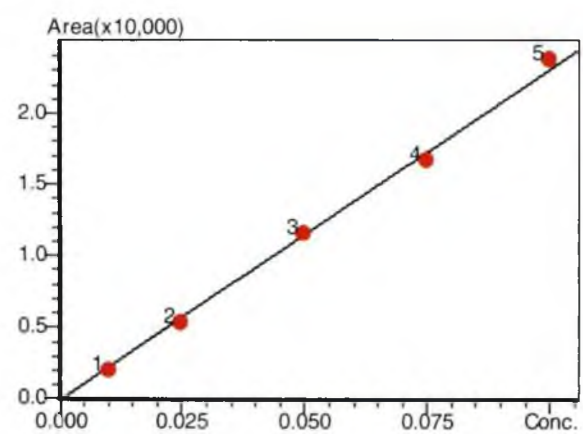
Y = aX + b, a = 1034642, b = 0.0, R^2 = 0.9989293, R = 0.9994645, RF %RSD : 7.250378

Fig 26. Calibration curve of cypermethrin- 4



Y = aX + b, a = 941525.0, b = 0.0, R^2 = 0.9984076, R = 0.9992035, RF %RSD : 5.702675

Fig 27. Calibration curve of fenvalerate-1



Y = aX + b, a = 231021.0, b = 0.0, R^2 = 0.9980012, R = 0.9990001, RF %RSD : 6.418373

Fig 28. Calibration curve of fenvalerate-2

4.3 Monitoring of pesticide residues in cardamom

The data on residues of pesticides in cardamom collected during August 2011 to January 2012 from the three major cardamom growing areas of Idukki district *viz.* Udumbanchola, Vandanmedu and Poopara are presented in tables 16 to 33.

4.3.1 Pesticide residues in cardamom capsules from Udumbanchola

The data on pesticide residues (µg g^{-1}) in cardamom collected from Udumbanchola during August 2011 (Table 16) indicated that all the samples showed the presence of multiple pesticide residues at varying levels. Pesticides detected were quinalphos, cypermethrin, lambda cyhalothrin and triazophos. Quinalphos and cypermethrin were present in all the samples with a range of 0.033 - 0.164 µg g^{-1} and 0.280 - 0.674 µg g^{-1} respectively. Five samples showed the presence of residues of lambda cyhalothrin, with the range 0.346 - 1.733 µg g^{-1} and triazophos in three samples with a range of 0.228 - 1.156 µg g^{-1}. In all the samples, residues of quinalphos were above PFA MRL and that of cypermethrin residues were above Codex MRL. No PFA or Codex MRL have been fixed for triazophos and lambda cyhalothrin in cardamom.

Monitoring of pesticide residues in Udumbanchola during September 2011 revealed that out of 10 samples analysed, all of them contained multiple residues with a range of 0.005 to 6.193 µg g^{-1}. Profenophos was seen in all the ten samples with a range of 0.043 - 6.193 µg g^{-1} for which no PFA or Codex MRL exists in cardamom. Quinalphos residues were detected in seven samples with a range of 0.053 - 1.879 µg g^{-1} and all the values were above the PFA MRL. Chlorpyriphos was detected in four samples with a range of 0.021 - 0.120 µg g^{-1}. However all were below the Codex MRL. Cypermethrin was detected in seven samples with a range of 0.068 - 0.429 µg g^{-1} , of which three were below the Codex MRL. Lambda cyhalothrin was detected in five samples with a range of 0.064-1.103 µg g^{-1}, and has no PFA or Codex MRL. Alpha endosulfan was detected in one sample (0.005 μg g^{-1}), beta endosulfan in three samples (0.005 - 0.01 μg g^{-1}) and endosulphan sulphate in four samples (0.012 - 0.020 μg g^{-1}). However, the level of these three pesticides were below PFA and Codex MRL. Ethion was seen in three samples at 0.152, 0.157 and 0.080 μg g^{-1} which were below Codex MRL. One sample showed the presence of methyl parathion at 0.042 μg g^{-1}, which is below Codex MRL. The highest level of pesticides observed during the month were profenophos (6.193 μg g^{-1}) followed by quinalphos (1.879 μg g^{-1}).

Similarly, all the samples collected from Udumbanchola during October, 2011 showed multiple residues of pesticides. Cypermethrin was detected in all the samples with a range of 0.032 - 0.231μg g^{-1} and six of them were above Codex MRL. Nine samples indicated the presence of quinalphos with a concentration of 0.045 - 0.45 μg g^{-1} falling above PFA MRL. Profenophos was detected in four samples with a range of 0.059 - 0.674 μg g^{-1} and Lambda cyhalothrin in six samples with a range of 0.01-0.065 μg g^{-1}.Though chlorpyriphos was seen in five samples at 0.153, 0.204, 0.012, 0.014 and 0.047 μg g^{-1}, all were below Codex MRL. Two samples contained residues of fenpropathrin at 0.043 and 0.079 μg g^{-1}. Methyl parathion was present in one sample at 0.240 μg g^{-1} which was below Codex MRL.

Out of 10 samples collected from Udumbanchola during November, 2011 all contained multiple residues of pesticides. Though chlorpyriphos was detected in all the samples with a range of 0.033 - 0.251 μg g^{-1} all of them were below the Codex MRL. Quinalphos and lambda cyhalothrin were present in nine samples each with a range of 0.038 - 0.632 μg g^{-1} and 0.029 - 1.399 μg g^{-1} respectively. All samples with quinalphos residues were above PFA MRL. Cypermethrin was seen in eight samples with a range of 0.024 - 0.24 μg g^{-1} , of which, three exceeded the Codex MRL limit of 0.1 μg g^{-1} Endosulfan sulphate was detected in three samples at 0.027, 0.04 and 0.031 μg g^{-1} and were below PFA and Codex MRLs. The level of residues of methyl parathion detected in two samples were 0.028 and 0.062 μg g^{-1}, and the residue was below codex MRL. Profenophos, ethion and malathion were seen in one sample each at 0.043, 0.113 and 0.158 $\mu g\ g^{-1}$ respectively.

In case of cardamom capsules collected from Udumbanchola during December 2011, a total of 14 different pesticides were detected from 10 samples at varying levels. Invariably all the samples contained multiple residues and as high as nine pesticides were detected from a single sample. Quinalphos was present in seven samples with a range of 0.012 - 2.063 $\mu g\ g^{-1}$ recording several fold increase over its MRL value of 0.01 $\mu g\ g^{-1}$.Though alpha and beta endosulfan were there in six samples, all values were below MRL. Similarly, methyl parathion was present in six samples at 0.185, 0.247, 0.024, 0.250, 0.055 and 0.417 $\mu g\ g^{-1}$, but below Codex MRL. Cypermethrin was detected in six samples with a range of 0.046 - 0.215 $\mu g\ g^{-1}$ of which two of them were above Codex MRL. Six samples contained lambda cyhalothrin with a range of 0.015 - 0.360 $\mu g\ g^{-1}$. Chlorpyriphos was detected in five samples with a range of 0.018 - 0.210 $\mu g\ g^{-1}$ and all the values were below Codex MRL and bifenthrin was detected in two samples at 0.107 and 0.053 $\mu g\ g^{-1}$. Two samples contained ethion at 0.128 and 0.401 $\mu g\ g^{-1}$. Five samples contained profenophos with a range of 0.080 - 0.222 $\mu g\ g^{-1}$. Malathion was detected in three samples at 0.353, 0.042 and 0.012 $\mu g\ g^{-1}$ and all the values were below the Codex MRL. Fenpropathrin and fenvalerate were detected in one sample each at 0.133 and 0.031 $\mu g\ g^{-1}$ respectively.

Data presented in table 21 revealed that, out of 10 samples analysed, multiple residues of pesticides could be detected in nine samples collected from Udumbanchola during January 2012. Pesticides detected from these samples include alpha endosulfan, beta cyfluthrin, chlorpyriphos, endosulfan sulphate, ethion, fenvalerate, methyl parathion, profenophos and quinalphos with the range of 0.007-1.163 $\mu g\ g^{-1}$ and the highest concentration observed being 1.163 $\mu g\ g^{-1}$ for ethion. Quinalphos was present in nine samples with the residue levels at 0.275, 0.134, 0.195, 0.148, 0.137, 0.083, 0.205, 0.106 and 0.202 $\mu g\ g^{-1}$ and all the values were above MRL. Endosulfan sulphate was detected in five samples with a range of

0.026-0.053 µg g^{-1}, which were below PFA and Codex MRL. Alpha endosulfan was detected in three samples at 0.010, 0.007 and 0.008 µg g^{-1} and beta cyfluthrin was present in two samples at 0.020 and 0.023 µg g^{-1}. Methyl parathion was detected in three samples at 0.097, 0.137 and 0.110 µg g^{-1}.Three samples contained profenophos at 0.016, 0.010 and 0.034 µg g^{-1}.Fenvalerate and ethion were detected in one sample each the level being 0.094 and 1.163 µg g^{-1} respectively.

4.3.2 Pesticide residues in cardamom capsules form Vandanmedu

The data on pesticide residues (µg g^{-1}) in cardamom samples collected from Vandenmedu during August 2011 revealed that out of 10 samples analyzed, one was free of residues, two contained residue of single insecticide and seven contained multiple residues of insecticides (Table 22). Among the different pesticides detected, quinalphos was detected in six samples with a range of 0.042 - 0.103 µg g^{-1} and all of them were above the PFA MRL. This was followed by chlorpyriphos which was present in five samples with a range of 0.020 - 0.033 µg g^{-1} and all were below PFA MRL. Other pesticides detected include lambda cyhalothrin in four samples with a range of 0.030- 0.915 µg g^{-1}, cypermethrin in three samples the range being 0.018 - 0.042 µg g^{-1}, malathion, methyl parathion and ethion were detected in one sample each, the level being 0.412, 0.099 and 0.026 µg g^{-1} respectively and all of them were below Codex MRL.

Out of the 10 cardamom samples collected from Vandanmedu during September 2011, nine showed the presence of multiple residues of pesticides. Nine samples showed the presence of cypermethrin residues at a range of 0.019-0.643 µg g^{-1} of which four were above Codex MRL. Quinalphos was detected in seven samples with a range of 0.052 - 1.386 µg g^{-1} and out of the seven samples six were several times higher than the MRL of 0.01 µg g^{-1}. Lambda cyhalothrin and profenophos which do not have PFA or Codex MRL were present in five samples each with a range of 0.164 - 0.984 µg g^{-1} and 0.040 - 0.318 µg g^{-1}. Alpha endosulfan and beta endosulfan were detected in three samples each with a range of 0.004 - 0.010 µg g^{-1} and endosulfan sulphate was detected in one sample at 0.012 µg g^{-1}.

However, all the values were below PFA and Codex MRL. Residues of methyl parathion (3), malathion (2), ethion (3) and Chlorpyriphos (8) were below Codex MRL.

Out of the 10 samples analyzed during October 2011, all of them contained multiple residues of pesticides with a range of 0.008 - 1.123 μg g^{-1} and the highest being quinalphos (1.123 μg g^{-1}). Chlorpyriphos was detected in all the samples with a range of 0.015-0.091μg g^{-1}, but all the values were below Codex MRL. Nine samples contained quinalphos with a range of 0.121-1.123 μg g^{-1} and all were above MRL. Cypermethrin was detected in six samples with a range of 0.023 - 0.309 μg g^{-1}, and five samples exceeded the Codex MRL. However, triazophos was present in one sample (0.836 μg g^{-1}). One of the samples showed the presence of alpha endosulfan (0.056 μg g^{-1}), beta endosulfan (0.050 μg g^{-1}) and endosulfan sulphate (0.032 μg g^{-1}), all below PFA and Codex MRL. Other pesticides detected include lambda cyhalothrin in eight samples with a range of 0.022 - 0.578 μg g^{-1}, profenophos in five samples with a range of 0.080 - 0.182 μg g^{-1} and ethion in two samples (0.135 and 0.098 μg g^{-1}) for which no PFA or Codex MRL exist.

Out of the 10 samples collected from Vandanmedu during November 2011, two samples were free of residues. Seven samples showed the presence of multiple residues with a range of 0.005 - 1.672 μg g^{-1} and one showed the presence of lambda cyhalothrin alone. Lambda cyhalothrin was present in eight samples (0.026 - 1.672 μg g^{-1}) and profenophos in five samples (0.078 - 0.367 μg g^{-1}) though chlorpyriphos was seen in three samples all of them were below Codex MRL. Alpha endosulfan and beta endosulfan were present in five samples with a range of 0.005 - 0.046 μg g^{-1} and 0.006 - 0.092 μg g^{-1}respectively whereas endosulfan sulphate was present in four samples with a range of 0.017 - 0.092 μg g^{-1}. However, all the values were below PFA and Codex MRL. Cypermethrin was present in four samples with a range of 0.055 - 0.685 μg g^{-1} of which three were above MRL. Quinalphos was present in one sample at 0.062 μg g^{-1} which was above PFA MRL.

All the cardamom samples collected from Vandanmedu during December 2011 revealed the presence of multiple residues of pesticides. Quinalphos was detected in eight samples with a range of 0.046 - 0.817 µg g^{-1}, all were above MRL. Lambda cyhalothrin was detected in seven samples with a range of 0.013 - 0.346 µg g^{-1}. Chlorpyriphos was detected in seven samples with a range of 0.017 - 0.382 µg g^{-1} and all the values were below Codex MRL. Profenophos was detected in five samples with a range of 0.036-0.599 µg g^{-1} and bifenthrin in one sample at 0.068 µg g^{-1}.Two samples showed the presence of residues of alpha endosulfan (0.088 and 0.060 µg g^{-1}), beta endosulfan (0.023 and 0.067 µg g^{-1}) and endosulfan sulphate (0.018 and 0.039 µg g^{-1}) at levels below PFA and Codex MRL.

Out of the 10 samples collected from Vandanmedu during January 2012, two of them were free of residues, while eight showed the residues of alpha endosulfan, beta cyfluthrin, chlorpyriphos, cypermethrin, fenpropathrin, quinalphos, fenvalerate, profenophos and endosulfan sulphate in varying levels. Alpha endosulfan and endosulfan sulphate was detected in two samples each with a range of 0.007 - 0.209 µg g^{-1}. Beta cyfluthrin, chlorpyriphos, cypermethrin, fenpropathrin and fenvalerate were present in one sample each at 0.124, 0.017, 0.025 , 0.093 and 0.101 µg g^{-1}. Profenophos was detected in four samples with a range of 0.011 - 0.060 µg g^{-1}. Quinalphos was detected in five samples with a range of 0.121 - 0.826 µg g^{-1} which were above MRL.

4.3.3 Pesticide residues in cardamom capsules from Poopara

All the samples of the cardamom collected from Pooppara region during August 2011 contained residues of pesticides, of which eight showed multiple residues in varying levels. Quinalphos was detected in two samples, the level being 0.031 and 0.184 µg g^{-1} respectively and both were above PFA MRL. Lambda cyhalothrin was detected in nine samples with a range of 0.210 to 0.585 µg g^{-1}. Six samples showed residues of ethion with a range of 0.014 - 0.049 µg g^{-1}. Fenvalerate was detected in two samples (0.020 and 0.050 μg g^{-1}), whereas chlorpyriphos (0.028 μg g^{-1}) and cypermethrin (0.020 μg g^{-1}) in one sample each. Level of residues of chlorpyriphos, ethion and cypermethrin detected were below Codex MRL. However, no PFA or Codex MRL have been fixed for lambda cyhalothrin and fenvalerate.

Monitoring of pesticide residues in Poopara during September 2011 indicated that of the 10 samples analyzed, nine contained multiple residues with a range of 0.017-0.739 μg g^{-1} whereas one sample contained residues of quinalphos only. Quinalphos was detected in nine samples with a range of 0.028 - 0.093μg g^{-1} which were above PFA MRL. Cypermethrin was detected in eight samples with the range of 0.017 - 0.247μg g^{-1}. However two samples exceeded the Codex MRL. Lambda cyhalothrin was detected in five samples (0.030 - 0.642 μg g^{-1}) and profenophos in five samples (0.035 - 0.739 μg g^{-1}), for which no PFA or Codex MRL have been fixed. Beta cyfluthrin was detected in two samples, the level being 0.087 and 0.118 μg g^{-1}. Malathion was detected in one sample (0.105 μg g^{-1}) which was below Codex MRL.

Pesticide residues in cardamom samples collected from Poopara during October 2011 indicated that all samples contained multiple residues with a range of 0.002-3.121 μg g^{-1}. Highest level of residues observed during the month was of malathion (3.121 μg g^{-1}) followed by quinalphos (1.163μg g^{-1}) and profenophos(1.087 μg g^{-1}). Quinalphos was detected in nine samples with a range of 0.091-1.163 μg g^{-1} and all were above PFA MRL. Two samples contained quinalphos to the tune of at 1.402 and 1.163 μg g^{-1}, which were several fold higher than its MRL of 0.01 μg g^{-1}. Chlorpyriphos was present in six samples (0.080-0.124 μg g^{-1}) which was below Codex MRL. Cypermethrin was detected in seven samples with a range of 0.192-0.239 μg g^{-1}, which were above Codex MRL. Profenophos was detected in four samples (0.109-1.087 μg g-1), lambda cyhalothrin in seven samples (0.070-0.229 μg g^{-1}) and methyl parathion in two samples (0.025and 0.045 μg g^{-1}). Alpha endosulfan (0.022 μg g^{-1}), beta endosulfan (0.039 μg g^{-1}) and endosulfan sulphate (0.026 µg g^{-1}) were detected in one sample each. However, all these values were below the PFA and Codex MRL. Ethion and malathion were detected in one sample each at 0.188 and 3.121 µg g^{-1} respectively, of which malathion was above and Ethion was below Codex MRL.

All the samples collected from Poopara during November 2011 contained multiple residues of pesticides at varying levels with a range of 0.003-0.666 µg g^{-1}. Quinalphos and lambda cyhalothrin were detected in all the samples with a range of 0.231-0.666 µg g^{-1} and 0.017-0.251 µg g^{-1} respectively. The level of quinalphos residues detected in all the samples were above PFA MRL. Chlorpyriphos was detected in eight samples with a range of 0.012-0.133 µg g^{-1}, which was below Codex MRL and cypermethrin was detected in six samples with a range of 0.015-0.122 µg g^{-1}, of which one was above Codex MRL. Endosulfan sulphate (0.026 and 0.056 µg g^{-1}), profenophos (0.026 and 0.052µg g^{-1}) and ethion (0.014 and 0.057µg g^{-1}) were present in two samples each. Beta cyfluthrin was detected in one sample at a level of 0.030 µg g^{-1}.

During December 2011, all the samples collected from Poopara contained multiple residues of pesticides at varying levels. The highest level observed was that of lambda cyhalothrin (1.502 µg g^{-1}) followed by profenophos (1.34µg g^{-1}). Chlorpyriphos and lambda cyhalothrin were detected in seven samples each with a range of 0.027-0.248 µg g^{-1} and 0.046-1.052µg g^{-1} respectively. The level of chlorpyriphos residues were below Codex MRL while no MRL values have been fixed for lambda cyhalothrin. Two samples contained quinalphos at 0.614 and 0.402 µg g^{-1}, which were above PFA MRL while ethion was also detected in one sample only (0.176 µg g^{-1}), which was below Codex MRL. Alpha endosulfan was present in six samples (0.005-0.088µg g^{-1}) and beta endosulfan in seven samples (0.012-0.245µg g^{-1}) and all of them were below PFA and Codex MRL.

