DYNAMICS OF PESTICIDE RESIDUES IN CARDAMOM GROWING SOILS OF IDUKKI DISTRICT

SIJI N. NATH

(2009-11-114)

THESIS

Submitted in partial fulfillment of the
requirement for the degree of

MASTER OF SCIENCE IN AGRICULTURE
(Soil Science and Agricultural Chemistry)

Faculty of Agriculture

Kerala Agricultural University

DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY
COLLEGE OF AGRICULTURE
VELLAYANI, THIRUVANANTHAPURAM- 695 522
KERALA, INDIA
2011

DECLARATION

I hereby declare that this thesis entitled **"Dynamics of pesticide residues in cardamom growing soils of Idukki district"** is a bonafide record of research 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.

Vellayani

09-08-2011

Siji N. Nath

(2009-11-114)

Dr. Thomas George
Associate Professor
Department of Soil Science& Agricultural Chemistry
College of Agriculture
Kerala Agricultural University
Vellayani, Thiruvanathapuram, Kerala

Date: 09/08/2011

CERTIFICATE

Certified that this thesis, entitled **"Dynamics of pesticide residues in cardamom growing soils of Idukki district"** is a record of research work done independently by Siji N. Nath (2009-11-114) under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to her.

09/8/2011

Thomas George
Chairman
Advisory Committee

Vellayani

Dr. Thomas George
Associate Professor
Department of Soil Science& Agricultural Chemistry
College of Agriculture
Kerala Agricultural University
Vellayani, Thiruvanathapuram, Kerala

Date: 09/08/2011

CERTIFICATE

Certified that this thesis, entitled **"Dynamics of pesticide residues in cardamom growing soils of Idukki district"** is a record of research work done independently by Siji N. Nath (2009-11-114) under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to her.

09/8/2011

Thomas George
Chairman
Advisory Committee

Vellayani

CERTIFICATE

We the undersigned members of the advisory committee of **Ms. Siji N. Nath (2009-11-114)** a candidate for the degree of **Master of Science in Agriculture** agree that this thesis entitled **"Dynamics of pesticide residues in cardamom growing soils of Idukki district"** may be submitted by of **Ms. Siji N. Nath (2009-11-114)**, in partial fulfillment of the requirement for the degree.

09/08/2011

Dr. Thomas George
Associate Professor
Department of Soil Science and Agricultural Chemistry
College of Agriculture
Vellayani.
(Major Advisor)

9/8/2011

Dr. N. Saifudeen
Professor and Head
Dept.of Soil Science and Agrl. Chemistry
College of Agriculture
Vellayani
(Member)

Sumam George
09-08-2011

Dr. Sumam George
Professor
Dept.of Soil Science and Agrl. Chemistry
College of Agriculture
Vellayani
(Member)

09-08-2011

Dr. S. Naseema Beevi
Professor
Dept. of Agricultural Entomology
College of Agriculture
Vellayani
(Member)

External Examiner who
evaluated the thesis
Dr. G. BYJU, PhD, ARS
Senior Scientist
CTCRI,
TRIVANDRUM
- 695017

ACKNOWLEDGEMENT

I bow my head before 'The Almighty ' for the bountiful blessings showered upon me, which helped me, pursue this endeavour to completion.

I express my exuberant pleasure to extend my deep sense of gratitude to ***Dr. Thomas George,*** *Associate Professor, Dept. of Soil Science and Agricultural Chemistry and chairman of my advisory committee for his affectionate guidance, valuable advice and constant encouragement during my research work. In spite of his busy schedule, he managed to suggest suitable ideas and extended his support at all stages of the work. I am indebted to him for the privilege to have worked under his guidance.*

I place on record my sincere gratitude to ***Dr. N. Saifuden****, Professor and Head, Dept. of Soil Science and Agricultural Chemistry for his valuable suggestions and encouragement during the course of study and preparation of thesis.*

I am extremely thankful to ***Dr. Sumam George,*** *Professor, Dept. of Soil Science and Agricultural Chemistry for her ever willing help, overwhelming support, affection and encouragement during the course of my investigation.*

I convey my heartful thanks to ***Dr. S. Naseema Beevi,*** *Professor, Dept. of Agricultural Entomology for her valuable suggestions, encouragement and constructive criticisms rendered during the course of my study and preparation of thesis.*

I owe my immense gratitude with pleasure to Dr. K. Harikrishnan Nair, Professor and Head (Retired), Department of Soil Science and Agricultural Chemistry and ex-member of my advisory committee for her critical suggestion and help during the course of my study.