Multiple residues of pesticides were detected in four cardamom samples, out of the 10 samples collected from Poopara during January 2012 whereas two samples were free of pesticide residues. Quinalphos was present in five samples with a range

Table 16. Pesticide residues (µg g^{-1}) in cardamom collected from Udumbanchola during August 2011

Sample No.	Pesticides Detected	Residue (µg g^{-1})	PFA MRL Status	Codex MRL Status
1.	Quinalphos	0.033	Above	No MRL
	Triazophos	0.228	No MRL	No MRL
	Lambda cyhalothrin	0.690	No MRL	No MRL
	Cypermethrin	0.280	No MRL	Above
2.	Quinalphos	0.067	Above	No MRL
	Triazophos	0.828	No MRL	No MRL
	Lambda cyhalothrin	0.346	No MRL	No MRL
	Cypermethrin	0.358	No MRL	Above
3.	Quinalphos	0.060	Above	No MRL
	Cypermethrin	0.394	No MRL	Above
4.	Quinalphos	0.113	Above	No MRL
	Cypermethrin	0.582	No MRL	Above
5.	Quinalphos	0.098	Above	No MRL
	Lambda cyhalothrin	1.133	No MRL	No MRL
	Cypermethrin	0.510	No MRL	Above
6.	Quinalphos	0.099	Above	No MRL
	Cypermethrin	0.413	No MRL	Above
7.	Quinalphos	0.157	Above	No MRL
	Cypermethrin	0.622	No MRL	Above
8.	Quinalphos	0.133	Above	No MRL
	Cypermethrin	0.507	No MRL	Above
9.	Quinalphos	0.164	Above	No MRL
	Triazophos	1.156	No MRL	No MRL
	Lambda cyhalothrin	1.733	No MRL	No MRL
	Cypermethrin	0.674	No MRL	Above
10.	Quinalphos	0.127	Above	No MRL
	Lambda cyhalothrin	1.300	No MRL	No MRL
	Cypermethrin	0.459	No MRL	Above

* LOD (OC : 0.005 µg g^{-1}, OP and SP : 0.01 µg g^{-1}), ** LOQ (OC, OP and SP : 0.05 µg g^{-1})

Table 17. Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Udumbanchola during September 2011

Sample No	Pesticides Detected	Residue ($\mu g\ g^{-1}$)	PFA MRL status	Codex MRL status
1.	Chlorpyriphos	0.103	No MRL	Below
	Profenophos	0.974	No MRL	No MRL
	Beta endosulfan	0.01	Below	Below
	Lambda cyhalothrin	0.806	No MRL	No MRL
	Cypermethrin	0.068	No MRL	Below
2	Quinalphos	0.353	Above	No MRL
	Profenophos	2.061	No MRL	No MRL
	Endosulfan sulphate	0.020	Below	Below
	Lambda cyhalothrin	0.704	No MRL	No MRL
3.	Chlorpyriphos	0.098	No MRL	Below
	Profenophos	0.117	No MRL	No MRL
	Ethion	0.152	No MRL	Below
	Lambda cyhalothrin	1.103	No MRL	No MRL
	Cypermethrin	0.410	No MRL	Above
4.	Quinalphos	0.183	Above	No MRL
	Profenophos	6.193	No MRL	No MRL
	Cypermethrin	0.337	No MRL	Above
5.	Chlorpyriphos	0.120	No MRL	Below
	Quinalphos	1.879	Above	No MRL
	Profenophos	0.247	No MRL	No MRL
	Ethion	0.157	No MRL	Below
	Cypermethrin	0.429	No MRL	Above
6.	Profenophos	0.043	No MRL	No MRL
	Lambda cyhalothrin	0.064	No MRL	No MRL
	Cypermethrin	0.095	No MRL	Below
7.	Methyl parathion	0.042	No MRL	Below
	Quinalphos	0.104	Above	No MRL
	Profenophos	0.079	No MRL	No MRL
	Endosulfan sulphate	0.012	Below	Below
	Lambda cyhalothrin	0.118	No MRL	No MRL
	Cypermethrin	0.107	No MRL	Above
8.	Quinalphos	0.061	Above	No MRL
	Profenophos	0.401	No MRL	No MRL
	Beta endosulfan	0.005	Below	Below
	Endosulfan sulphate	0.013	Below	Below
	Quinalphos	0.053	Above	No MRL
	Alpha endosulfan	0.005	Below	Below
9.	Profenophos	0.437	No MRL	No MRL
	Beta endosulfan	0.005	Below	Below
	Endosulfan sulphate	0.015	Below	Below
10.	Chlorpyrifos	0.021	No MRL	Below
	Quinalphos	0.189	Above	No MRL
	Profenophos	0.398	No MRL	No MRL
	Ethion	0.080	No MRL	Below
	Cypermethrin	0.074	No MRL	Below

* LOD (OC : 0.005 $\mu g\ g^{-1}$, OP and SP : 0.01 $\mu g\ g^{-1}$), ** LOQ (OC, OP and SP : 0.05 $\mu g\ g^{-1}$)

Table 18. Pesticide residues (µg g^{-1}) in cardamom collected from Udumbanchola during October 2011

Sample No	Pesticides Detected	Residue (µg g^{-1})	PFA MRL status	Codex MRL status
1.	Quinalphos	0.045	Above	No MRL
	Profenophos	0.059	No MRL	No MRL
	Lambda cyhalothrin	0.065	No MRL	No MRL
	Cypermethrin	0.038	No MRL	Below
2.	Quinalphos	0.172	Above	No MRL
	Profenophos	0.646	No MRL	No MRL
	Fenpropathrin	0.043	No MRL	No MRL
	Cypermethrin	0.190	No MRL	Below
3.	Chlorpyriphos	0.153	No MRL	Below
	Quinalphos	0.351	Above	No MRL
	Lambda cyhalothrin	0.014	No MRL	No MRL
	Cypermethrin	0.122	No MRL	Above
4.	Chlorpyriphos	0.204	No MRL	Below
	Quinalphos	0.115	Above	No MRL
	Lambda cyhalothrin	0.010	No MRL	No MRL
	Cypermethrin	0.043	No MRL	Below
5.	Quinalphos	0.052	Above	No MRL
	Lambda cyhalothrin	0.010	No MRL	No MRL
	Cypermethrin	0.041	No MRL	Below
6.	Quinalphos	0.450	Above	No MRL
	Lambda cyhalothrin	0.027	No MRL	No MRL
	Cypermethrin	0.231	No MRL	Above
7.	Methyl parathion	0.240	No MRL	Below
	Chlorpyriphos	0.012	No MRL	Below
	Profenophos	0.674	No MRL	No MRL
	Cypermethrin	0.222	No MRL	Above
8.	Quinalphos	0.251	Above	No MRL
	Cypermethrin	0.126	No MRL	Above
9.	Chlorpyriphos	0.014	No MRL	Below
	Quinalphos	0.163	Above	No MRL
	Profenophos	0.169	No MRL	No MRL
	Fenpropathrin	0.079	No MRL	No MRL
	Cypermethrin	0.129	No MRL	Above
10.	Chlorpyriphos	0.047	No MRL	Below
	Quinalphos	0.120	Above	No MRL
	Lambda cyhalothrin	0.051	No MRL	No MRL
	Cypermethrin	0.032	No MRL	Above

* LOD (OC : 0.005 µg g^{-1}, OP and SP : 0.01 µg g^{-1}), ** LOQ (OC, OP and SP : 0.05 µg g^{-1})

Table 19. Pesticide residues (μg g^{-1}) in cardamom collected from Udumbanchola during November 2011

Sample No	Pesticides Detected	Residue (μg g^{-1})	PFA MRL Status	Codex MRL Status
1.	Chlorpyriphos	0.071	No MRL	Below
	Quinalphos	0.596	Above	No MRL
	Endosulfan sulphate	0.027	Below	Below
	Lambda cyhalothrin	0.043	No MRL	No MRL
	Cypermethrin	0.046	No MRL	Below
2.	Chlorpyriphos	0.081	No MRL	Below
	Quinalphos	0.632	Above	No MRL
	Ethion	0.113	No MRL	Below
	Lambda cyhalothrin	0.060	No MRL	No MRL
	Cypermethrin	0.086	No MRL	Below
3.	Chlorpyriphos	0.057	No MRL	Below
	Quinalphos	0.441	Above	No MRL
	Endosulfan sulphate	0.040	Below	Below
	Lambda cyhalothrin	0.037	No MRL	No MRL
4.	Malathion	0.158	No MRL	Below
	Chlorpyriphos	0.054	No MRL	Below
	Quinalphos	0.570	Above	No MRL
	Endosulphan sulphate	0.031	Below	Below
	Lambda cyhalothrin	0.034	No MRL	No MRL
	Cypermethrin	0.089	No MRL	Below
5.	Chlorpyriphos	0.033	No MRL	Below
	Quinalphos	0.358	Above	No MRL
	Lambda cyhalothrin	0.029	No MRL	No MRL
	Cypermethrin	0.065	No MRL	Below
6.	Chlorpyriphos	0.037	No MRL	Below
	Quinalphos	0.073	Above	No MRL
	Cypermethrin	0.133	No MRL	Above
7.	Methyl parathion	0.062	No MRL	Below
	Chlorpyriphos	0.066	No MRL	Below
	Quinalphos	0.045	Above	No MRL
	Lambda cyhalothrin	1.399	No MRL	No MRL
	Cypermethrin	0.024	No MRL	Below
8.	Methyl parathion	0.028	No MRL	Below
	Chlorpyriphos	0.028	No MRL	Below
	Quinalphos	0.038	Above	No MRL
	Profenophos	0.043	No MRL	No MRL
	Lambda cyhalothrin	0.097	No MRL	No MRL
	Cypermethrin	0.130	No MRL	Above
9.	Chlorpyriphos	0.077	No MRL	Below
	Quinalphos	0.375	Above	No MRL
	Lambda cyhalothrin	0.033	No MRL	No MRL
10.	Chlorpyriphos	0.251	No MRL	Below
	Lambda cyhalothrin	0.052	No MRL	No MRL
	Cypermethrin	0.240	No MRL	Above

* LOD (OC : 0.005 μg g^{-1}, OP and SP : 0.01 μg g^{-1}), ** LOQ (OC, OP and SP : 0.05 μg g^{-1})

Table 20 Pesticide residues (µg g^{-1}) in cardamom collected from Udumbanchola during December 2011

Sample No	Pesticides Detected	Residue (µg g^{-1})	PFA MRL Status	Codex MRL Status
1.	Quinalphos	0.181	Above	No MRL
	Lambda cyhalothrin	0.023	No MRL	No MRL
	Cypermethrin	0.076	No MRL	Below
2.	Lambda cyhalothrin	0.084	No MRL	No MRL
	Cypermethrin	0.046	No MRL	Below
3.	Quinalphos	0.149	Above	No MRL
	Lambda cyhalothrin	0.015	No MRL	No MRL
	Cypermethrin	0.066	No MRL	Below
4.	Methyl parathion	0.185	No MRL	Below
	Chlorpyriphos	0.072	No MRL	Below
	Alpha endosulfan	1.415	Above	Below
	Profenophos	0.222	No MRL	No MRL
	Beta endosulfan	0.372	Below	Below
	Lambda cyhalothrin	0.133	No MRL	No MRL
	Cypermethrin	0.125	No MRL	Above
5.	Methyl parathion	0.247	No MRL	Below
	Chlorpyriphos	0.210	No MRL	Below
	Alpha endosulfan	0.015	Below	Below
	Profenophos	0.038	No MRL	No MRL
	Beta endosulfan	0.023	Below	Below
	Ethion	0.128	No MRL	Below
	Bifenthrin	0.107	No MRL	No MRL
	Fenvalerate	0.031	No MRL	No MRL
6.	Methyl parathion	0.024	No MRL	Below
	Chlorpyriphos	0.018	No MRL	Below
	Quinalphos	0.026	Above	No MRL
	Alpha endosulfan	0.011	Below	Below
	Profenophos	0.112	No MRL	No MRL
	Beta endosulfan	0.233	Below	Below
	Ethion	0.401	No MRL	Below
7.	Malathion	0.353	No MRL	Below
	Quinalphos	1.569	Above	No MRL
	Alpha endosulfan	0.076	Below	Below
	Endosulfan sulphate	0.231	Below	Below
	Cypermethrin	0.064	No MRL	Below
8.	Methyl parathion	0.250	No MRL	Below
	Malathion	0.042	No MRL	Below
	Chlorpyriphos	0.030	No MRL	Below
	Quinalphos	0.012	Above	No MRL
	Profenophos	0.080	No MRL	No MRL
	Beta endosulfan	0.011	Below	Below
	Fenpropathrin	0.133	No MRL	No MRL
	Lambda cyhalothrin	0.081	No MRL	No MRL
9.	Methyl parathion	0.055	No MRL	Below
	Malathion	0.012	No MRL	Below

	Quinalphos	0.413	Above	No MRL
	Alpha endosulfan	0.028	Below	Below
	Profenophos	0.134	No MRL	No MRL
	Beta endosulfan	0.099	Below	Below
	Endosulfan sulphate	0.111	Below	Below
	Lambda cyhalothrin	0.067	No MRL	No MRL
	Cypermethrin	0.205	No MRL	Above
10.	Methyl parathion	0.417	No MRL	Below
	Chlorpyrifos	0.155	No MRL	Below
	Quinalphos	2.063	Above	No MRL
	Alpha endosulfan	0.012	Below	Below
	Beta endosulfan	0.018	Below	Below
	Endosulfan sulphate	0.019	Below	Below
	Bifenthrin	0.053	No MRL	No MRL
	Lambda cyhalothrin	0.360	No MRL	No MRL

* LOD (OC : 0.005 $\mu g\ g^{-1}$, OP and SP : 0.01 $\mu g\ g^{-1}$), ** LOQ (OC, OP and SP : 0.05 $\mu g\ g^{-1}$)

Table 21. Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Udumbanchola during January 2012

Sample No	Pesticides Detected	Residue ($\mu g\ g^{-1}$)	PFA MRL Status	Codex MRL Status
1.	Methyl parathion	0.097	No MRL	Below
	Quinalphos	0.275	Above	No MRL
	Alpha endosulfan	0.010	Below	Below
	Beta cyfluthrin	0.020	No MRL	No MRL
2.	Methyl parathion	0.137	No MRL	Below
	Quinalphos	0.134	Above	No MRL
	Profenophos	0.016	No MRL	No MRL
	Ethion	1.163	No MRL	Below
3.	Quinalphos	0.195	Above	No MRL
	Endosulfan sulphate	0.053	Below	Below
4.	Quinalphos	0.148	Above	No MRL
	Alpha endosulfan	0.007	Below	Below
	Profenophos	0.010	No MRL	No MRL
	Fenvalerate	0.094	No MRL	No MRL
5.	Chlorpyriphos	0.018	No MRL	Below
	Quinalphos	0.137	Above	No MRL
	Profenophos	0.034	No MRL	No MRL
	Endosulfan sulphate	0.026	Below	Below
6.	Quinalphos	0.083	Above	No MRL
	Endosulfan sulphate	0.034	Below	Below
7.	Quinalphos	0.205	Above	No MRL
	Endosulfan sulphate	0.034	Below	Below
8.	Quinalphos	0.106	Above	No MRL
	Alpha endosulfan	0.008	Below	Below
	Endosulfan sulphate	0.035	Below	Below
	Beta cyfluthrin	0.023	No MRL	No MRL
9.	Methyl parathion	0.110	No MRL	Below
10.	Chlorpyriphos	0.050	No MRL	Below
	Quinalphos	0.202	Above	No MRL

* LOD (OC : 0.005 $\mu g\ g^{-1}$, OP and SP : 0.01 $\mu g\ g^{-1}$), ** LOQ (OC, OP and SP : 0.05 $\mu g\ g^{-1}$)

Table 22. Pesticide residues (µg g^{-1}) in cardamom collected from Vandanmedu during August 2011

Sample No	Pesticides Detected	Residue (µg g^{-1})	PFA MRL status	Codex MRL status
1.	Chlorpyriphos	0.017	No MRL	Below
2.	Malathion	0.412	No MRL	Below
	Chlorpyriphos	0.011	No MRL	Below
	Quinalphos	0.064	Above	No MRL
	Ethion	0.026	No MRL	Below
	Cypermethrin	0.042	No MRL	Below
3.	Quinalphos	0.069	Above	No MRL
	Cypermethrin	0.018	No MRL	Below
4.	Chlorpyriphos	0.020	No MRL	Below
	Quinalphos	0.103	Above	No MRL
	Lambda cyhalothrin	0.318	No MRL	No MRL
5.	Methyl parathion	0.099	No MRL	Below
	Chlorpyriphos	0.033	No MRL	Below
6.	Chlorpyriphos	0.080	No MRL	Below
	Quinalphos	0.084	Above	No MRL
	Cypermethrin	0.020	No MRL	Below
7.	Quinalphos	0.058	Above	No MRL
	Lambda cyhalothrin	0.030	No MRL	No MRL
8.	Lambda cyhalothrin	0.350	No MRL	No MRL
9.	Not Detected	-	-	-
10.	Quinalphos	0.042	Above	No MRL
	Lambda cyhalothrin	0.915	No MRL	No MRL
	Cypermethrin	0.459	No MRL	above

* LOD (OC : 0.005 µg g^{-1}, OP and SP : 0.01 µg g^{-1}), ** LOQ (OC, OP and SP : 0.05 µg g^{-1})

Table 23. Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Vandanmedu during September 2011

Sample No	Pesticides Detected	Residue ($\mu g\ g^{-1}$)	PFA MRL status	Codex MRL status
1.	Methyl parathion	0.070	No MRL	Below
	Chlorpyriphos	0.013	No MRL	Below
	Profenophos	0.040	No MRL	No MRL
	Beta endosulfan	0.008	Below	Below
	Cypermethrin	0.019	No MRL	Below
2	Chlorpyriphos	0.018	No MRL	Below
	Cypermethrin	0.032	No MRL	Below
3.	Malathion	0.109	No MRL	Below
	Chlorpyriphos	0.017	No MRL	Below
	Quinalphos	0.797	Above	No MRL
	Alpha endosulfan	0.008	Below	Below
	Lambda cyhalothrin	0.663	No MRL	No MRL
	Cypermethrin	0.076	No MRL	Below
4.	Malathion	0.191	No MRL	Below
	Chlorpyriphos	0.184	No MRL	Below
	Quinalphos	0.264	Above	No MRL
	Alpha endosulfan	0.010	Below	Below
	Profenophos	0.318	No MRL	No MRL
	Beta endosulfan	0.014	Below	Below
	Ethion	0.185	No MRL	Below
	Lambda cyhalothrin	0.231	No MRL	No MRL
	Endosulphan Sulphate	0.012	Below	Below
	Cypermethrin	0.643	No MRL	Above
5.	Chlorpyriphos	0.077	No MRL	Below
	Quinalphos	0.565	Above	No MRL
	Profenophos	0.103	No MRL	No MRL
	Ethion	0.087	No MRL	Below
	Cypermethrin	0.290	No MRL	Above
6.	Methyl parathion	0.010	No MRL	Below
	Chlorpyriphos	0.018	No MRL	Below
	Quinalphos	0.052	Above	No MRL
	Profenophos	0.013	No MRL	No MRL
	Lambda cyhalothrin	0.405	No MRL	No MRL
	Cypermethrin	0.031	No MRL	Below
7.	Quinalphos	0.810	Above	No MRL
	Lambda cyhalothrin	0.984	No MRL	No MRL
	Cypermethrin	0.084	No MRL	Below
8.	Chlorpyriphos	0.022	No MRL	Below
	Quinalphos	1.386	Above	No MRL
	Alpha endosulfan	0.004	Below	Below
	Beta endosulfan	0.011	Below	Below
	Cypermethrin	0.102	No MRL	Above
9.	Methyl parathion	0.028	No MRL	Below
	Chlorpyriphos	0.108	No MRL	Below
	Quinalphos	0.217	Above	No MRL
	Profenophos	0.146	No MRL	No MRL
	Ethion	0.330	No MRL	Below
	Cypermethrin	0.505	No MRL	Above
10.	Lambda cyhalothrin	0.167	No MRL	No MRL

* LOD (OC : 0.005 $\mu g\ g^{-1}$, OP and SP : 0.01 $\mu g\ g^{-1}$), ** LOQ (OC, OP and SP : 0.05 $\mu g\ g^{-1}$)

Table 24. Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Vandanmedu during October 2011

Sample No	Pesticides Detected	Residue ($\mu g\ g^{-1}$)	PFA MRL Status	Codex MRL Status
1.	Chlorpyriphos	0.084	No MRL	Below
	Quinalphos	0.188	Above	No MRL
	Ethion	0.135	No MRL	Below
	Lambda cyhalothrin	0.087	No MRL	No MRL
	Cypermethrin	0.023	No MRL	Below
2.	Chlorpyriphos	0.015	No MRL	Below
	Quinalphos	0.151	Above	No MRL
	Ethion	0.098	No MRL	Below
	Lambda cyhalothrin	0.193	No MRL	No MRL
	Cypermethrin	0.213	No MRL	Above
3.	Chlorpyriphos	0.021	No MRL	Below
	Quinalphos	0.956	Above	No MRL
	Lambda cyhalothrin	0.114	No MRL	No MRL
4.	Chlorpyriphos	0.031	No MRL	Below
	Quinalphos	0.703	Above	No MRL
	Profenophos	0.117	No MRL	No MRL
	Lambda cyhalothrin	0.022	No MRL	No MRL
	Cypermethrin	0.191	No MRL	Above
5.	Chlorpyriphos	0.049	No MRL	Below
	Quinalphos	0.121	Above	No MRL
	Alpha endosulfan	0.056	Below	Below
	Profenophos	0.080	No MRL	No MRL
	Beta endosulfan	0.050	Below	Below
	Endosulfan sulphate	0.032	Below	Below
	Lambda cyhalothrin	0.084	No MRL	No MRL
	Cypermethrin	0.309	No MRL	Above
6.	Chlorpyriphos	0.091	No MRL	Below
	Quinalphos	0.369	Above	No MRL
	Lambda cyhalothrin	0.033	No MRL	No MRL
	Cypermethrin	0.143	No MRL	Above
7.	Chlorpyriphos	0.020	No MRL	Below
	Quinalphos	0.257	Above	No MRL
	Cypermethrin	0.193	No MRL	Above
8.	Chlorpyriphos	0.015	No MRL	Below
	Profenophos	0.149	No MRL	No MRL
	Lambda cyhalothrin	0.118	No MRL	No MRL
9.	Chlorpyriphos	0.026	No MRL	Below
	Quinalphos	0.292	Above	No MRL
	Profenophos	0.018	No MRL	No MRL
10.	Chlorpyriphos	0.019	No MRL	Below
	Quinalphos	1.123	Above	No MRL
	Profenophos	0.182	No MRL	No MRL
	Triazophos	0.836	No MRL	No MRL
	Lambda cyhalothrin	0.578	No MRL	No MRL
	Cypermethrin	0.065	No MRL	Below

* LOD (OC : 0.005 $\mu g\ g^{-1}$, OP and SP : 0.01 $\mu g\ g^{-1}$), ** LOQ (OC, OP and SP : 0.05 $\mu g\ g^{-1}$)

Table 25. Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Vandanmedu during November 2011

Sample No	Pesticides Detected	Residue ($\mu g\ g^{-1}$)	PFA MRL Status	Codex MRL Status
1.	Not Detected	-	-	-
2.	Not Detected	-	-	-
3.	Profenophos	0.218	No MRL	No MRL
	Lambda cyhalothrin	1.672	No MRL	No MRL
	Cypermethrin	0.176	No MRL	Above
4.	Alpha endosulfan	0.007	Below	Below
	Profenophos	0.367	No MRL	No MRL
	Beta endosulfan	0.006	Below	Below
	Endosulfan sulphate	0.017	Below	Below
	Lambda cyhalothrin	0.070	No MRL	No MRL
	Cypermethrin	0.685	No MRL	Above
5.	Chlorpyriphos	0.032	No MRL	Below
	Quinalphos	0.062	Above	No MRL
	Alpha endosulfan	0.032	Below	Below
	Beta endosulfan	0.056	Below	Below
	Endosulfan sulphate	0.092	Below	Below
	Lambda cyhalothrin	1.331	No MRL	No MRL
6.	Chlorpyriphos	0.063	No MRL	Below
	Profenophos	0.336	No MRL	No MRL
	Lambda cyhalothrin	0.068	No MRL	No MRL
7.	Lambda cyhalothrin	0.049	No MRL	No MRL
8.	Alpha endosulfan	0.005	Below	Below
	Beta endosulfan	0.036	Below	Below
	Lambda cyhalothrin	0.032	No MRL	No MRL
9.	Alpha endosulfan	0.026	Below	Below
	Profenophos	0.078	No MRL	No MRL
	Beta endosulfan	0.069	Below	Below
	Endosulfan sulphate	0.048	Below	Below
	Lambda cyhalothrin	0.026	No MRL	No MRL
	Cypermethrin	0.157	No MRL	Above
10.	Chlorpyriphos	0.095	No MRL	Below
	Alpha endosulfan	0.046	Below	Below
	Profenophos	0.243	No MRL	No MRL
	Beta endosulfan	0.092	Below	Below
	Endosulfan sulphate	0.092	Below	Below
	Lambda cyhalothrin	0.133	No MRL	No MRL
	Cypermethrin	0.055	No MRL	Below

* LOD (OC : 0.005 $\mu g\ g^{-1}$, OP and SP : 0.01 $\mu g\ g^{-1}$), ** LOQ (OC, OP and SP : 0.05 $\mu g\ g^{-1}$)

Table 26 Pesticide residues (μg g^{-1}) in cardamom collected from Vandanmedu during December 2011

Sample No	Pesticides Detected	Residue (μg g^{-1})	PFA MRL Status	Codex MRL Status
1.	Quinalphos	0.093	Above	No MRL
	Lambda cyhalothrin	0.016	No MRL	No MRL
2.	Chlorpyriphos	0.382	No MRL	Below
	Quinalphos	0.061	Above	No MRL
	Lambda cyhalothrin	0.036	No MRL	No MRL
	Cypermethrin	0.462	No MRL	Above
3.	Chlorpyriphos	0.017	No MRL	Below
	Quinalphos	0.086	Above	No MRL
	Profenophos	0.139	No MRL	No MRL
	Lambda cyhalothrin	0.042	No MRL	No MRL
	Cypermethrin	0.050	No MRL	Below
4.	Quinalphos	0.136	Above	No MRL
	Alpha endosulfan	0.088	Below	Below
	Profenophos	0.036	No MRL	No MRL
	Beta endosulfan	0.023	Below	Below
	Endosulfan sulphate	0.018	Below	Below
	Cypermethrin	0.034	No MRL	Below
5.	Chlorpyriphos	0.038	No MRL	Below
	Alpha endosulfan	0.060	Below	Below
	Profenophos	0.113	No MRL	No MRL
	Beta endosulfan	0.067	Below	Below
	Endosulfan sulphate	0.039	Below	Below
	Lambda cyhalothrin	0.056	No MRL	No MRL
	Cypermethrin	0.059	No MRL	Below
6.	Lambda cyhalothrin	0.346	No MRL	No MRL
	Cypermethrin	0.030	No MRL	Below
7.	Chlorpyriphos	0.265	No MRL	Below
	Quinalphos	0.162	Above	No MRL
	Lambda cyhalothrin	0.018	No MRL	No MRL
	Cypermethrin	0.553	No MRL	Above
8.	Chlorpyriphos	0.107	No MRL	Below
	Quinalphos	0.046	Above	No MRL
	Lambda cyhalothrin	0.013	No MRL	No MRL
	Cypermethrin	0.250	No MRL	Above
9.	Chlorpyriphos	0.053	No MRL	Below
	Quinalphos	0.817	Above	No MRL
	Profenophos	0.599	No MRL	No MRL
	Cypermethrin	0.214	No MRL	Above
10.	Chlorpyriphos	0.056	No MRL	Below
	Quinalphos	0.124	Above	No MRL
	Profenophos	0.077	No MRL	No MRL
	Bifenthrin	0.068	No MRL	No MRL
	Cypermethrin	0.144	No MRL	Above

* LOD (OC : 0.005 μg g^{-1}, OP and SP : 0.01 μg g^{-1}), ** LOQ (OC, OP and SP : 0.05 μg g^{-1})

Table 27. Pesticide residues (μg g^{-1}) in cardamom collected from Vandanmedu during January 2012

Sample No	Pesticides Detected	Residue (μg g^{-1})	PFA MRL Status	Codex MRL Status
1.	Quinalphos	0.826	Above	No MRL
	Alpha endosulfan	0.209	Below	Below
	Profenophos	0.011	No MRL	No MRL
	Fenpropathrin	0.093	No MRL	No MRL
2.	Quinalphos	0.200	Above	No MRL
	Endosulfan sulphate	0.099	Below	Below
3.	Alpha endosulfan	0.007	Below	Below
	Endosulfan sulphate	0.128	Below	Below
4.	Quinalphos	0.353	Above	No MRL
	Profenophos	0.017	No MRL	No MRL
5.	Not Detected		-	-
6.	Quinalphos	0.332	Above	No MRL
7.	Chlorpyriphos	0.017	No MRL	Below
	Profenophos	0.060	No MRL	No MRL
	Cypermethrin	0.025	No MRL	Below
8.	Not Detected		-	-
9.	Profenophos	0.029	No MRL	No MRL
10.	Quinalphos	0.121	Above	No MRL
	Beta cyfluthrin	0.124	No MRL	No MRL
	Fenvalerate	0.101	No MRL	No MRL

* LOD (OC : 0.005 μg g^{-1}, OP and SP : 0.01 μg g^{-1}), ** LOQ (OC, OP and SP : 0.05 μg g^{-1})

Table 28. Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Pooppara during August 2011

Sample No	Pesticides Detected	Residue ($\mu g\ g^{-1}$)	PFA MRL status	Codex MRL status
1.	Ethion	0.023	No MRL	Below
	Lambda cyhalothrin	0.407	No MRL	No MRL
2.	Lambda cyhalothrin	0.290	No MRL	No MRL
3.	Ethion	0.040	No MRL	Below
	Lambda cyhalothrin	0.210	No MRL	No MRL
	Cypermethrin	0.020	No MRL	Below
	Fenvalerate	0.020	No MRL	No MRL
4.	Chlorpyriphos	0.028	No MRL	Below
	Lambda cyhalothrin	0.335	No MRL	No MRL
5.	Ethion	0.049	No MRL	Below
	Lambda cyhalothrin	0.412	No MRL	No MRL
6.	Lambda cyhalothrin	0.436	No MRL	No MRL
7.	Ethion	0.021	No MRL	Below
	Lambda cyhalothrin	0.438	No MRL	No MRL
8.	Ethion	0.017	No MRL	Below
	Lambda cyhalothrin	0.585	No MRL	No MRL
	Fenvalerate	0.050	No MRL	No MRL
9.	Quinalphos	0.031	Above	No MRL
	Lambda cyhalothrin	0.512	No.MRL	No MRL
10.	Quinalphos	0.184	Above	No MRL
	Ethion	0.014	No MRL	Below

* LOD (OC : 0.005 $\mu g\ g^{-1}$, OP and SP : 0.01 $\mu g\ g^{-1}$), ** LOQ (OC, OP and SP : 0.05 $\mu g\ g^{-1}$)

Table 29. Pesticide residues (μg g^{-1}) in cardamom collected from Poopara during September 2011

Sample No.	Pesticides Detected	Residue (μg g^{-1})	PFA MRL status	Codex MRL status
1.	Quinalphos	0.093	Above	No MRL
	Profenophos	0.159	No MRL	No MRL
	Lambda cyhalothrin	0.059	No MRL	No MRL
	Cypermethrin	0.065	No MRL	Below
2.	Profenophos	0.292	No MRL	No MRL
	Lambda cyhalothrin	0.030	No MRL	No MRL
	Cypermethrin	0.148	No MRL	Above
3.	Profenophos	0.739	No MRL	No MRL
	Cypermethrin	0.068	No MRL	Below
4.	Quinalphos	0.039	Above	No MRL
	Profenophos	0.344	No MRL	No MRL
5.	Quinalphos	0.029	Above	No MRL
	Profenophos	0.035	No MRL	No MRL
	Lambda cyhalothrin	0.060	No MRL	No MRL
	Cypermethrin	0.071	No MRL	Below
6.	Quinalphos	0.028	Above	No MRL
	Lambda cyhalothrin	0.098	No MRL	No MRL
	Beta Cyfluthrin	0.087	No MRL	No MRL
	Cypermethrin	0.097	No MRL	Below
7.	Malathion	0.105	No MRL	Below
	Beta Cyfluthrin	0.118	No MRL	No MRL
	Cypermethrin	0.019	No MRL	Below
8.	Lambda cyhalothrin	0.642	No MRL	No MRL
	Cypermethrin	0.017	No MRL	Below
9.	Quinalphos	0.046	Above	No MRL
	Lambda cyhalothrin	0.036	No MRL	No MRL
	Cypermethrin	0.247	No MRL	Above
10.	Quinalphos	0.030	Above	No MRL

* LOD (OC : 0.005 μg g^{-1}, OP and SP : 0.01 μg g^{-1}), ** LOQ (OC, OP and SP : 0.05 μg g^{-1})

Table 30 Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Poopara during October 2011

Sample No	Pesticides Detected	Residue ($\mu g\ g^{-1}$)	PFA MRL Status	Codex MRL Status
1.	Methyl parathion	0.045	No MRL	Below
	Chlorpyriphos	0.066	No MRL	Below
	Quinalphos	0.581	Above	No MRL
	Alpha endosulfan	0.022	Below	Below
	Beta endosulfan	0.039	Below	Below
	Endosulfan sulphate	0.026	Below	Below
	Lambda cyhalothrin	0.106	No MRL	No MRL
	Cypermethrin	0.192	No MRL	Above
2.	Methyl parathion	0.025	No MRL	Below
	Chlorpyriphos	0.080	No MRL	Below
	Quinalphos	0.634	Above	No MRL
	Profenophos	0.138	No MRL	No MRL
	Lambda cyhalothrin	0.109	No MRL	No MRL
	Cypermethrin	0.168	No MRL	Above
3.	Malathion	3.121	No MRL	Above
	Chlorpyriphos	0.042	No MRL	Below
	Quinalphos	0.296	Above	No MRL
	Ethion	0.188	No MRL	Below
	Lambda cyhalothrin	0.229	No MRL	No MRL
	Cypermethrin	0.272	No MRL	Above
4.	Chlorpyriphos	0.023	No MRL	Below
	Quinalphos	0.224	Above	No MRL
	Profenophos	1.087	No MRL	No MRL
	Cypermethrin	0.203	No MRL	Above
5.	Quinalphos	1.402	Above	No MRL
	Lambda cyhalothrin	0.023	No MRL	No MRL
6.	Quinalphos	1.163	Above	No MRL
	Profenophos	0.109	No MRL	No MRL
	Cypermethrin	0.164	No MRL	Above
7.	Profenophos	0.241	No MRL	No MRL
	Lambda cyhalothrin	0.045	No MRL	No MRL
8.	Chlorpyriphos	0.014	No MRL	Below
	Quinalphos	0.091	Above	No MRL
	Alpha endosulfan	0.010	Below	Below
	Beta endosulfan	0.002	Below	Below
	Lambda cyhalothrin	0.025	No MRL	No MRL
	Cypermethrin	0.218	No MRL	Above
9.	Quinalphos	0.452	Above	No MRL
	Cypermethrin	0.239	No MRL	Above
10.	Chlorpyriphos	0.124	No MRL	Below
	Quinalphos	0.249	Above	No MRL
	Lambda cyhalothrin	0.070	No MRL	No MRL

* LOD (OC : 0.005 $\mu g\ g^{-1}$, OP and SP : 0.01 $\mu g\ g^{-1}$), ** LOQ (OC, OP and SP : 0.05 $\mu g\ g^{-1}$)

Table 31. Pesticide residues (μg g^{-1}) in cardamom collected from Poopara during November 2011

Sample No	Pesticides Detected	Residue (μg g^{-1})	PFA MRL Status	Codex MRL Status
1.	Chlorpyriphos	0.106	No MRL	Below
	Quinalphos	0.360	Above	No MRL
	Lambda cyhalothrin	0.060	No MRL	No MRL
	Cypermethrin	0.078	No MRL	Below
2.	Chlorpyriphos	0.052	No MRL	Below
	Quinalphos	0.504	Above	No MRL
	Profenophos	0.026	No MRL	No MRL
	Ethion	0.014	No MRL	Below
	Lambda cyhalothrin	0.039	No MRL	No MRL
	Cypermethrin	0.015	No MRL	Below
3.	Chlorpyriphos	0.133	No MRL	Below
	Quinalphos	0.354	Above	No MRL
	Ethion	0.057	No MRL	Below
	Lambda cyhalothrin	0.024	No MRL	No MRL
	Cypermethrin	0.122	No MRL	Above
4.	Quinalphos	0.666	Above	No MRL
	Lambda cyhalothrin	0.089	No MRL	No MRL
5.	Chlorpyriphos	0.066	No MRL	Below
	Quinalphos	0.231	Above	No MRL
	Endosulfan sulphate	0.026	Below	Below
	Lambda cyhalothrin	0.017	No MRL	No MRL
	Cypermethrin	0.033	No MRL	Below
6.	Chlorpyriphos	0.042	No MRL	Below
	Quinalphos	0.481	Above	No MRL
	Lambda cyhalothrin	0.058	No MRL	No MRL
7.	Chlorpyriphos	0.033	No MRL	Below
	Quinalphos	0.480	Above	No MRL
	Endosulfan sulphate	0.056	Below	Below
	Lambda cyhalothrin	0.100	No MRL	No MRL
	Beta cyfluthrin	0.030	No MRL	No MRL
	Cypermethrin	0.037	No MRL	Below
8.	Chlorpyriphos	0.012	No MRL	Below
	Quinalphos	0.296	Above	No MRL
	Lambda cyhalothrin	0.018	No MRL	No MRL
9.	Chlorpyriphos	0.081	No MRL	Below
	Quinalphos	0.587	Above	No MRL
	Profenophos	0.052	No MRL	No MRL
	Lambda cyhalothrin	0.251	No MRL	No MRL
	Cypermethrin	0.088	No MRL	Below
10.	Chlorpyriphos	0.044	No MRL	Below
	Quinalphos	0.500	Above	No MRL
	Lambda cyhalothrin	0.055	No MRL	No MRL

* LOD (OC : 0.005 μg g^{-1}, OP and SP : 0.01 μg g^{-1}), ** LOQ (OC, OP and SP : 0.05 μg g^{-1})

Table 32. Pesticide residues (μg g^{-1}) in cardamom collected from Poopara during December 2011

Sample No	Pesticides Detected	Residue (μg g^{-1})	PFA MRL Status	Codex MRL Status
1.	Chlorpyriphos	0.050	No MRL	Below
	Quinalphos	0.614	Above	No MRL
	Alpha endosulfan	0.006	Below	Below
	Profenophos	0.495	No MRL	No MRL
	Beta endosulfan	0.012	Below	Below
	Lambda cyhalothrin	0.082	No MRL	No MRL
2.	Quinalphos	0.402	Above	No MRL
	Lambda cyhalothrin	0.115	No MRL	No MRL
3.	Methyl parathion	0.095	No MRL	Below
	Chlorpyriphos	0.174	No MRL	Below
	Alpha endosulfan	0.005	Below	Below
	Profenophos	0.021	No MRL	No MRL
	Beta endosulfan	0.015	Below	Below
	Lambda cyhalothrin	0.046	No MRL	No MRL
4.	Chlorpyriphos	0.248	No MRL	Below
	Alpha endosulfan	0.021	Below	Below
	Profenophos	1.340	No MRL	No MRL
	Beta endosulfan	0.054	Below	Below
	Ethion	0.176	No MRL	Below
	Cypermethrin	0.904	No MRL	Above
5.	Alpha endosulfan	0.037	Below	Below
	Profenophos	0.186	No MRL	No MRL
	Beta endosulfan	0.113	Below	Below
	Endosulfan sulphate	0.125	Below	Below
	Lambda cyhalothrin	0.057	No MRL	No MRL
	Cypermethrin	0.282	No MRL	Above
6.	Methyl parathion	0.322	No MRL	Below
	Chlorpyriphos	0.105	No MRL	Below
	Alpha endosulphan	0.088	Below	Below
	Profenophos	0.725	No MRL	No MRL
	Beta endosulfan	0.245	Below	Below
	Endosulfan sulphate	0.344	Below	Below
	Cypermethrin	0.148	No MRL	Above
7.	Chlorpyriphos	0.243	No MRL	Below
	Beta endosulfan	0.036	Below	Below
	Lambda cyhalothrin	1.502	No MRL	No MRL
	Cypermethrin	0.498	No MRL	Above
8.	Chlorpyriphos	0.027	No MRL	Below
	Alpha endosulfan	0.049	Below	Below
	Beta endosulfan	0.133	Below	Below
	Endosulfan sulphate	0.027	Below	Below
9.	Chlorpyriphos	0.111	No MRL	Below
	Lambda cyhalothrin	0.210	No MRL	No MRL
10.	Methyl parathion	0.172	No MRL	Below
	Profenophos	0.010	No MRL	No MRL
	Lambda cyhalothrin	0.137	No MRL	No MRL

* LOD (OC : 0.005 μg g^{-1}, OP and SP : 0.01 μg g^{-1}), ** LOQ (OC, OP and SP : 0.05 μg g^{-1})

Table 33 . Pesticide residues (μg g^{-1}) in cardamom collected from Poopara during January 2012

Sample No	Pesticides Detected	Residue (μg g^{-1})	PFA MRL status	Codex MRL Status
1.	Alpha endosulfan	0.008	Below	Below
	Endosulfan sulphate	0.061	Below	Below
	Cypermethrin	0.147	No MRL	Above
2.	Methyl parathion	0.083	No MRL	Below
	Quinalphos	0.060	Above	No MRL
3.	Quinalphos	0.180	Above	No MRL
4.	Not Detected	-	-	-
5.	Quinalphos	0.018	Above	No MRL
6.	Lambda cyhalothrin	0.260	No MRL	No MRL
	Cypermethrin	0.015	No MRL	Below
7.	Cypermethrin	0.109	No MRL	Above
8.	Quinalphos	0.188	Above	No MRL
	Endosulfan sulphate	0.067	Below	Below
9.	Quinalphos	0.068	Above	No MRL
10.	Not Detected	-	-	-

* LOD (OC : 0.005 μg g^{-1}, OP and SP : 0.01 μg g^{-1}), ** LOQ (OC, OP and SP : 0.05 μg g^{-1})

of 0.018- 0.188 µg g^{-1} and all the values were above MRL. Alpha Endosulfan, lambda cyhalothrin and methyl parathion were detected in one sample each at a level of 0.008, 0.260 and 0.083 µg g^{-1}. Cypermethrin was detected in three samples (0.015-0.147µg g^{-1}), of which two were above Codex MRL. Endosulfan sulphate detected in two samples (0.061 and 0.067 µg g^{-1}) and the values were below PFA and Codex MRL.