I wish to express my special thanks to ***Dr. Thomas Biju Mathew****, Professor, Dept. of Agricultural Entomology,* ***Dr. Ambily Paul,*** *Assistant Professor, Dept. of Agricultural Entomology for the guidance, support and constant encouragement offered throughout my study period.*

I pay my heartful thanks to ***Dr. P. B. Usha,, Dr. Sam T. Kurumthottical, Dr. Sumam Susan Varghese Dr. C. R . Sudharmaidevi, Dr. K. C. Manorama Thampatti, Dr. Usha Mathew, Dr. S. Shehana*** *and* ***Dr. K. Ushakumari,*** *for their friendly approach and constant encouragement during the study.*

I convey my heartful thanks to ***Dr. Dhanya M. K,*** *Professor and Head, CRS Pampadumpara and* ***Dr. M. Murugan,*** *Associate Professor, Soil Science and*

Agricultural Chemistry, CRS Pampadumpara for providing necessary facilities during my study.

I wish to record my special thanks to the generous and selfless help of ***Dr. John Jo Varghese,*** *Senior scientist, Division of Agronomy and Soil Science, ICRI, Myladumpara rendered to me during the course of my investigation.*

I am grateful to ***Sri. C. E. Ajithkumar,*** *Programmer. Dept. of Agrl. Extension for his valuable help in analyzing the experimental data.*

I owe my gratitude to the non teaching staff of Dept. of Soil Science and Agricultural Chemistry, for their sincere co-operation during the course of study.

I am thankful to the project, Central Sector Scheme on Monitoring of Pesticide Residues at National level (CSS on MPR) for awarding fellowship during my M.Sc. programme.

My special thanks to Alikhan uncle, Anil chetan (CRS, Pampadumpara), Sujitha, Xavier, Soumya and Jimi(ICRI, Myladumpara) for their whole hearted co-operation and help during my study.

I am thankful to all my friends in Pesticide residue lab, Seena chechi, Beena chechi, Emile, Pallavi, Thania chechi, Vijayasree chechi, Binu chetan, Georgechetan Rajith, Aravind chetan, Pratheepchetan, Pratheeshchetan, , Rajesh chetan, Reshmi chechi, Deepa chechi,Prathibha chichi, Neethu chechi and Preetha chechi for their constant help and support during various stages of my work.

Words fail to express my sincere thanks to my friends Maryia, Shameena, Anju, and Vipitha for their sincere love emotional support and affection during these days without which my work wouldn't have been completed.

I remember the support and love offered by all my colleagues and friends especially Adrika chechi, Kavitha, Kranthi, Dhanya, Deepa, Agey, Athulya, Priya, Divya chechi, Appu, Asha, Shruthi, Jinsy chechi and Gayathri chechi and all other senior and junior friends.

I owe immeasurable indebtedness to my Pappa, Amma, Chetan and Liji chechi for their love, affection and blessings which enabled me to complete this attempt a successful one.

SIJI N. NATH

Dedicated to

MY

Parents

CONTENTS

LIST OF TABLES

LIST OF TABLES CONTINUED

LIST OF TABLES CONTINUED

LIST OF FIGURES

LIST OF PLATES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

%	Per cent
@	At the rate of
a.i.	Active ingredient
BDL	Below detectable level
CRM	Certified reference material
C.D.	Critical difference
cm	Centimetre(s)
*et a*l	And others
Fig.	Figure
g	Gram
µg	Microgram
ha^{-1}	per hectare
l^{-1}	per litre
kg	Kilogram
m	Metre
ml	Millilitre
PPM	Parts per million
RSD	Relative standard deviation
SD	Standard deviation
SL	Soluble liquid
Spp	Species
Viz.	*namely*

Introduction

1. INTRODUCTION

Environmentally and economically viable agriculture requires a variety of cultivation practices and pest management options as no one system will be appropriate for every situation. Since the dawn of time, mankind has had two primary goals, obtaining enough food to survive and improving the quality of life. The single most important task facing a society is the production of food to feed its population. Pesticides have played and will continue to play a significant role in food security in India. In modern agriculture, the advent of nutrient responsive cultivars and high yielding varieties resulted in intensive agriculture, which along with mono cropping system leads to outbreak of various pests and diseases. Thus the use of agricultural chemicals becomes imminent in present day agriculture.