4.4 Effect of curing on removal of residues

The results of the field study conducted to assess the effect of curing process is presented below.

4.4.1. Effect of curing process on removal of residues of quinalphos from cardamom capsules

The mean residues of quinalphos was 3.26, 2.55, 1.94 and 1.85 µg g^{-1} in cardamom before curing at 2, 24, 72 and 120 hours after spraying (HAS) respectively. However, the mean residues of quinalphos on cured samples of cardamom at 2, 24, 72 and 120 HAS was 6.23, 4.77, 3.22 and 2.98 µg g^{-1} respectively. The processing factor of quinalphos on 2, 24, 72 and 120 HAS was 1.90, 1.86, 1.65 and 1.60 respectively. The highest percentage removal of residues was on 120 HAS (67.78) followed by 72 (66.8), 24 (62.59) and 2 HAS (61.78).

4.4.2 Effect of curing process on removal of residues of chlorpyriphos from cardamom capsules

The mean initial deposit of chlorpyriphos in the fresh capsules was 3.11, 1.91, 0.967 and 0.70 µg g^{-1} at 2, 24, 72 and 120 HAS respectively. On the other hand, the mean residues of chlorpyriphos in the cured cardamom capsules were 4.63, 2.50, 1.21 and 0.817 µg g-1 at 2, 24, 72 and 120 HAS respectively.

The processing factor of chlorpyriphos in cardamom was 1.48 at 2 HAS, 1.31 at 24 HAS, 1.25 at 72 HAS and 1.17 at 120 HAS. Curing process removed residues of chlorpyriphos to the tune of 70.23 %, 73.82 %, 74.97 % and 76.66 % at 2, 24, 72 and 120 HAS respectively.

4.4.3 Effect of curing process on removal of residues of triazophos from cardamom capsules

The mean level of residues of triazophos in fresh cardamom capsules was 3.93, 3.8, 3.32 and 3.01 µg g^{-1} at 2, 24, 72 and 120 HAS respectively and the corresponding values in cured samples were 9.90, 8.85, 7.54 and 6.77 µg g^{-1}. Processing factor for triazophos on 2, 24, 72 and 120 HAS were 2.51, 2.33, 2.27 and 2.25 respectively. The percentage removal of triazophos residues as a result of curing process was 49.62, 53.42, 54.58 and 55.02 at 2, 24, 72 and 120 HAS.

4.4.4 Effect of curing process on removal of residues of lambda cyhalothrin from cardamom capsules

The mean level of residues of lambda cyhalothrin in the fresh capsules were 0.73, 0.64, 0.60 and 0.57 µg g^{-1} at 2, 24, 72 and 120 HAS. On the other hand, the residue level of l ambda cyhalothrin in the cured cardamom capsules were 3.17, 2.56, 1.84 and 1.71 µg g-1 at 2, 24, 72 and 120 HAS respectively.The processing factor of lambda cyhalothrin in cardamom was 4.34 at 2 HAS whereas at 24 HAS it was reduced to 4.02. Corresponding values at 72 and 120 HAS were 3.06 and 3.01 respectively. The percentage removal of residues at2, 24, 72 and 120 HAS were 13.15, 20, 38.67 and 40 respectively.

4.4.5 Effect of curing process on removal of residues of cypermethrin from cardamom capsules

The mean residues of cypermethrin in the fresh cardamom capsules at 2, 24, 72 and 120 HAS were 0.40, 0.35, 0.34 and 0.30 µg g^{-1} respectively. After curing process, the mean level of residues were 0.691, 0.580, 0.550 and 0.484 µg g^{-1} at 2, 24, 72 and 120 HAS respectively. Processing factor of cypermethrin in cardamom was 1.71, 1.67, 1.63 and 1.62 respectively at 24, 72 and 120 HAS. Residues of cypermethrin was removed to the extent of 65.71% at 2 HAS as a result of curing. Curing process removed the residues of cypermethrin to the tune of 66.47% at 24 HAS. The extent of removal of residues at 72 and 120 HAS were 67.36 and 67.63 percentages respectively.

4.4.6 Effect of curing process on removal of residues of imidacloprid from cardamom capsules

The mean initial deposit of imidacloprid in fresh capsules of cardamom was 0.402, 0.325, 0.282 and 0.115 μg g^{-1} at 2, 24, 72 and 120 HAS respectively. In cured cardamom capsules, the mean level of residues at 2 HAS was 0.487 μg g-1 and the corresponding values at 24, 72 and 120 HAS were 0.386, 0.330 and 0.130 μg g^{-1} respectively. Processing factor of imidacloprid at 2, 24, 72 and 120 HAS was 1.21, 1.18. 1.16 and 1.12 respectively. Curing process removed the residues of imidacloprid to a considerable extent of 75.76 %, 76.23 %, 76.63 % and 77.32 % respectively at 2, 24, 72 and 120 HAS.

Table 34. Effect of curing on removal of residues of quinalphos in cardamom capsules

Hours after spraying	Mean residues before curing (µg g-1)	Moisture content (%)	Mean residues after curing (µg g-1)	Mean residues on cured samples on fresh weight basis (µg g-1)	Processing factor	Percentage removal of residues (%)
2	3.26	80	6.23	1.25	1.90	61.78
24	2.55	80	4.77	0.95	1.86	62.59
72	1.94	80	3.22	0.64	1.65	66.8
120	1.85	80	2.98	0.6	1.60	67.78

Table 35. Effect of curing on removal of residues of chlorpyriphos in cardamom capsules in cardamom

Hours after spraying	Mean residues before curing (µg g-1)	Moisture content (%)	Mean residues after curing (µg g-1)	Mean residues on cured samples on fresh weight basis (µg g-1)	Processing factor	Percentage removal of residues (%)
2	3.11	80	4.63	0.93	1.48	70.23
24	1.91	80	2.5	0.5	1.31	73.82
72	0.97	80	1.21	0.24	1.25	74.97
120	0.7	80	0.82	0.16	1.17	76.66

Table 36. Effect of curing on removal of residues of triazophos in cardamom capsules in cardamom

Hours after spraying	Mean residues before curing (µg g-1)	Moisture content (%)	Mean residues after curing (µg g-1)	Mean residues on cured samples on fresh weight basis (µg g-1)	Processing factor	Percentage removal of residues (%)
2	3.93	80	9.9	1.98	2.51	49.62
24	3.8	80	8.85	1.77	2.33	53.42
72	3.32	80	7.54	1.51	2.27	54.58
120	3.01	80	6.77	1.35	2.25	55.02

Table 37. Effect of curing on removal of residues of Lambda cyhalothrin in cardamom capsules in cardamom

Hours after spraying	Mean residues before curing (µg g-1)	Moisture content (%)	Mean residues after curing (µg g-1)	Mean residues on cured samples on fresh weight basis (µg g-1)	Processing factor	Percentage removal of residues (%)
2	0.73	80	3.17	0.63	4.34	13.15
24	0.64	80	2.56	0.51	4.02	20
72	0.6	80	1.84	0.37	3.06	38.67
120	0.57	80	1.71	0.34	3.01	40

Table 38. Effect of curing on removal of residues of cypermethrin in cardamom capsules in cardamom

Hours after spraying	Mean residues before curing (µg g-1)	Moisture content (%)	Mean residues after curing (µg g-1)	Mean residues on cured samples on fresh weight basis (µg g-1)	Processing factor	Percentage removal of residues (%)
2	0.4	80	0.69	0.14	1.71	65.71
24	0.35	80	0.58	0.12	1.67	66.47
72	0.34	80	0.55	0.11	1.63	67.36
120	0.3	80	0.48	0.1	1.62	67.63

Table 39. Effect of curing on removal of residues of imidacloprid in cardamom capsules in cardamom

Hours after spraying	Mean residues before curing (µg g-1)	Moisture content (%)	Mean residues after curing (µg g-1)	Mean residues on cured samples on fresh weight basis (µg g-1)	Processing factor	Percentage removal of residues (%)
2	0.4	80	0.49	0.1	1.21	75.76
24	0.33	80	0.39	0.08	1.19	76.23
72	0.28	80	0.33	0.07	1.16	76.63
120	0.12	80	0.13	0.03	1.12	77.32

Table 40. Pesticide residues (µg g^{-1}) in cardamom collected from Udumbanchola during August 2011- October 2011

Pesticides detected	Aug-11		Sep-11		Oct-11	
	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)
Alpha endosulfan	0		1	0.002	0	
Beta Endosulfan	0		3	0.003-0.01	0	
Beta Cyfluthrin	0		0		0	
Bifenthrin	0		0		0	
Chlorpyriphos	0		4	0.021-0.12	5	0.012-0.204
Cypermethrin	10	0.028-0.674	7	0.068-0.095	10	0.032-0.231
Endosulfan sulphate	0		4	0.012-0.02	0	
Ethion	0		3	0.008-0.157	0	
Fenpropathrin	0		0		2	0.043-0.079
Fenvalerate	0		0		0	
Lambda cyhalothrin	5	0.346-1.733	5	0.064-1.103	6	0.01-0.065
Malathion	0		1	0.042	0	
Methyl parathion	0		0		1	0.24
Profenophos	0		10	0.043-6.193	4	0.059-0.674
Quinalphos	10	0.033-0.164	7	0.053-1.879	9	0.045-0.45
Triazophos	3	0.028-1.156	0		0	

Discussion

5. DISCUSSION

India accounts for the largest area under cardamom at the global level, but the productivity is very low compared to other major producing countries (Thomas and Kuruvila, 2007). Cardamom is susceptible to an array of pests and diseases, which cause significant crop loss. Investigations carried out to study the pesticide use pattern, pesticide consumption in cardamom plantations of Idukki district, monitoring the level of pesticide residues in cardamom are discussed hereunder. Studies on validation of multiresidue method for estimation of residues and the effect of curing on the removal of residues from cardamom are also discussed below.

5.1 Development of database on pesticide use pattern in cardamom plantations of Idukki district

The current agricultural practices for intensive cardamom production which involve deliberate maintenance of the ecosystem in a nutrient rich state has resulted in the wide spread incidence of pests and diseases in cardamom which warranted application of pesticides to the status of an inevitable agricultural operation in the Indian Cardamom Hills. Hence an attempt was made to study the pesticide use pattern in cardamom in Idukki district.

Based on the productivity of cardamom in the cardamom hills of Idukki district, three zones in decreasing order of productivity *viz.* A- zone comprising of Vandanmedu, B-zone comprising of Udumbanchola and C-zone comprising of Poopara were selected for the development of the database on pesticide use pattern in cardamom plantations. Ten farmers were selected randomly from each location making a total sample size of 30. A detailed field investigation was carried out with the help of a questionnaire.

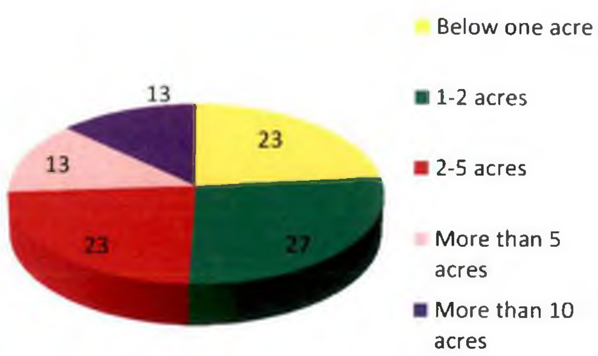
Data on average holding size of farmers revealed that 27 per cent possessed one to two acres, 23 per cent each possessed below one acre and two to five acres whereas 13 per cent each possessed more than five and ten acres of land. Regarding the educational status of the planters, it was revealed that 40 per cent of the farmers were educated below matriculation level only. However, remaining 60 per cent were having an education status from matriculation to post graduation. About 90 per cent of the farmers consider cardamom shoot and capsule borer (*Conogethes punctiferalis* Guen.) and 10 per cent consider cardamom thrips (*Sciothrips cardamomi* Ramk.) as major pests of cardamom. The present study revealed that out of the 30 farmers surveyed 93 per cent followed prophylactic spraying of insecticides rather than the remedial measures and only 7 per cent followed integrated pest management strategies. Most of them were experienced farmers and hence they followed their own spraying schedules and doses. The respondents of the survey used fungicides as well as insecticides in higher quantities than herbicides. Farmers depend largely on synthetic chemical pesticides. None of the respondents used any botanical for pest control. Farmers justify the use of chemical insecticides as their rapid action on crop pests and their easy availability in the local market. Organophosphorous insecticides were preferred by most of the respondents though they do not have any information on the chemical nature, persistence and properties of the applied pesticides. The indiscriminate use of broad spectrum synthetic pesticides resulted in reduction of biodiversity, outbreak of secondary pests, development of pesticide resistance, pesticide-induced resurgence and contamination of food and the ecosystem (Singh, 2000). For the management of these major pests of cardamom, lionshare pesticides are occupied by organophosphorous insecticides like quinalphos, triazophos, monocrotophos, chlorpyriphos and profenophos. Synthetic pyrethroids like lambda cyhalothrin, beta cyfluthrin, fenvalerate *etc.* are also used for pest control. Even though new generation insecticides like imidacloprid, thiacloprid flubendiamide *etc.* were available in the pesticide shops, farmers were totally ignorant about their importance. They still rely upon the traditional organophosphate and synthetic pyrethroid compounds. About 26.66 per cent of the farmers still use endosulfan which reveals that in spite of its ban during 2001, it is still being used in Kerala. They purchased it from neighboring state like Tamil Nadu. Thus the impact of ban of endosulfan in Kerala in cardamom hills had only negligible effect, because of the easy availability from the neighboring state of Tamil Nadu. The use of a single insecticide was found to be ineffective during a high pest infestation period and the respondents were found mixing two or more insecticides either of the same chemical group or different groups. Several insecticides were used in rotation and among fungicides, carbendazim and bordeaux mixture are widely used.

The study has revealed that majority of farmers follow their own spraying schedules (53 %) and doses for pest and disease control and 70 per cent of farmers used power sprayer for application of pesticides. Only 3 per cent of the farmers visited krishi bhavans for technical information regarding crop protection. The dosages used by the planters are 4 - 6 folds higher than the Package of Practices Recommendations of Kerala Agricultural University. Regarding the dosage of pesticides, most of the farmers are of the opinion that the recommended doses of pesticides in the POP are ineffective in controlling the pests and diseases. About 99 per cent of the planters are unaware of the active ingredients of these plant protection chemicals and it was not a matter of concern for them. Majority of the planters use their own experience as well as the instructions from the pesticide retailers/dealers for pest management. Cent per cent of the planters are unaware of the Central Insecticide Board and Registration committee recommendations. It was observed that restricted use pesticides (RUP) like monocrotophos and methyl parathion are popular and available in many regions of Idukki district during the period of study. Monocrotophos is an organophosphorous systemic insecticide extremely toxic to birds and poisonous to mammals. All applications of this chemical were discontinued in the US since 1998 (Devi, 2010). In India it is banned for use in vegetables. Similarly methyl parathion also has been included in the list of chemicals permitted for restricted use in India by CIB-RC.

As the prices of cardamom are soaring, farmers are using pesticides indiscriminately as their main aim is to produce cardamom capsules with good appearance. The need of the hour is production of quality cardamom without pesticide residues, as importing countries such as Japan have already rejected cardamom containing residues of triazophos and profenophos. Japan was the steady and reliable market for cardamom and was importing 30 to 40 % of the total export from India (Thomas and Kuruvila, 2007). In addition, the indiscriminate uses of plant protection chemicals are wiping out the populations of natural enemies leading to pest outbreaks and resurgence (Shetty, 2000). It was found that the gap between two consecutive pesticide sprayings has narrowed to 15-30 days, compared with 50-60 days in the 1970s and 1980s. The interval between two successive sprayings is dependant upon the pest load as well as the persistence of the chemical used. In rain fed condition, seven rounds of insecticide spraying starting from February to December and under irrigated condition nine rounds of spraying was the optimum spray schedule as per the recommendation of spices board. Overall comparison of the three regions shows that 57 per cent of the respondents spray insecticides at 30 days interval. About 23 per cent of respondents spray at fortnightly intervals and the remaining 20 per cent at 40 days interval.

As cardamom is cultivated in vast areas, farmers employ laborers for carrying out the plant protection operations. Most of them were natives of Tamil Nadu with very low economic and educational status and the planters are not directly involved in spraying operations. Majority of the respondents (57 %) were aware of some health hazards due to the injudicious use of pesticides to a negligible extent. Regarding the adoption of safety measures while spraying, 66 per cent are not adopting any safety precautions while handling these chemicals, 17 per cent each wear mask or gloves while spraying. About 60 per cent of the respondents point outs the reason for non adoption of any safety precautions while handling plant protection of chemicals as inconvenience while spraying, 30 per cent as ignorance and the rest 10 per cent as additional cost. The results of a study conducted by Grace *et al.*, (2006) among 631 farmers of Thanjavur district the following acute signs and symptoms are reported, excessive sweating (36.5 %), burning/stinging/itching of eyes (35.7 %), dry/sore throat (25.5 %) and excessive salivation (14.1 %). According to the Directorate of plant protection, quarantine and storage, Faridabad, in 1996 and 1999, the number of pesticide related poisoning cases and deaths in the country was about 15,500 and 7,500 respectively (Shetty, 2000).

The direct health impacts to spray men on repeated pesticide exposure were collected during the survey. Most of the respondents (60 %) experienced headache and dizziness. Dermal diseases on exposure to pesticides were another important health hazard. Another health problems faced by the pesticide spray men was stomach pain and general weakness. The expression of unscientific handling of pesticides in agriculture in terms of the direct impact on human health is published by state department of health on status of pesticide poisoning in human beings for the period from 1998- 99 to 2006-07. The study revealed that careless storage and disposal of pesticide containers often lead to unintentional poisoning. The farm workers who enter immediately after the spraying also get exposed. Occupational poisoning occurs due to an expose during the handling and spraying operations by the farm workers and the traders who sell it. The occupational exposure data show only 16 cases in 2003-04, seven cases in 2004-05 and two cases in 2005-06. Taking into account the possibility of under reporting of poisoning cases is quiet high; this data can only be taken with some caution and perhaps can be considered as the lower bound of the actual value. Study conducted by Rakhesh (1999) indicated that the pesticide poisoning led to both explicit and implicit costs for the applicator/farmer, which could be considered as a health cost. Majority of farmers (60 %) were reported to be suffering from health problems caused by pesticides. Among the health hazards induced by pesticide, skin allergy and headache were most prominent in Kuttanad (Krishna, 2001). Similar studies conducted by Mohan (2012), reveals that headache and dizziness were the main problem for majority (43.3 %) of the respondents in Kuttanad. Dermal disorders on exposure to pesticides were another important health



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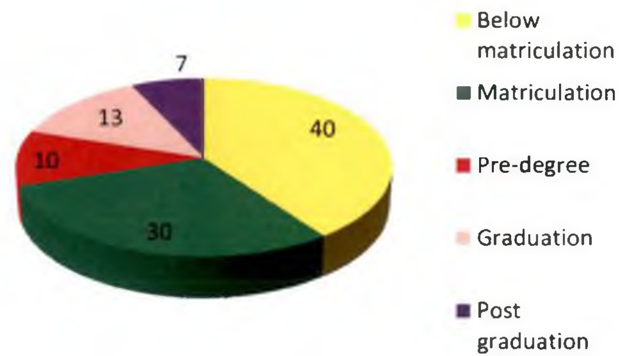
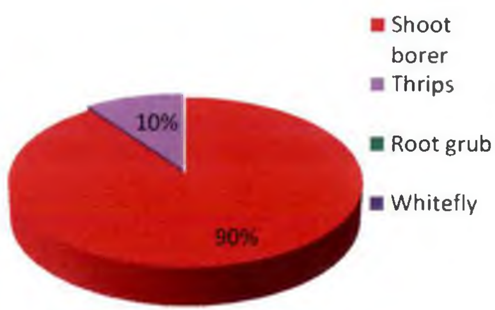
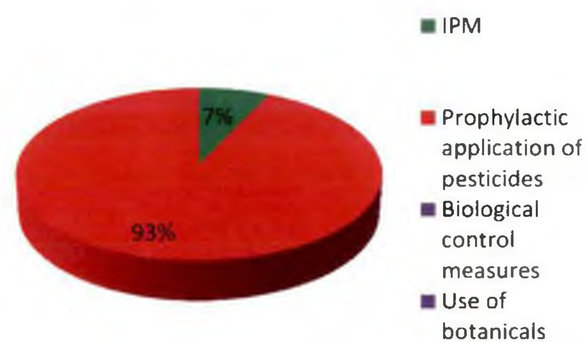


Educational status

Fig 29. Socio economic status of the farmers in the study region (Idukki district)

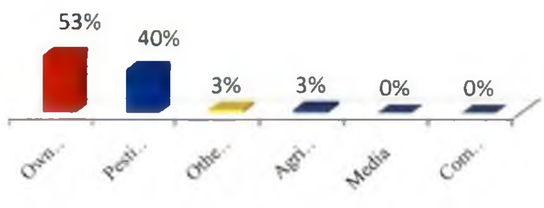


Major pests

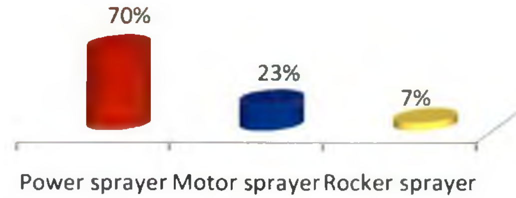


Pest management strategies

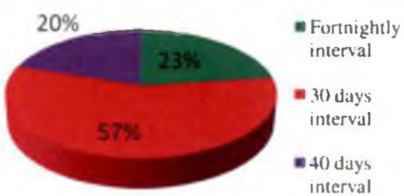
Fig 30. Major pests and management strategies followed in the study region



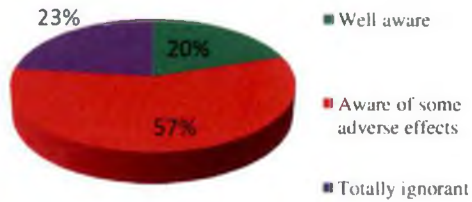
Source of technical information



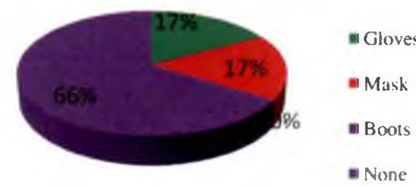
Type of sprayer used



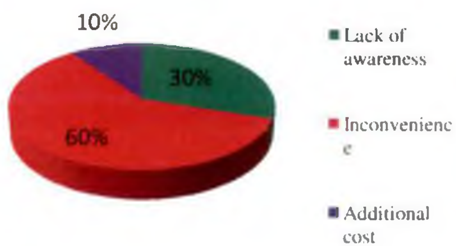
Frequency of application of pesticides



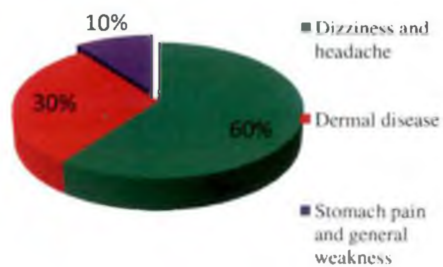
Awareness regarding adverse effects of pesticides



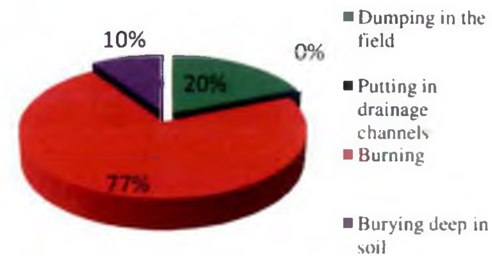
Adoption of safety measures while spraying



Reasons for non-adoption of safety measures



Adverse health effect experienced



Disposal of pesticide containers

Fig 31. Information on pesticide use in cardamom plantations in Idukki district hazard. Among 60 farmers, 28.33 per cent were suffering from dermal disorders. During long periods of pesticide application, unconsciousness occurred in case of 3.33 per cent of spray men.

5.2 Method validation

Method validation is an important requirement in the practice of chemical analysis (Holcombe, 1998). By means of validation procedure, the performance of test method is investigated systematically (Morkowski, 1996). There are several key parameters for ensuring the suitability of the method like recovery, selectivity, calibration, repeatability, reproducibility, limit of detection (LOD) and limit of quantification (LOQ). Developing sensitive and reliable analytical methods incorporating validation parameters such as repeatability, reproducibility and quality parameters such as precision, linearity and detection limits capable of detecting pesticides at very low levels is an urgent requirement in chemical analysis especially in monitoring of pesticide residues in food and environmental samples to produce accurate and reproducible results. The acceptability of the validated method for general use is best evaluated on the basis of precision and accuracy of the result confirmed by repeat analysis in different replicates. (Garg *et al.*, 2009). Accordingly, performance can be compared with the previously posed requirements and the suitability of the test method established (Sherma and Beroza, 1980). Validation of multiresidue methods for pesticide residue analysis in cardamom was done as per single laboratory validation approach of Thompson *et al.* (2002) to standardise a procedure for the extraction of pesticides from cardamom using different solvents/solvent systems. Three methods *viz.* CDFA method, QuEChERS method and modified QuEChERS were tried with 22 pesticide molecules at five different fortification levels *viz.* 1, 0.50, 0.10, 0.05 and 0.01 $\mu g\ g^{-1}$ and the results of which are discussed below.

In CDFA method, all the 22 compounds were detected at the higher two levels of 1µg g^{-1} and 0.50 µg g^{-1} only. Even then the recovery percentages were not satisfactory and compounds exhibited wide variation in per cent recovery. At 0.10 µg g^{-1} only five compounds *viz.* phorate, lindane, delta HCH and PP DDT were detected while three compounds were detected at 0.05 µg g^{-1}. None of the compounds was detected at the fortification level of 0.01 µg g^{-1}. Low recovery percentages, wide variation in the recovery among the pesticides were the important factors which made this method unsuitable for the multiresidue estimation of pesticides from cardamom. In addition, none of the compounds was recovered at the lowest level. Considering all these factors it can be concluded that this method is not suitable for the residue estimation from cardamom.

The QuEChERS method was tried in which acetonitrile was used as the solvent. At 1µg g^{-1}, all the compounds were detected with the mean recovery percentages ranging from 60.56 to 112.84. At 0.5 µg g^{-1} level of fortification, mean recovery percentage varied from 44.85 to 121.84. At both levels, PP DDT showed the lowest recovery. The mean recovery percentage at 0.1 µg g^{-1} level varied from 19.28 to 83.28. The range of mean per cent recovery at 0.05 µg g^{-1} was 9.52- 61.20. At this level, PP DDT gave the lowest mean recovery of 9.52 per cent. At 1, 0.50, 0.10 and 0.05 µg g^{-1} levels phorate and PP DDT showed lower recovery values whereas compounds like chlorpyriphos, quinalphos, lambda cyhalothrin gave higher as well as more or less stable recovery values. At the lowest level of 0.01 µg g^{-1} only nine compounds were detected out of the 22 compounds spiked and the mean recovery ranged from 12.09-35.12 per cent.

The method was effective in extracting all the compounds at higher levels of fortification and the per cent recovery of some of the compounds are very low at the lower levels of fortification. In this method satisfactory recovery percentage was obtained for all the compounds except for p-p'- DDT and phorate with lower recovery percentage. It was found that the recovery declined at the lower levels of fortification of 0.05 μg g^{-1} and 0.01 μg g^{-1}. An obviously wide variation was there in the recovery percentage of different pesticides at the same level of fortification too, thus failing to offer a satisfactory recovery of all the compounds fortified. Hence this method was also not recommended for multiresidue extraction of pesticides from cardamom.

Another method with slight modifications in the QuEChERS method in which extraction using acetonitrile and chilled water was carried out. The method resulted in a the mean recovery percentage which ranged from 70 and 110. The mean recovery percentage of various compounds spiked at 1 μg g^{-1}, ranged from 83.46 to 106.65. This method gave satisfactory recovery of organochlorine and organophosphorous compounds and synthetic pyrethroids at 1 μg g^{-1} with RSD ranging from 3.3- 8.1. At 0.5 μg g^{-1}, the mean recovery percentage ranged from 80.64 to 106.92. All the compounds gave satisfactory recovery values and RSD values were < 20. At the fortification level of 0.1μg g^{-1}, the mean recovery values ranged between 81.50 to 110.00 per cent It gave satisfactory recovery values for OC, OP and SP compounds with RSD < 20. At 0.05 and 0.01 μg g^{-1} levels also out of the 22 compounds spiked, all were resolved with good recovery values. At both the levels all the compounds gave RSD < 20 and the mean recovery percentage ranged from 69.76- 97.53 and 84.43-116.07 for 0.05 and 0.01 μg g^{-1} respectively. A satisfactory recovery even at the lowest level of fortification coupled with minimal variation and acceptable RSD values together with the easiness are added advantages of the method. All these clearly demonstrate the superiority of the method over other two methods tried. Method validation was accomplished with good linearity and satisfactory recoveries (69.7–110%) were obtained with 22 pesticides at 1, 0.5, 0.1, 0.05 and 0.01 μg g^{-1} levels of fortification making this modified QuEChERS method a simple and cost-effective method for the routine detection and analysis of pesticides in cardamom samples.

5.3 Monitoring pesticide residues in cardamom capsules

Results of the monitoring study conducted in the three major cardamom growing zones *viz.* Vandanmedu, Udumbanchola and Poopara during August 2011- January 2012 are discussed below.

Out of the 180 samples analysed, 173 showed the presence of residues of various pesticides, whereas seven samples were free of residues. Among the total 180 samples, thirteen samples showed residues of a single pesticide while 160 samples showed residues of multiple pesticides. Monitoring of pesticide residues in cardamom capsules in the three locations revealed the presence of 16 different pesticide molecules *viz.* alpha endosulfan, beta endosulfan, beta cyfluthrin, bifenthrin, chlorpyriphos, cypermethrin, endosulfan sulphate, ethion, fenpropathrin, fenvalerate, lambda cyhalothrin, malathion, methyl parathion, profenophos, quinalphos and triazophos belonging to organochlorines (3), organophosphates (7) and synthetic pyrethroids (6). Among the different pesticides, quinalphos was the major contaminant in all the three locations. It was detected in 121 out of the 180 samples analysed from the three locations. This was followed by lambda cyhalothrin which was detected in 104 samples, cypermethrin in 100 and chlorpyriphos in 87 samples respectively. Profenophos, alpha endosulfan, beta endosulfan and endosulfan sulphate were detected in 64, 32, 30 and 33 samples respectively whereas ethion, methyl parathion and malathion were detected in 23, 22 and 10 samples respectively. Among the detected pesticides bifenthrin was found to be the least occured one which was detected in three samples. Fenpropathrin and triazophos were detected in four samples each whereas beta cyfluthrin and fenvalerate were detected in five samples each. The present finding on the occurrence of quinalphos residues is in agreement with Murugan *et al.*, 2011 who reported the occurrence of residues of quinalphos to the tune of 0.01 to 0.25ppm in 60 per cent of the cardamom samples collected from the planters of Indian cardamom hills. As seen in the present study, occurrence of alpha endosulfan, beta endosulfan, endosulfan sulphate, chlorpyriphos, profenophos and lambda cyhalothrin were also reported by the same authors. Considering the pesticide groups, it can be concluded that OP and SP compounds predominates over the OC compounds which is very similar to the pesticide use pattern in the study area.

The study revealed that, 67.22 per cent of the analysed samples contained residues of quinalphos, which indicates that about only 30 per cent of the cardamom samples were free of residues of quinalphos. Per cent contamination by cypermethrin and lambda cyhalothrin were 57.78 and 55.56 respectively. Chlorpyriphos and profenophos contaminated the samples to the extent of 48.33 per cent and 35.56 per cent respectively.

While analyzing the occurrence of residues of quinalphos in the three locations each month, it can be seen that maximum number of samples contained quinalphos residues in October, in which 27 samples were contaminated out of the 30 samples analysed. In September and November 20 samples each contained quinalphos residues. Least occurrence of quinalphos residues were found in the month of December. Coming to the extent of contamination with cypermethrin, maximum occurrence was recorded in September and October *ie.* 24 samples in these months contained cypermethrin residues. Least occurrence with residues was found in January where only 4 samples were detected with Cypermethrin residues. In the case of lambda cyhalothrin, October, November and December months the occurrence of residues were high. Here also least number of samples were detected with residues of lambda cyhalothrin in the month of January. Similar trend was observed in the case of chlorpyriphos where maximum contaminantion was noticed in the months of October, November and December. Here also least contamination was noticed in January. In general it can be concluded that October, November and December are the months were the detection of residues are in peak in the case of cypermethrin, lamda cyhalothrin and chlorpyriphos whereas quinalphos showed more or less similar pattern in all the six months.

Considering the samples detected with multiple residues as separate a total of 647 pesticides were detected from 180 samples, of which 182 were above

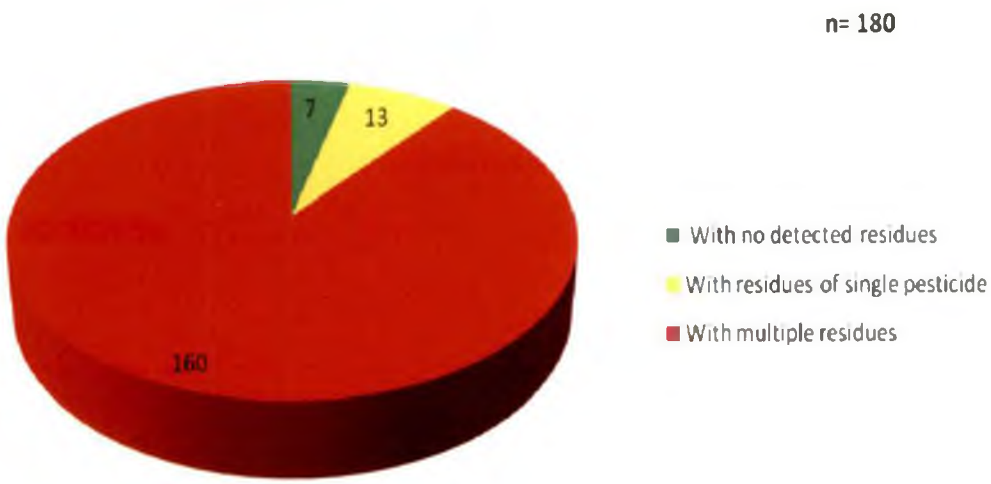


Fig 32. Extent of contamination of cardamom with pesticides in Idukki district

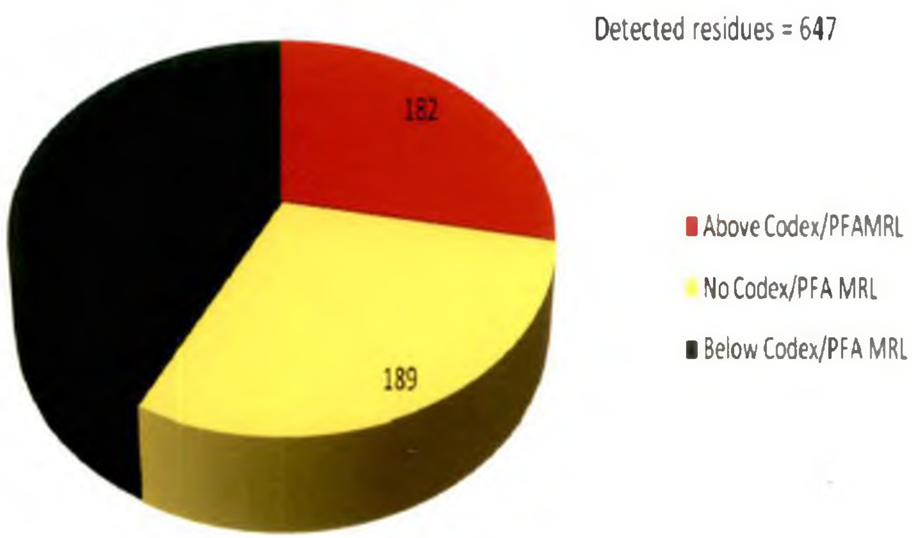


Fig 33. Pesticide contamination in cardamom in Idukki district with respect to MRL status