Considering the Worldwide consumption of pesticides, 85 per cent of pesticides are used in agriculture. India has 170 m ha of arable land with average pesticide consumption of 0.5 kg per ha and is ranked tenth in the world in pesticide consumption (Hundal, 2006). Agrochemicals are some of the many pest control tools used in an integrated approach to pest management. Agrochemical distribution into environmental compartments is influenced by the physical and chemical properties of the chemical and environmental conditions, *ie* soil type, structure and meteorological conditions.

Despite the beneficial impacts of pesticides in improving and stabilizing agricultural productivity by control of obnoxious weeds, fungi and insects, these allocthonous organic chemicals are known to contaminate the soil ecosystem and pose threat to a balance equilibrium among various groups of micro organisms in soil. Soil, being the storehouse of multitudes of microbes, receives the chemicals in various forms and acts as a scavenger of harmful substances. The efficiency and the competence to handle these chemicals vary with the soil and its physical, chemical and biological characteristics.

Crop protection by pesticides results in pesticide residues in the soil, which is ultimately the sink of all the xenobiotic compounds. To ensure the safety of groundwater, it is necessary to study the dissipation and mobility behavior of pesticides. However, their judicious use demands a practical knowledge of their fate and effects in agricultural and natural ecosystems. According to a recent study, practically 1 per cent loss of one pound pesticide applied in an acre can contaminate all of the drainage from a fied in a normal rainfall year at 5 ppb level (Colborn, 2006).

Cardamom, the "Queen of spices", is the fruit of *Elettaria cardamomum* L.Maton and is one of the most important spice crops of Kerala. It is indigenous to the southern stretch and thrives well in the tropical rain forests of Western Ghats of India. It is cultivated in the hilly forest regions of southern states of Kerala (60%), Karnataka, (32%) and Tamil Nadu (8%) and is one of the important commodities for export. Cardamom is a sensitive plant and is often infested with a wide variety of insect pests and in a desperate bid to control them, farmers resort to frequent application of pesticides, either as foliar or soil treatment starting from 15- 20 days interval. As far as Kerala is concerned, 50 per cent of the total pesticide consumption goes to cardamom (Shetty, 2008). Small cardamom consumes more than 100 kg per hectare per year of phorate in Kerala (Usha, 2007). The impact of pesticides on the environment is alarming in cardamom growing plantations of Idukki district. The indiscriminate use of these toxic xenobiotics in the cardamom growing hot spots not only pollutes the ecosystem but also affects the physico-chemical and biological properties of soil

Imidacloprid is a neonicotinoid insecticide widely used for soil, foliar and seed treatment. It is reported to be persistent in soil and the potential for the chemical to bioaccumulate in the environment is low, due to its high photodegradation tendency and higher water solubility. Moreover, literature on the dissipation pattern of Imidacloprid in soil and the residues of pesticides in forest soils of cardamom plantations are scanty inspite of the wide use of pesticides.

In this context an investigation was carried out to assess the pesticide residues in soil and water samples from cardamom plantations and to study the dissipation pattern of imidacloprid in cardamom growing soils of idukki with the following objectives:

1. To develop a database on pesticide use pattern in cardamom growing plantations of Idukki district.
2. To validate the method for estimation of multiple residues of pesticides in soil.
3. To monitor the persistence level of pesticides in soil and water during the period December to May.
4. To study the dissipation kinetics of imidacloprid applied at different dosage in cropped and uncropped condition.

Review of literature

2. REVIEW OF LITERATURE

Cardamom is the most important spice crop of Kerala grown both for domestic consumption and for export. It is prone to infestation by different pests and is frequently applied with a variety of pesticides. This leads to contamination of cardamom capsules and soil with residues of toxic pesticides. It is in this context that a study was undertaken to find out the dynamics of pesticide residues in cardamom soils of Idukki district. The previous work done in relation to the above topic is reviewed under the following heads.

2.1 PESTS OF CARDAMOM

Ecological changes, particularly edaphic factors have added new pest problems in cardamom plantation in recent years. Many pests considered minor are assuming alarming proportions. There are 56 different insect and mite species reported as pests of cardamom in India (Kumaresan and George, 1999). 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).

Cardamom is affected by several diseases and infested by many insects, mite and nematodes. Among the insect pests, thrips, capsule/panicle/shoot borer, root grubs and root knot nematode are the major pests. Minor pests 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 (Spices Board, 2009).

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 (Table1) a schedule for its effective control (Spices Board, 2009).