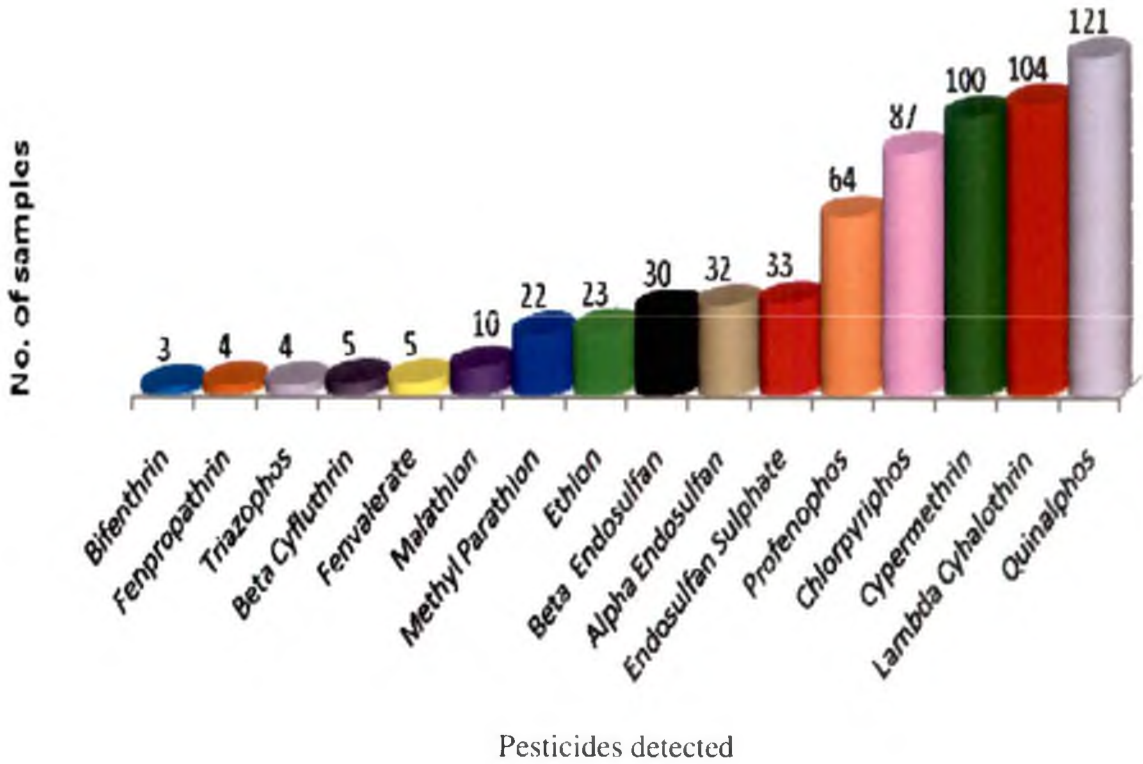


Fig 34. Pesticides detected in cardamom samples in Idukki district

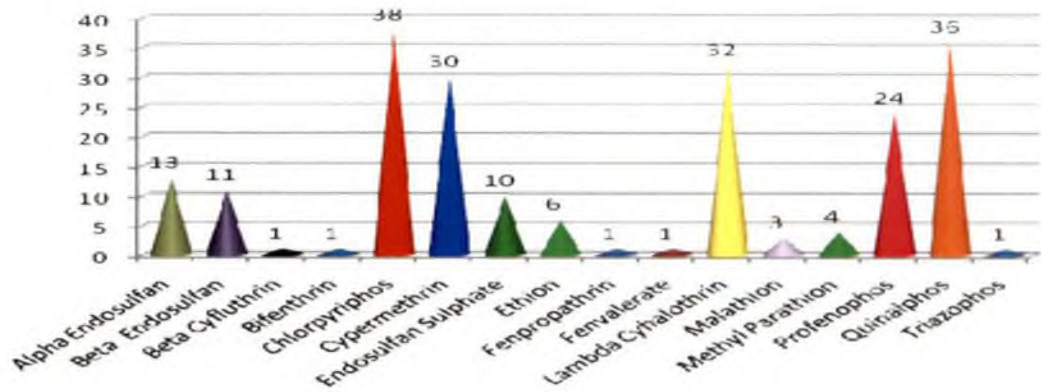


Fig 35. Occurance of pesticide residues in cardamom in Vandanmedu

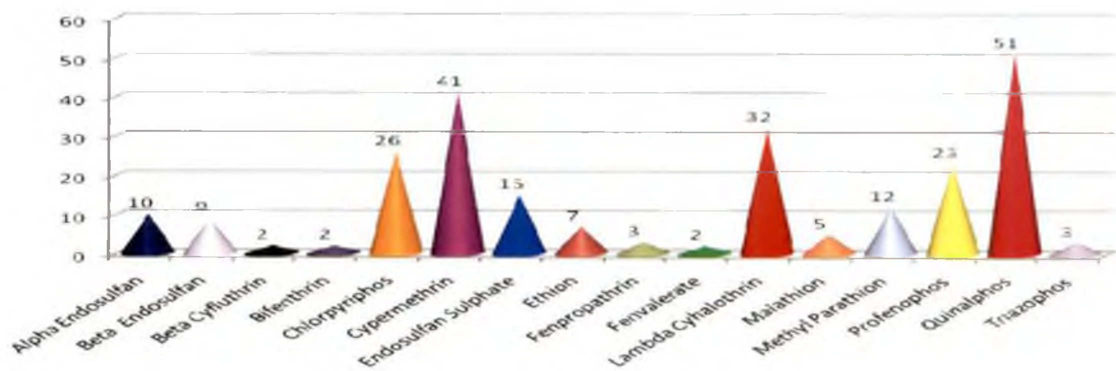


Fig 36. Occurance of pesticide residues in cardamom in Udumbanchola

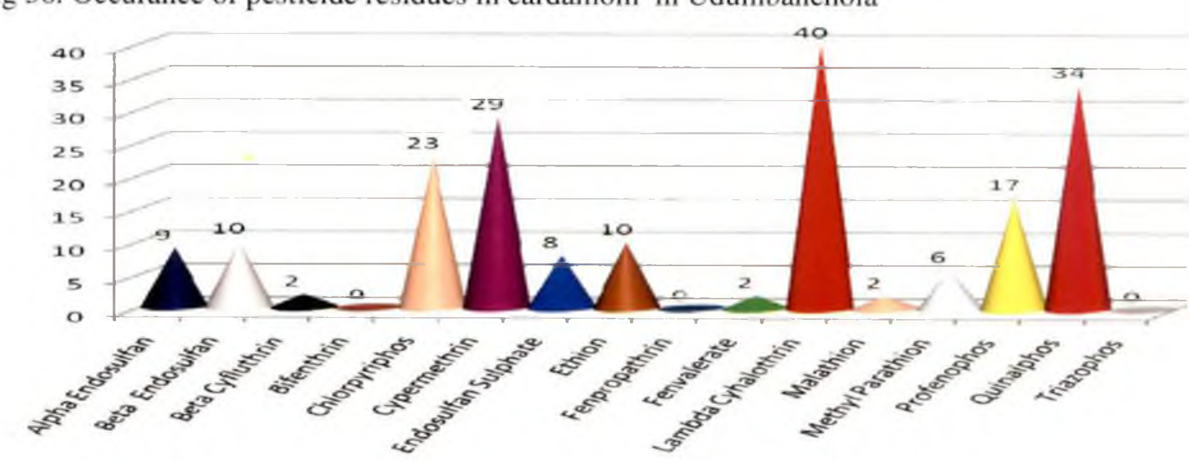


Fig 37. Occurance of pesticide residues in cardamom in Poopara

Table 41. Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Udumbanchola during during November 2011-January 2012

Pesticides detected	Nov-11		Dec-11		Jan-12	
	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)
Alpha endosulfan	0		6	0.011-1.415	3	0.007-0.01
Beta Endosulfan	0		6	0.011-0.372	0	
Beta Cyfluthrin	0		0		2	0.02-0.023
Bifenthrin	0		2	0.053-0.107	0	
Chlorpyriphos	10	0.028-0.251	5	0.018-0.21	2	0.005-0.018
Cypermethrin	8	0.024-0.24	6	0.046-0.205	0	
Endosulfan sulphate	3	0.027-0.031	3	0.019-0.231	5	0.026-0.053
Ethion	1	0.113	2	0.128-0.401	1	1.163
Fenpropathrin	0		1	0.133	0	
Fenvalerate	0		1	0.031	1	0.094
Lambda cyhalothrin	9	0.029-1.399	7	0.015-0.036	0	
Malathion	1	0.158	3	0.012-0.353	0	
Methyl parathion	2	0.028-0.062	6	0.024-0.417	3	0.097-0.137
Profenophos	1	0.043	5	0.038-0.222	3	0.01-0.034
Quinalphos	9	0.038-0.632	7	0.012-2.063	9	0.083-0.275
Triazophos	0		0		0	

Table 42 Pesticide residues (μg g^{-1}) in cardamom collected from Vandanmedu during August 2011-Ocober 2011

Pesticides detected	Aug-11		Sep-11		Oct-11	
	No of samples	Range (μg g-1)	No of samples	Range (μg g-1)	No of samples	Range (μg g-1)
Alpha endosulfan	0		3	0.004-0.01	1	0.056
Beta Endosulfan	0		3	0.008-0.014	1	0.05
Beta Cyfluthrin	0		0		0	
Bifenthrin	0		0		0	
Chlorpyriphos	9	0.002-0.459	8	0.013-0.184	10	0.015-0.091
Cypermethrin	0		9	0.019-0.643	7	0.023-0.309
Endosulfan sulphate	0		1	0.012	1	0.032
Ethion	1	0.026	3	0.087-0.33	2	0.098-0.135
Fenpropathrin	0		0		0	
Fenvalerate	0		0		0	
Lambda cyhalothrin	4	0.03-0.915	5	0.167-0.984	8	0.022-0.578
Malathion	1	0.412	2	0.109-0.191	0	
Methyl parathion	1	0.099	3	0.007-0.028	0	
Profenophos	0		5	0.004-0.318	5	0.008-0.182
Quinalphos	6	0.042-0.103	7	0.052-1.386	9	0.121-1.123
Triazophos	0		0		1	0.836

Table 43. Pesticide residues (µg g^{-1}) in cardamom collected from Vandanmedu during November 2011-January 2012

Pesticides detected	Nov-11		Dec-11		Jan-12	
	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)
Alpha endosulfan	5	0.005-0.046	2	0.060-0.088	2	0.007-0.209
Beta Endosulfan	5	0.006-0.092	2	0.023-0.067	0	
Beta Cyfluthrin	0		0		1	0.124
Bifenthrin	0		1	0.068	0	
Chlorpyriphos	3	0.032-0.095	7	0.017-0.382	1	0.017
Cypermethrin	4	0.055-0.685	9	0.03-0.553	1	0.025
Endosulfan sulphate	4	0.017-0.092	2	0.018-0.039	2	0.099-0.128
Ethion	0		0		0	
Fenpropathrin	0		0		1	0.093
Fenvalerate	0		0		1	0.101
Lambda cyhalothrin	8	0.026-1.672	7	0.013-0.346	0	
Malathion	0		0		0	
Methyl parathion	0		0		0	
Profenophos	5	0.078-0.367	5	0.036-0.599	4	0.011-0.06
Quinalphos	1	0.062	8	0.046-0.817	5	0.121-0.826
Triazophos	0		0		0	

Table 44. Pesticide residues (µg g^{-1}) in cardamom collected from Poopara during August 2011-Ocober 2011

Pesticides detected	Aug-11		Sep-11		Oct-11	
	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)
Alpha endosulfan	0		0		2	0.01-0.022
Beta Endosulfan	0		0		2	0.002-0.039
Beta Cyfluthrin	0		2	0.087-0.118	0	
Bifenthrin	0		0		0	
Chlorpyriphos	1	0.028	0		6	0.008-0.124
Cypermethrin	1	0.02	8	0.017-0.247	7	0.164-0.272
Endosulfan sulphate	0		0		1	0.026
Ethion	6	0.014-0.049	0		1	0.188
Fenpropathrin	0		0		0	
Fenvalerate	2	0.02-0.05	0		0	
Lambda cyhalothrin	9	0.21-0.585	6	0.03-0.642	7	0.005-0.229
Malathion	0		1	0.105	1	3.121
Methyl parathion	0		0		2	0.025-0.045
Profenophos	0		5	0.035-0.739	4	0.109-1.087
Quinalphos	2	0.031-0.184	6	0.028-0.093	9	0.091-1.402
Triazophos	0		0		0	

Table 45. Pesticide residues ($\mu g\ g^{-1}$) in cardamom collected from Poopara during November 2011-January 2012

Pesticides detected	Nov-11		Dec-11		Jan-12	
	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)	No of samples	Range (µg g-1)
Alpha endosulfan	0		6	0.005-0.088	1	0.008
Beta Endosulfan	1	0.003	7	0.012-0.245	0	
Beta Cyfluthrin	0		0		0	
Bifenthrin	0		0		0	
Chlorpyriphos	9	0.012-0.133	7	0.027-0.248	0	
Cypermethrin	6	0.015-0.122	4	0.148-0.904	3	0.015-0.147
Endosulfan sulphate	2	0.026-0.056	3	0.027-0.344	2	0.061-0.067
Ethion	2	0.014-0.057	1	0.176	0	
Fenpropathrin	0		0		0	
Fenvalerate	0		0		0	
Lambda cyhalothrin	10	0.017-0.251	7	0.046-1.502	1	0.26
Malathion	0		0		0	
Methyl parathion	0		3	0.095-0.322	1	0.083
Profenophos	2	0.026-0.052	6	0.01-1.34	0	
Quinalphos	10	0.231-0.666	2	0.402-0.614	5	0.018-0.188
Triazophos	0		0		0	

Table 46 – Occurrence of pesticides in cardamom collected from different locations in Idukki District.

Pesticides detected	Number of samples			
	Udumbanchola	Vandanmedu	Poopara	Total
Alpha endosulfan	10	13	9	32
Beta Endosulfan	9	11	10	30
Beta Cyfluthrin	2	1	2	5
Bifenthrin	2	1	0	3
Chlorpyriphos	26	38	23	87
Cypermethrin	41	30	29	100
Endosulfan sulphate	15	10	8	33
Ethion	7	6	10	23
Fenpropathrin	3	1	0	4
Fenvalerate	2	1	2	5
Lambda cyhalothrin	32	32	40	104
Malathion	5	3	2	10
Methyl parathion	12	4	6	22
Profenophos	23	24	17	64
Quinalphos	51	36	34	121
Triazophos	3	1	0	4

Table 47. Level of pesticides in cardamom in Idukki district with respect to Codex/PFA MRL

Pesticides detected	Number of samples			
	Analyzed	Detected	Above PFA/Codex MRL	No MRL
Alpha endosulfan	180	32	1	0
Beta Endosulfan	180	30	0	0
Beta Cyfluthrin	180	5	0	5
Bifenthrin	180	3	0	3
Chlorpyriphos	180	87	0	0
Cypermethrin	180	100	59	0
Endosulfan sulphate	180	33	0	0
Ethion	180	23	0	0
Fenpropathrin	180	4	0	4
Fenvalerate	180	5	0	5
Lambda cyhalothrin	180	104	0	104
Malathion	180	10	1	0
Methyl parathion	180	22	0	0
Profenophos	180	64	0	64
Quinalphos	180	121	121	0
Triazophos	180	4	0	4

PFA/Codex MRL whereas 276 were below PFA/Codex MRL The most ımportant thıng was that the remaınıng 189 do not have any Codex or PFA MRL Out of the 16 detected pestıcıdes beta cyfluthrın (5) bıfenthrın (3) fenpropathrın(4) fenvalerate (5) lambda cyhalothrın (104) profenophos (64) and trıazophos (4) were the pestıcıdes whıch do not have label claım ın cardamom So emphasıs should be gıven to fix MRL val ıes for these pestıcıdes ın cardamom

Most frequently occurrıng pestıcıdes *vız* quınalphos lambda cyhalothrın cypermethrın and chlorpyrıphos were predomınant ın Udumbanchola compared to the other locatıons where the extent of contamınatıon wıth these pestıcıdes were 51 32 31 and 26 respectıvely Maxımum occurrence wıth lambda cyhalothrın was notıced ın Poopara whereas Udumbanchola predommated ın the occurrence of quınalphos and cypermethrın Maxımum occurrence of chlorpyrıphos was recorded ın Vandanmedu Udumbanchola predomınates over Vandanmedu and Poopara wıth respect to the occurrence of pestıcıde resıdues

Chlorpyrıphos (38) was the most frequently occurrıng pestıcıde ın Vandanmedu followed by quınalphos (36) lambda cyhalothrın (32) cypermethrın (30) and profenophos(24) whereas quınalphos (51) was the most frequently occurrıng one ın Udumnchola, followed by cypermethrın (41) lambda cyhalothrın (32) chlorpyrıphos (26) and profenophos (23) In Poopara lambda cyhalothrın (40) takes the lead followed by quınalphos (34) cypermethrın (29) chlorpyrıphos (23) and profenophos(17)

5 4 Effect of curıng process on removal of resıdues of ınsectıcıdes ın cardamom capsules

To estımate the potentıal pestıcıde exposure from contamınated food ıt ıs ımportant to approxımate the level of exposure at the poınt of consumptıon after processmg It has already been reported that processıng such as washıng dryıng peelıng etc can reduce resıdue levels whıch further reduces the ımpact on human health (Abou arab 1999 Solıman 2001 Zohaır 2001) Each operatıon ın processıng has a cumulatıve effect on the reductıon of pestıcıdes present ın the produce Hence the study on effect of curing on removal of residues in cardamom is significant Cardamom curing is a process in which the moisture of freshly harvested capsule is reduced from 80 per cent to 10 to 12 per cent at an optimum temperature of 50 ^{0}C so as to retain green colour After drying polishing is done by rubbing against hard surface or using polishing machine There is every chance for removal of residues in each stage of processing of cardamom Hence studies were conducted to assess the extent of removal of residues of six pesticides viz quinalphos chlorpyriphos triazophos cypermethrin lambda cyhalothrin and imidacloprid Residues were estimated at intervals of 2 24 72 and 120 hours after spraying from both fresh and processed cardamom capsules

The mean level of residues of quinalphos m fresh pods at 2 24 72 and 120 hours after sampling were 3 26 2 55 2 94 and 1 82 µg g respectively The corresponding level of residues in cured cardamom were 6 23 4 77 3 22 and 2 98 µg g^{1} During the process of curing 75 78 per cent of the moisture got depleted which would have resulted in an accumulation of residues and a portion of residues would also have dissipated due to the effect of heat and rubbing Hence the level of residues in cured sample got magnified in the range of 1 60 1 90 The results obtained in the present study corroborated the findings of Pathan *et al* 2009 wherein the effect of processing on diss pation of residues of dicofol ethion and cypermethrin on chilli was reported with processing factor of 5 59 3 52 and 7 50 respectively The processing factor arrived in the present study lead to the conclusion that quinalphos at 0 05 per cent on cardamom followed by curing resulted in a mean initial deposit of 1 90 times more residues in cured pods This could be due to a relatively high resistance of the compound to degradation forces like prolonged exposure to high temperature as well as loss of moisture leading to lowering of the weight of the fresh product The residues in fresh product were estimated on fresh weight basis while that on cured product was estimated and expressed on dry weight basis Fresh cardamom conta ns around 75 80 per cent moisture and the dry yield of cardamom is generally in the range of 20 to 25 per cent Assuming a zero dissipation of the insecticide during curing the initial deposit after curing would have been 16 30 µg g In the present study initial deposit obtained in the cured produce was 6 23 µg g ^{1} indicating a lower residue than the maximum possible deposit The difference of the two corresponds to the residues lost during curing However the curing process in cardamom ultimately resulted in a magnification of residues in the final product which could be mainly due to the moisture loss during curing A similar trend is observed in the case of samples drawn at intervals of 24 72 and 120 HAS

In the case of chlorpyriphos the mean initial deposit of 3 11 µg g in fresh cardamom was magnified to the tune of 1 48 times resulting in 4 63 µg g in cured samples As in the case of quinalphos assuming a zero dissipation of the insecticide during curing the initial deposit after curing would have been 15 55 µg g In the present study initial deposit obtained in the cured produce was 4 63 µg g ^{1} which was much lower than the maximum possible and the per cent reduction due to curing being 70 23 A per cent reduction to the tune of 73 82 74 97 and 76 66 were seen in the subsequent intervals of sampling of 24 72 and 120 hours

In the case of triazophos the mean initial deposit of 3 93 µg g in fresh cardamom was magnified to the tune of 2 51 times resulting in 9 9 µg g ^{1} in cured samples Assuming a zero dissipation of the residue during curing the initial deposit after curing would have been 19 65 µg g In the present study initial deposit obtained in the cured produce was 9 90 µg g ^{1} which was much lower than the maximum possible and the per cent reduction due to curing being 49 62 A per cent reduction to the tune of 53 42 54 58 and 55 02 were seen in the subsequent intervals of sampling of 24 72 and 120 hours

On the contrary lambda cyhalothrin had a higher processing factor leading to lower rate of removal of residues Thus the mean initial deposit of 0 73 µg g in fresh cardamom was magnified to 4 34 times leading to 3 17 µg g ^{1} after curing process which would have been 3 65 µg g with out loss due to curing The removal of residues in subsequent intervals of 24 72 and 120 hours were 20 00 38 67 and 40 00 per cent respectively