2.1.1.1 Chemical methods of pest control in small cardamom

Table 1. Chemical methods of pest control in small cardamom

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
Seventhspray(December)Methylparathion @100ml 100 l^{-1} of water	Seventhspray(September)Profenophos @ 150 ml 100 l^{-1} of water
	Eighthspray(earlyNovember)Monocrotophos @ 200 ml 100 l^{-1} of water
	Ninth spray (December third week) Methylparathion @100 ml 100 l^{-1} of water

2.1.2 Pesticides used in control 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 per cent, dimethoate 0.05 per cent, fenthion 0.05 per cent, methylparathion 0.05 per cent and monocrotophos 0.025 per cent (a.i) were recommended.

A study showed that pesticide use in cardamom plantations of Idukki was one of the world's highest. On an average, farmers use 27 kg of pesticides in a hectare (ha) of cardamom plantation (Shetty, 2000) and in small cardamom, twelve insecticide and six fungicide sprays per year are required.

There has been an increase in the pesticide consumption in cardamom during the last ten years and the results of a survey during 2000-2001 revealed an unscientific and non-judicious use of pesticides by farmers in Kattappana block of Idukki district (Usha, 2007). It was reported that small cardamom consumes more than 100 kg ha^{-1} $year^{-1}$ of phorate in Kerala. The other pesticides used are quinalphos, monocrotophos, chlorpyriphos, fenthion, methyl parathion, endosulfan and emisan (Usha, 2007).

Shetty (2008) reported that residues of seven pesticides 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 cardamom. In cardamom ecosystem, the number of pesticide sprays was as high as 20 per seasons in Kerala and Tamil Nadu.

Application of phorate 10G or carbofuran 3G may be done for the management of root grubs or root knot nematode subject to the condition that enough soil moisture is available at the time of application. Under poor soil moisture condition, chlorpyriphos 20EC @ 0.04% (2 to 5 litres per clump) may be drenched in soil around and inside the clump for root grub management (Spices Board, 2009)

In an experiment with organic and inorganic insecticides evaluated against shoot fly infestation in cardamom, imidacloprid 200SL @ 0.5 ml l^{-1} of water was found very effective (Naik *et al.,* 2010). An experiment was conducted to evaluate imidacloprid (0.5 ml l^{-1}) for the management of hairy caterpillars in cardamom. Among the different chemicals compared, mean population of hairy caterpillars was significantly lower in acetamiprid followed by imidacloprid (Naik *et al.*, 2010).

The Central Insecticides Board advises quinalphos, monocrotophos and phenthoate for the management of cardamom thrips and diafenthiuron against cardamom thrips and capsule borer (www. Cibrc.nic.in/major uses/insecticides).

2.1.3 Pesticide residues in cardamom

In a monitoring study done by Chozhen and Regupathy (1994), in which pesticide residues in 130 cardamom samples were analysed and the residues of quinalphos, monocrotophos and fenthion ranged from 0.008-0.72 ppm, 0.001-0.54 ppm and 0.004-0.98 ppm, respectively. Residues of more than one insecticide were also detected in some samples.

Spice samples including cardamom monitored during 1980-89 in India indicated 75-100 per cent contamination of DDT and HCH (Kathpal and Kumari., 2000).

Studies conducted under the All India Network Project on Pesticide Residues indicated the presence of residues of insecticides in varying levels in small cardamom and quinalphos, monocrotophos and endosulphan were the common pesticides which exceeded the maximum residue limit (AICRP(PR), 2001).

Renuka (2001) and Rajabaskar (2003) reported that complete disappearence of profenophos was occurred after 15 days of application, both in green and cured cardamom capsules when sprayed at 0.075 per cent.

A field experiment was conducted in Green gold variety of cardamom by spraying imidacloprid 200 SL which is highly effective against sucking pests at 25 g a.i ha^{-1} and 50 g a.i $^{-1}$ as foliar spray. Samples were drawn 30 days after the last spraying and the residues were below detectable level (Vinoth *et al.*, 2006).

The incidence of pest activity and its management coincides with harvesting of produce. To manage the pest problem, farmers are applying higher dose of conventional insecticides available in the market. The indiscriminate use of several rounds of heavy doses of insecticides resulted in high levels of residue problems in cardamom. These insecticides adversely affect the quality of the produce and pollute the environment. The export of cardamom has reduced by 80 per cent because of the high pesticide residue problem (Beevi *et al.*, 2007).

Stanely (2007) reported that the residues of diafenthiuron dissipated to 0.08 and 0.16 per cent in green cardamom capsules at 15 days after application.