In the case of cypermethrin the mean initial deposit of 0 40 µg g^{1} in fresh cardamom was magnified to the tune of 1 71 times resulting in 0 69 µg g in cured samples Assuming a zero dissipation of the residue during curing the initial deposit after curing would have been 2 00 µg g^{1} In the present study initial deposit obtained in the cured produce was 0 69 µg g^{1} which was much lower than the maximum possible and the per cent reduction due to curing being 65 71 A per cent reduction to the tune of 66 47 67 36 and 67 63 were seen in the subsequent intervals of sampling of 24 72 and 120 hours

In the case of imidacloprid the mean initial deposit of 0 40 µg g in fresh cardamom was magnified to the tune of 1 21 times resulting in 0 49 µg g^{1} in cured samples Assuming a zero dissipation of the residue during curing the initial deposit after curing would have been 2 00 µg g In the present study initial deposit obtained in the cured produce was 0 49 µg g^{1} which was much lower than the maximum possible and the per cent reduction due to curing being 75 76 A per cent reduction to the tune of 76 23 76 63 and 77 32 were seen in the subsequent intervals of sampling of 24 72 and 120 hours

The present study on Pesticide use pattern and monitoring of residues in cardamom in Idukki district revealed the indiscriminate use of pesticides for pest control in cardamom plantations in Idukki district Ninety per cent of the respondents adopt application of plant protection chemicals at 15 40 days interval using 32 different chemicals of which 25 are insecticides Majority of the farmers resort to the advice from the plant protection chemical dealers or follow their own experience for adopting the pest control strategies Only 10 per cent of the farmers adopt the recommendation from Agricultural Officers/ other technical source Ninety per cent of the respondents consider shoot & capsule borer as the most noxious pest while 10 per cent believe thrips as the most noxious one

Result of the monitoring of pesticide residues in cardamom samples revealed that out of 180 samples analyzed 173 were detected with pesticides of which 160 samples showed multiple residues Sixteen different pesticides were detected in samples among which quinalphos is the most predominant contaminant detected in 121 samples followed by lambda cyhalothrin cypermethrin and chlorpyriphos in 104 100 and 87 samples respectively Bifenthrin was the least predominant one and was detected in three samples

The presence of multiple residues in the samples led to the conclusion that altogether the incidence of pesticide residues in 182 occasions were above the MRL prescribed by PFA/ codex 272 below MRL and 189 did not have MRL values fixed in cardamom The presence of residues of pesticides which do not have MRL indicate the degree of misuse of unregistered pesticides Extensive training programmes should be conducted among farmers/ planters for creating proper awareness regarding judicious and scientific use of pesticides in cardamom

The situation also warrants the development and popularization Good Agricultural Practices(GAP) in cultivation of cardamom among the various stake holders to meet the export requirements and to build up their capabilities and enable them to be globally competitive for which evaluation of effectiveness of new generation insecticides having lower dosage and faster degradation should be taken up to bring up as recommendations for pest management in cardamom instead of the conventional pesticides Further effectiveness of those pesticides which are not having label claim in cardamom as on date should be studied and steps for label expansion may be taken up The combination products of newer molecules may also be evaluated for plant protection in cardamom especially from the point of view of minimizing the risk of resistance development in pest population

Summary

6 SUMMARY

Cardamom *Elettaria cardamomum* L Maton the produce of commerce is the dried ripe fruit (capsules of cardamom plant) and is often referred to as the Queen of Spices owing to its very pleasant aroma flavor taste and culinary characteristics It is used as an exquisite flavored spice all around the globe The Indian cardamom hills are considered one of the ideal geographically preferred location for intensive cardamom cultivation and biodiversity in the world One of the major constraints in the cultivation and production of cardamom is the excessive damage inflicted by insect pests and diseases At present these pests are kept under check with the help of synthetic insecticides Considering the number of rounds of pesticide sprays and quantity of pesticides used in cardamom one can rate cardamom as the highest pesticide consuming rainfed crop in the world Unscientific use of dangerously high levels of pesticides on cardamom plantations is hazardous to human health and environment and may result in several social problems in the fragile ecosystems of the Cardamom Hill Reserve At the same time the spurious use of pesticides has resulted in high levels of harvest time residues of pesticides in cardamom which is being rejected by the hitherto importing countries which in turn would have a major say in foreign exchange revenues Though the insecticides deposited by plant protection operations might be reduced during curing garbling and storage it is emphasized to have monitoring of pesticide residues in cardamom capsules before being exported

In this context an investigation was carried out to study the pesticide use pattern pesticide consumpt on in cardamom plantations of Idukki district and also to monitor the level of pesticide residues in cardamom A field survey was conducted in cardamom plantations of Idukki district to assess the pesticide use pattern A multiresidue method was validated for the estimation of the different pesticides in cardamom by trying different procedures The multiresidue method satisfying requirement of selectivity precision reproducibility accuracy linearity limit of detection limit of quantification was selected for the estimation of multiple residues in cardamom Cardamom samples were collected randomly from the three major cardamom growing zones for monitoring of pesticide residues for a period of six months from August 2011 to January 2012 The samples were analysed and the residues were estimated using GC ECD

A field experiment was conducted at Cardamom Research Station Pampadumpara to study the effect of curing process on removal of pesticide residues Six insecticides belonging to different pesticide groups were sprayed in triplicate in the experimental field Samples were drawn at 0 24 72 and 120 hours after sparying The samples were analysed and insecticide residues were estimated using GC and HPLC

The results are summarized below

1 The major pest infesting cardamom were shoot and capsule borer and cardamom thrips apart from root grub whitefly and nematode which cause significant loss to cardamom For the timely management of these pests farmers are following strict plant protection measures at an interval of 15 to 40 days with conventional insectic des Farmers are widely applying heavy doses of chemicals especially the organophosphorus insecticides like phorate chlorpyriphos quinalphos profenophos methyl parathion and synthetic pyrethroids like cypermethrin and lambda cyhalothrin

2 Around 32 plant protection chemicals are applied frequently to the crop of which 25 are insecticides six fungicides and one herbicide 2 4 D Among the insecticides major share is contributed by organophosphorus insecticides followed by synthetic pyrethroids and organochlorines Newer molecules are not that much popular among the farming community in the region

3 Majorıty of the farmers resort to prophylactıc sprayıng of plant protectıon chemıcals rather than remedıal Adoptıon of IPM strategıes are also neglıgıble Most of the farmers used theır own sprayıng schedules for pest management Some of them depended pestıcıde retaılers as a source of technıcal ınformatıon

4 The effıcıency of extractıon of multıresıdues of pestıcıdes from cardamom was standardızed through recovery experıments The modıfied QuEChERS method wıth extractıon usıng acetonıtrıle and chılled water was found to be the best method The analytıcal procedure gave good recovery for mutıresıdues 69 7 110 per cent from cardamom when spıked at 0 01 1 μg g A calıbratıon curve was drawn by plottıng dıfferent concentratıons (0 01 μg g 0 05 μg g 0 1 μg g^{1} 0 5 μg g 1 μg g) *vs* peak area Good lınearıty was found wıthın the range of 0 01 1 μg g concentratıon

5 Data on monıtorıng of pestıcıde resıdues ın cardamom samples collected from the study regıons for a perıod of sıx months revealed varyıng level of resıdues of several pestıcıdes Out of the total 180 samples analyzed resıdues were detected ın 173 samples and only seven samples were free of resıdues Out of the 173 samples detected wıth pestıcıde resıdues 160 contaıned multıple resıdues of pestıcıdes whereas only 13 contaıned resıdues of sıngle pestıcıde

6 Cardamom capsules contaıned resıdues of 16 dıfferent pestıcıde molecules belongıng to organochlorınes organophosphates and synthetıc pyrethroıds The most common contamınant was quınalphos whıch was detected ın 121 out of 180 samples analysed Other major contamınants ınclude lambda cyhalothrın (104) cypermethrın (100) chlorpyrıphos (87) and profenophos (64)

7 The level of resıdues of quınalphos ın all the samples were above PFA MRL Other resıdues of pestıcıdes detected above the PFA/Codex MRL were alpha endosulfan (1) cypermethrın (59) and malathıon (1)

8 Pesticides detected in cardamom which have no label claim in cardamom include Beta cyfluthrin (5) bifenthrin (3) fenpropathrin (4) fenvalerate (5) lambda cyhalothrin (104) methyl parathion (64) and triazophos (4)

9 Curing process removed the residues of pesticides at varying level Processing factor was worked out for each chemical Extent of removal of residues as a result of curing was quinalphos (61 78 67 78%) chlorpyriphos (70 23 76 66%) triazophos (49 62 55 02%) cypermethrin (65 71 67 63%) lambda cyhalothrin (13 15 40 00%) and imidacloprid (75 56 77 32%)

To conclude in the effort to develop Good Agricultural Practices (GAP) for the cultivation of cardamom the effectiveness of new generation insecticides which have lower dosage of application and faster degradation rate may be evaluated and brought up as recommendations for pest management m cardamom instead of conventional pesticides Further the effectiveness of those pesticides which are not having label claim on cardamom as on date may be studied and steps for label expansion may be taken up The effectiveness of combination products of newer insecticides may also be evaluated for plant protection in cardamom especially from the point of view of minimizing the risk of resistance development in the pest population

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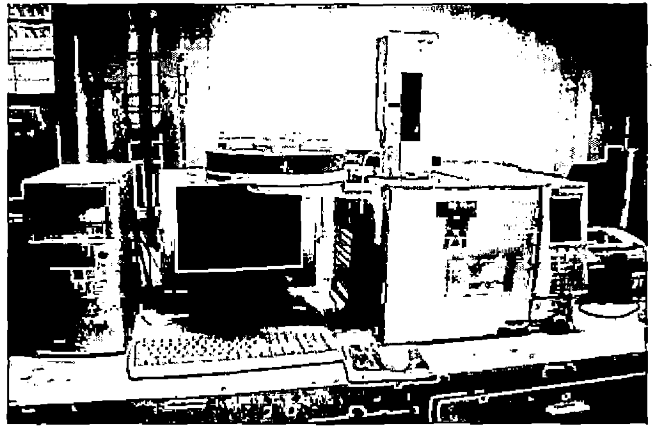
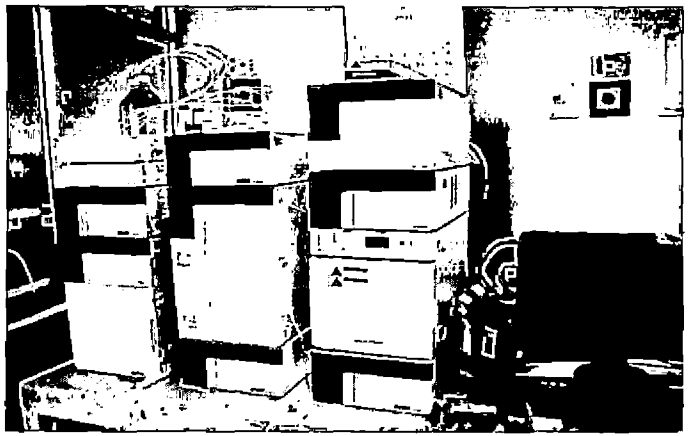
A. Sample extraction unit



B. Gas Chromatograph



C. High Performance Liquid Chromatograph

Plate 1. Infrastructure facilities availed for the study

A. Sample extraction unit

B. Gas Chromatograph

C. High Performance Liquid Chromatograph

Plate 1. Infrastructure facilities availed for the study

Appendices

AINP ON PESTICIDE RESIDUES VELLAYANI CENTRE
CSS on MPR at National Level ,COLLEGE OF AGRICULTURE, VELLAYANI,THIRUVANANTHAPURAM

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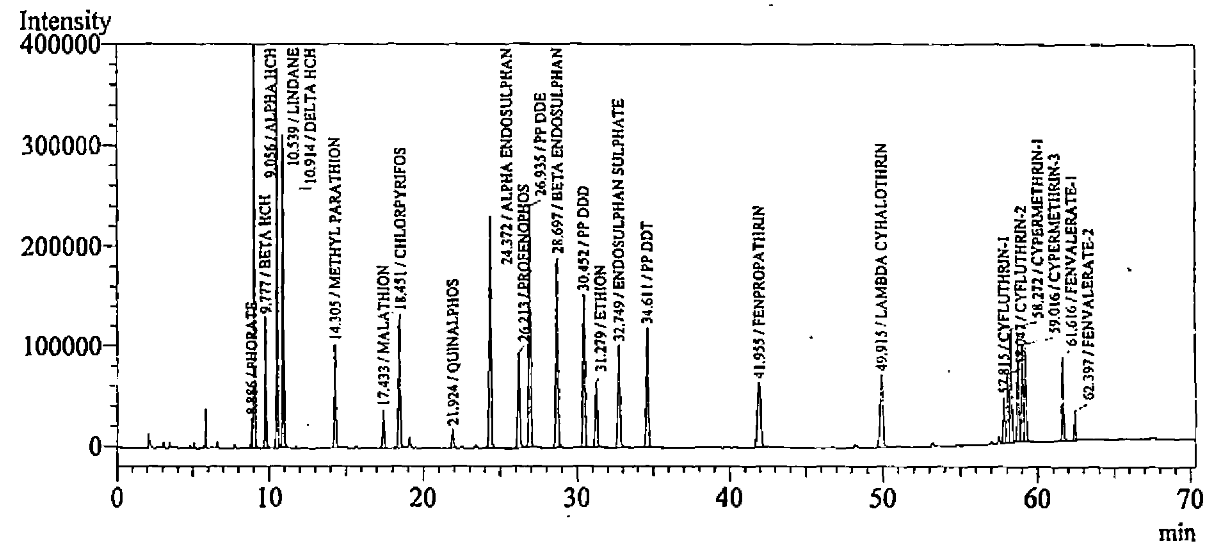

Quantitative Results - Channel 1

ID#	Name	Ret.Time	Area	Height	Conc.	Units
1	PHORATE	8.886	143594	29611	0.000	ppm
2	ALPHA HCH	9.056	2343796	511616	0.000	ppm
3	BETA HCH	9.777	725021	130175	0.000	ppm
4	LINDANE	10.539	1924954	377537	0.000	ppm
5	DELTA HCH	10.914	1739769	309335	0.000	ppm
6	METHYL PARATHION	14.305	673997	102764	0.000	ppm
7	MALATHION	17.433	284039	38068	0.000	ppm
8	CHLORPYRIFOS	18.451	974089	125280	0.000	ppm
9	QUINALPHOS	21.924	150584	18634	0.000	ppm
10	ALPHA ENDOSULPHAN	24.372	1874289	230896	0.000	ppm
11	PROFENOPHOS	26.213	859203	94261	0.000	ppm
12	PP DDE	26.935	1984146	240240	0.000	ppm
13	BETA ENDOSULPHAN	28.697	1649845	183056	0.000	ppm
14	PP DDD	30.452	1347283	152514	0.000	ppm
15	ETHION	31.279	594693	64384	0.000	ppm
16	ENDOSULPHAN SULPHATE	32.749	986594	102050	0.000	ppm
17	PP DDT	34.611	1058279	119128	0.000	ppm
18	FENPROPATHRIN	41.955	985654	64625	0.000	ppm
19	LAMBDA CYHALOTHRIN	49.915	924203	72453	0.000	ppm
20	CYFLUTHRIN-1	57.815	314176	45113	0.000	ppm
21	CYFLUTHRIN-2	58.047	476632	67291	0.000	ppm
22	CYPERMETHRIN-1	58.272	846803	113064	0.000	ppm
23	CYPERMETHRIN-2	58.723	774812	106181	0.000	ppm
24	CYPERMETHRIN-3	59.016	683556	96934	0.000	ppm
25	CYPERMETHRIN-4	59.221	601969	85566	0.000	ppm
26	FENVALERATE-1	61.616	538185	83558	0.000	ppm
27	FENVALERATE-2	62.397	178462	29180	0.000	ppm

AINP ON PESTICIDE RESIDUES VELLAYANI CENTRE
CSS on MPR at National Level ,COLLEGE OF AGRICULTURE, VELLAYANI,THIRUVANANTHAPURAM

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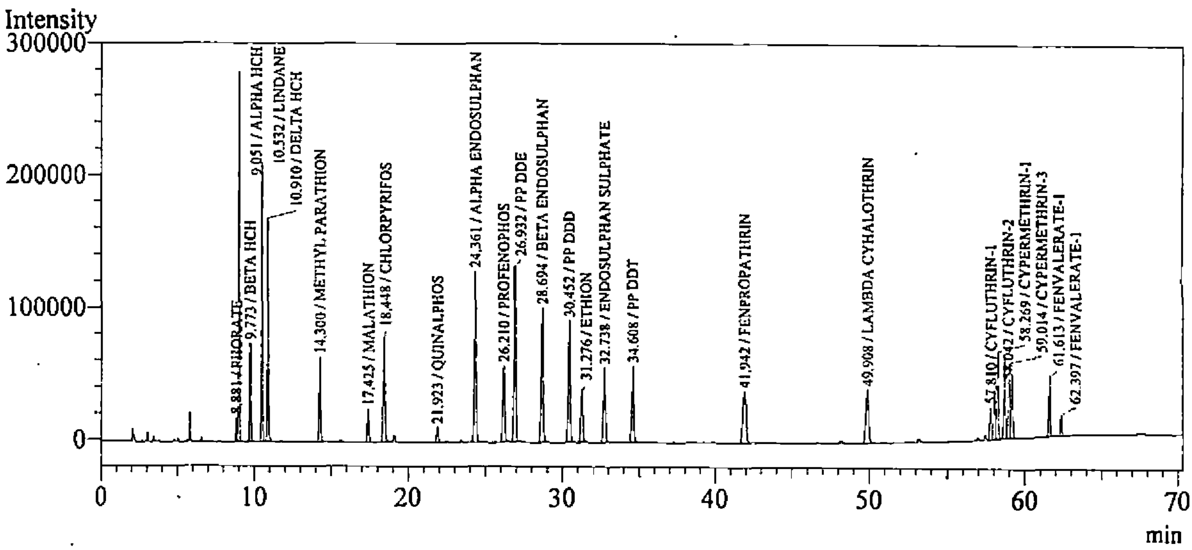

Quantitative Results - Channel 1

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1	PHORATE	8.881	85579	17844	0.000	ppm
2	ALPHA HCH	9.051	1266303	278888	0.000	ppm
3	BETA HCH	9.773	405508	73585	0.000	ppm
4	LINDANE	10.532	1044577	208982	0.000	ppm
5	DELTA HCH	10.910	934499	167671	0.000	ppm
6	METHYL PARATHION	14.300	418985	63743	0.000	ppm
7	MALATHION	17.425	177312	24613	0.000	ppm
8	CHLORPYRIFOS	18.448	590112	78504	0.000	ppm
9	QUINALPHOS	21.923	92375	11604	0.000	ppm
10	ALPHA ENDOSULPHAN	24.361	1027823	128750	0.000	ppm
11	PROFENOPHOS	26.210	495820	57179	0.000	ppm
12	PP DDE	26.932	1056771	132237	0.000	ppm
13	BETA ENDOSULPHAN	28.694	908291	101250	0.000	ppm
14	PP DDD	30.452	782630	91409	0.000	ppm
15	ETHION	31.276	358089	38782	0.000	ppm
16	ENDOSULPHAN SULPHATE	32.738	524889	55703	0.000	ppm
17	PP DDT	34.608	519431	57131	0.000	ppm
18	FENPROPATHRIN	41.942	587592	38700	0.000	ppm
19	LAMBDA CYHALOTHRIN	49.908	487606	40111	0.000	ppm
20	CYFLUTHRIN-1	57.810	166738	24259	0.000	ppm
21	CYFLUTHRIN-2	58.042	257969	37325	0.000	ppm
22	CYPERMETHRIN-1	58.269	476155	65648	0.000	ppm
23	CYPERMETHRIN-2	58.725	434650	62025	0.000	ppm
24	CYPERMETHRIN-3	59.014	379585	56144	0.000	ppm
25	CYPERMETHRIN-4	59.207	335085	48224	0.000	ppm
26	FENVALERATE-1	61.613	295211	44953	0.000	ppm
27	FENVALERATE-1	62.397	97130	16023	0.000	ppm

AINP ON PESTICIDE RESIDUES VELLAYANI CENTRE
CSS on MPR at National Level ,COLLEGE OF AGRICULTURE, VELLAYANI,THIRUVANANTHAPURAM

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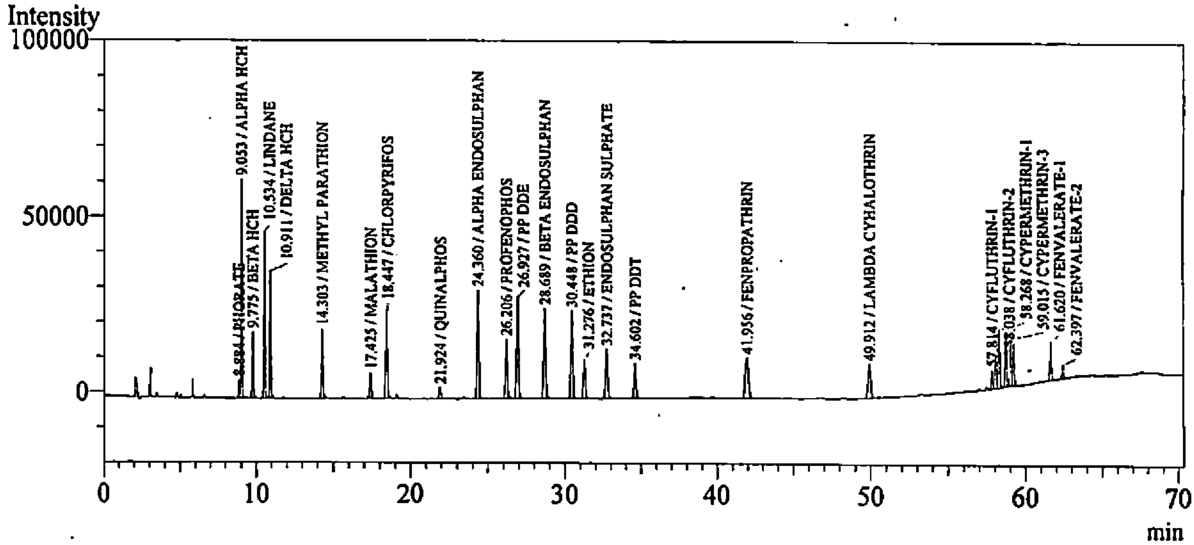

Quantitative Results - Channel 1

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1	PHORATE	8.884	24303	5227	0.000	ppm
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3	BETA HCH	9.775	101799	18975	0.000	ppm
4	LINDANE	10.534	230157	47617	0.000	ppm
5	DELTA HCH	10.911	192091	36151	0.000	ppm
6	METHYL PARATHION	14.303	126197	19605	0.000	ppm
7	MALATHION	17.425	47463	7066	0.000	ppm
8	CHLORPYRIFOS	18.447	178110	24876	0.000	ppm
9	QUINALPHOS	21.924	24057	3233	0.000	ppm
10	ALPHA ENDOSULPHAN	24.360	242556	30900	0.000	ppm
11	PROFENOPHOS	26.206	142495	16813	0.000	ppm
12	PP DDE	26.927	227436	28818	0.000	ppm
13	BETA ENDOSULPHAN	28.689	220004	25719	0.000	ppm
14	PP DDD	30.448	211190	24905	0.000	ppm
15	ETHION	31.276	102304	11125	0.000	ppm
16	ENDOSULPHAN SULPHATE	32.737	128459	13891	0.000	ppm
17	PP DDT	34.602	81837	9778	0.000	ppm
18	FENPROPATHRIN	41.956	164084	11471	0.000	ppm
19	LAMBDA CYHALOTHRIN	49.912	115861	9557	0.000	ppm
20	CYFLUTHRIN-1	57.814	35592	5385	0.000	ppm
21	CYFLUTHRIN-2	58.038	58458	8813	0.000	ppm
22	CYPERMETHRIN-1	58.268	116000	16604	0.000	ppm
23	CYPERMETHRIN-2	58.727	103980	15827	0.000	ppm
24	CYPERMETHRIN-3	59.015	86336	13240	0.000	ppm
25	CYPERMETHRIN-4	59.208	78264	12036	0.000	ppm
26	FENVALERATE-1	61.620	68110	10879	0.000	ppm
27	FENVALERATE-2	62.397	21239	3782	0.000	ppm

AINP ON PESTICIDE RESIDUES VELLAYANI CENTRE
CSS on MPR at National Level ,COLLEGE OF AGRICULTURE, VELLAYANI,THIRUVANANTHAPURAM

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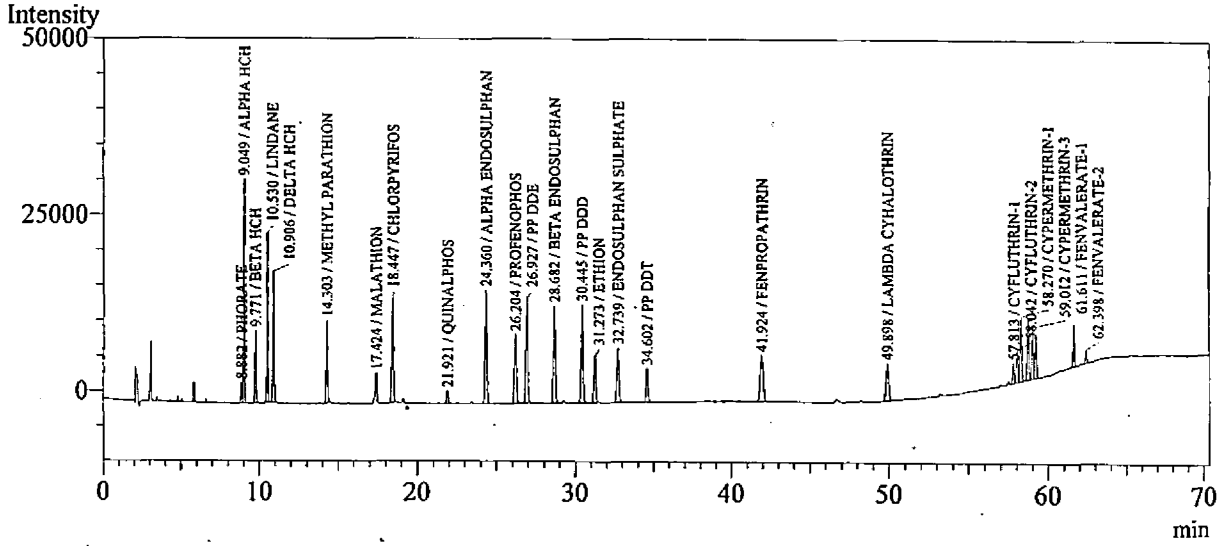

Quantitative Results - Channel 1

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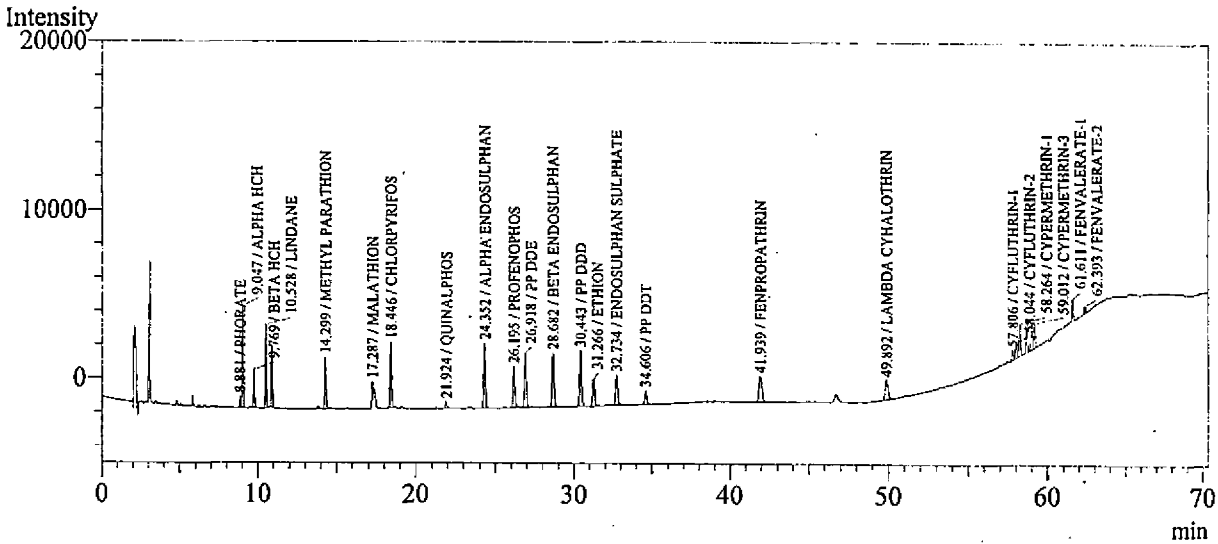
2	ALPHA HCH	9.049	134265	31557	0.000	ppm
3	BETA HCH	9.771	53155	10151	0.000	ppm
4	LINDANE	10.530	115178	24149	0.000	ppm
5	DELTA HCH	10.906	96026	18470	0.000	ppm
6	METHYL PARATHION	14.303	72349	11645	0.000	ppm
7	MALATHION	17.424	24083	3855	0.000	ppm
8	CHLORPYRIFOS	18.447	103975	14616	0.000	ppm
9	QUINALPHOS	21.921	13119	1842	0.000	ppm
10	ALPHA ENDOSULPHAN	24.360	130702	16072	0.000	ppm
11	PROFENOPHOS	26.204	81701	9695	0.000	ppm
12	PP DDE	26.927	117309	14943	0.000	ppm
13	BETA ENDOSULPHAN	28.682	118439	13737	0.000	ppm
14	PP DDD	30.445	115400	13775	0.000	ppm
15	ETHION	31.273	57406	6653	0.000	ppm
16	ENDOSULPHAN SULPHATE	32.739	70970	7768	0.000	ppm
17	PP DDT	34.602	41082	4810	0.000	ppm
18	FENPROPATHRIN	41.924	90901	6533	0.000	ppm
19	LAMBDA CYHALOTHRIN	49.898	61246	5304	0.000	ppm
20	CYFLUTHRIN-1	57.813	18905	2853	0.000	ppm
21	CYFLUTHRIN-2	58.042	30778	4623	0.000	ppm
22	CYPERMETHRIN-1	58.270	62008	9141	0.000	ppm
23	CYPERMETHRIN-2	58.722	57775	8480	0.000	ppm
24	CYPERMETHRIN-3	59.012	47714	7305	0.000	ppm
25	CYPERMETHRIN-4	59.210	42488	6256	0.000	ppm
26	FENVALERATE-1	61.611	36129	5886	0.000	ppm
27	FENVALERATE-2	62.398	11083	1875	0.000	ppm

AINP ON PESTICIDE RESIDUES VELLAYANI CENTRE
CSS on MPR at National Level ,COLLEGE OF AGRICULTURE, VELLAYANI,THIRUVANANTHAPURAM

User Name : Admin
Sample Name : OC+OS 0.01 ppm
Sample ID : OC+OS 0.01 ppm
Sample Type : Unknown
Injection Volume : 2.00
Data Name : D:\C of GC-2\SEENA\MV\25-08-2011\OC+OS 0-01 ppm.gcd
Method Name : D:\Fortification study\Fort method\pc cell methods-2.gcm



Quantitative Results - Channel 1

ID#	Name	Ret.Time	Area	Height	Conc.	Units
1	PHORATE	8.881	2789	664	0.000	ppm
2	ALPHA HCH	9.047	26623	6068	0.000	ppm
3	BETA HCH	9.769	11418	2275	0.000	ppm
4	LINDANE	10.528	23482	4917	0.000	ppm
5	DELTA HCH	10.906	19105	3650	0.000	ppm
6	METHYL PARATHION	14.299	18046	3030	0.000	ppm
7	MALATHION	17.287	5405	1032	0.000	ppm
8	CHLORPYRIFOS	18.446	25530	3867	0.000	ppm
9	QUINALPHOS	21.924	2704	386	0.000	ppm
10	ALPHA ENDOSULPHAN	24.352	29446	3854	0.000	ppm
11	PROFENOPHOS	26.195	19317	2402	0.000	ppm
12	PP DDE	26.918	25622	3208	0.000	ppm
13	BETA ENDOSULPHAN	28.682	26408	3147	0.000	ppm
14	PP DDD	30.443	27586	3283	0.000	ppm
15	ETHION	31.266	13530	1583	0.000	ppm
16	ENDOSULPHAN SULPHATE	32.734	15820	1777	0.000	ppm
17	PP DDT	34.606	6977	808	0.000	ppm
18	FENPROPATHRIN	41.939	20416	1513	0.000	ppm
19	LAMBDA CYHALOTHRIN	49.892	12881	1119	0.000	ppm
20	CYFLUTHRIN-1	57.806	3846	574	0.000	ppm
21	CYFLUTHRIN-2	58.044	6254	905	0.000	ppm
22	CYPERMETHRIN-1	58.264	12829	1927	0.000	ppm
23	CYPERMETHRIN-2	58.721	12337	1967	0.000	ppm
24	CYPERMETHRIN-3	59.012	9789	1510	0.000	ppm
25	CYPERMETHRIN-4	59.205	8820	1420	0.000	ppm
26	FENVALERATE-1	61.611	7341	1282	0.000	ppm
27	FENVALERATE-2	62.393	2088	390	0.000	ppm

APPENDIX II
PROFORMA FOR SURVEY ON PESTICIDE USE PATTERN IN CARDAMOM PLANTATIONS OF IDUKKI DISTRICT

Sl no.	Particulars	
1	Location	
	Block	
	Taluk	
	Panchayat	
2	Nam & Address of Farmer	
3	Age	
4	Education	
5	Size of holding(ha)	
6	Land Status	
a	Own Land	
b	Leased Land	
7	Cropping pattern	
8	Irrigation Status	
a	Irrigated	
b	Rainfed	
9	Average Yield (kg/ha)	
10	Annual income	
11	Soil Type	
12	Pesticide availability	
13	Source of technical information regarding crop protection	
a	Agriculture officers	
b	Company representatives	
c	Other progressive farmers	
d	Own decisions	
e	Media	
14	Cost for plant protection measures	
a	Cost of Chemicals	
b	Cost of Labour	
c	Total cost	

15	Is there any practice of manual mixing of pesticides and spraying?	
16	Any Changes in pest Scenario?	
17	Is there any prophylactic application of PP chemicals?	
18	Type of sprayer used	
19	Whether applying pesticides continuously for the last ten years. If withdrawn, when? And why?	
20	Whether it is possible to avoid pesticide application	Yes/No
21	Whether following integrated pest management strategies?	Yes/No
22	Practicing any biological control measures?	Yes/No
23	Applying any botanicals for pest management? If yes, which are they? Are they effective?	
24	Application of plant protection chemicals as per the recommendations of LAU or not.	Yes/No
25	Whether following the directions in the pesticide label during handling and application of pesticides?	Yes/No
26	Most frequently used	
a	Insecticide	
b	Fungicide	
c	Herbicide	
27	Habit of taking food, water, smoke or chew tobacco while spraying of pesticides	Yes/No
28	Time of application of pesticides	
a	Early Morning	
b	Morning	
c	Afternoon	
d	Evening	
29	Aware of the direction of wind while spraying effects of pesticides	Yes/No
30	Degree of awareness regarding the adverse health effects of pesticides	
a	Well aware	
b	Aware of some adverse health effects	
c	Totally ignorant	

31	Pesticide application by	
a	Himself	
b	Labour	
32	Type of clothing while spraying	
33	Safety precautions taken while spraying	
a	Use of gloves	
b	Wearing mask	
c	Wearing boots	
d	Nothing adopted	
34	Reasons for non-adoption of safety measures	
a		
b		
35	Method of disposal of pesticide containers	
a	Dumping in the field	
b	Putting in drainage channels	
c	Burning	
d	Burrying deep in soil	
36	Type of health hazard due to pesticide application	
a	Some irritation during the time of spraying	
b	Continuous coughing, difficulty to breathe, skin diseases etc.	
37	Cases of poisoning/death due to pesticide use	
38	Percentage increase in crop yield due to pesticide application	
39	Noticed incidence of pesticide resistance/resurgence? If yes, which pest? Against which pesticide?	

40 Details of major inspect pests and diseases and weeds:

Sl No.	Name of pest/disease/weeds		Percentage of yield dose
	Nursery	Mainfield	

41 Information regarding plant protection chemicals used

Sl No	Particulars of insecticide used			Particulars of fungicide used		
	Name of chemical	Aware of active ingredient	Dosage/Quantity applied	Name of chemical	Aware of active ingredient	Dosage/Quantity applied

Source of information: Cardamom farmers

PESTICIDE USE PATTERN AND MONITORING OF RESIDUES IN CARDAMOM IN IDUKKI DISTRICT

SEENA. S. M

(2009-11-119)

Abstract of the thesis submitted in partial fulfillment of the requirement

for the degree of

MASTER OF SCIENCE IN AGRICULTURE

Faculty of Agriculture

Kerala Agricultural University, Thrissur.

DEPARTMENT OF AGRICULTURAL ENTOMOLOGY

COLLEGE OF AGRICULTURE,

VELLAYANI, THIRUVANANTHAPURAM - 695 522

2013

ABSTRACT

The field survey conducted among the farmers of Idukki district revealed that major pest infesting cardamom were shoot and capsule borer and cardamom thrips For the timely management of these pests farmers are following strict plant protection measures at an interval of 15 to 40 days with conventional insecticides Farmers are widely applying heavy doses of chemicals especially the organophosphorus insecticides like phorate chlorpyriphos quinalphos profenophos methyl parathion and synthetic pyrethroids l ke cypermethrin and lambda cyhalothrin Majority of the farmers resort to prophylactic spraying of plant protection chemicals rather than remedial measures Adoption of IPM strategies are also negligible Most of the farmers used their own spraying schedules for pest management The pesticide use pattern in cardamom growing tracts of Idukki district shows that the farmers are applying plant protection chemicals aggressively and the liberal and continual use of pesticides has disturbing consequences on the ecosystem

In multiresidue mehod validation cardamom samples were spiked at five different levels *viz* 0 01 µg g^{1} 0 05 µg g^{1} 0 10 µg g^{1} 0 50 µg g^{1} and 1 µg g and extraction was carried out using various solvent/ solvent system and the modified QuEChERS method which gave 69 7 110% per cent recovery with RSD < 20 was selected and the same method was adopted for the estimation of pesticide residues from cardamom samples

In order to assess the residue level and to study the extent of contamination due to pesticides in cardamom samples were collected from the cardamom growing plantations of Idukki district Three major cardamom growing zones were selected namely Vandanmedu Udumbanchola and Poopara in Idukki district and ten samples were collected from each location for a period of six months Data on monitoring of pesticide residues m cardamom samples collected from the study regions for a period of six months revealed varying level of residues of several pesticides Out of the total 180 samples analyzed residues were detected in 173 samples and only seven samples

were free of residues Out of the 173 samples detected with pesticide residues 160 contained multiple residues of pest cides whereas only 13 contained residues of single pesticide Cardamom capsules contained residues of 16 different pesticide molecules belonging to organochlorines organophosphates and synthetic pyrethroids The most common contaminant was quinalphos which was detected in 121 out of 180 sample analysed Other major contaminants include lambda cyhalothrin (104) cypermethrin (100) chlorpyriphos (87) and profenophos (64) Pesticides detected in cardamom which have no label claim in cardamom include Beta cyfluthrin (5) bifenthrin (3) fenpropathrin (4) fenvalerate (5) lambda cyhalothrin (104) methyl parathion (64) and triazophos (4)

A field experiment was carried out in order to study the curing process on removal of residues of quinalphos chlorpyriphos triazophos cypermethrin lambda cyhalothrin and imidacloprid Curing process removed the residues of pesticides at varying levels Processing factor was worked out for each chemical Extent of removal of residues as a result of curing were quinalphos (61 78 67 78%) chlorpyriphos (70 23 76 66%) triazophos (49 62 55 02%) cypermethrin (65 71 67 63%) lambda cyhalothrin (13 15 40 00%) and imidacloprid (75 56 77 32%)

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