2.2 SOIL PESTS

Agricultural soils provide the life requirements of a wide variety of insect pests. Soil infesting insects are termites, white grubs, cutworms *etc.* The majority of the termite species are soil inhabiting, either as mound builders or as subterranean nest builders. Economically, termites are serious pests of agriculture, horticultre, plantations, forest, trees of garden plants and vegetables. In all tropical countries, the annual losses caused by their depredation run to millions of dollars (Roonwal, 1999).

Termites attack both annual and perennial crops, especially in the semi-arid and sub-humid tropics. A loss of 10-25 per cent is estimated in most field and forest crops due to termite attack. Severe loss in different regions of India has been recorded on highly susceptible crops like wheat, maize, sugarcane, cotton, groundnut, sunflower and tea (Rajagopal, 2002).

In India, termites are widely distributed in red, sandy loams, lateritic and red loam soils and they damage major field crops at all stages of their growth cycle (Sanyal *et al.*, 2006).

Bhattacharyya *et.al.*, (2007) reported that termite was a perennial problem in most of the sugarcane growing areas in Assam and the attack of *Odontotermes obesus* (Ramb.) and *Microtermes obesi* (Holgren) are often noticed in 50 per cent of the sugarcane (preserved and planted) while infestation in standing crop may vary from 10-20 per cent.

2.2.1 Chemical control of soil pests

The use of chemicals for the control of agricultural pests is an established practice in farming system throughout the world. Application of insecticides as seed and soil treatments has become a common practice to control the soil inhabiting insect pests. Besides controlling these insect pests, insecticides and their metabolites come into direct or indirect contact to the beneficial soil microorganisms and may affect their population as well as activities (Moorman, 1995).

Singh *et al.* (2002) reported that lindane, an organochlorine insecticide and a fumigant which was commonly used in India on a wide variety of crops and soil and there are several reports about its accumulation in soil.

Chlorpyriphos was found effective to control the incidence of termites in sugarcane and its effectiveness in reducing termite infestation was also observed in maize (Sharma *et al.*, 2003) and ground nut (Mishra, 1999).

The termiticides available includes chlorpyriphos, permethrin, cypermethrin, bifenthrin, fenvalerate, imidacloprid and fipronil (Su, 2002., Wagner, 2003). Horwood (2007) reported that bifenthrin and chlorfenapyr were the most persistent termiticides in soil.

Chlorpyriphos is a moderately stable organophosphorus insecticide widely used for the control of soil inhabiting insects like termites, field crickets, ants, white grubs, wire worms and black field earwig (Rekha, 2005).

The use of soil applied insecticide was a widely adopted management strategy to control insect pests. Systemic insecticides like phorate, carbofuran and aldicarb could be applied to soil for protecting crops from soil pests as well as sucking pests infesting aerial parts of the plant (Chadha and Swaminathan, 2006)

2.2.2 Pesticide application for management of soil pests

Crop protection is an integral part of modern agriculture with pesticide application as a major component. The indiscriminate use of broad spectrum synthetic pesticides has resulted in reduction of biodiversity, outbreak of secondary pests, development of pesticide resistence and contamination of food and ecosystem (Singh, 2000).

2.2.2.1 *Foliar application*

As much as 50 per cent of the pesticide applied to foliage falls on soil depending on crop canopy and the method of application (Sharma *et al.*, 2007). The direct exposure of crop to pesticides, includes the application of target crop and drift to non-target crop and second is indirect exposure of non-target plants.

2.2.2.2 *Soil application*

Pesticides may reach the soil through direct application to the soil surface, incorporation in the top few inches of soil, or during application to crops (Mc Ewen and Stephenson, 1979). Pesticides easily find their way into the soil (Harvey, 1983) and it has been reported that only 0.1 per cent of applied pesticides reach the target pests and remaining 99.9 per cent enters the environment (Pimental, 1995).

Kovacs (1986) reported that pesticides can enter ground water resources and surface run off during rainfall, thereby contributing to the risk of environmental contamination and can persist in soil by several kinds of intermolecular interactions .

Pal *et al.* (2000) reported that pesticide reaching the soil may affect the non-target soil micro organisms, thereby disturbing pesticide degradation processes. The amount of pesticide that migrates from the intended application area is influenced by the chemical's properties like its propensity for binding to soil, vapour pressure, water solubility and resistance to being broken down over time. Kellogg *et al.* (2000) reported that factors in the soil, such as texture, ability to retain water and the amount of organic matter contained in the soil also affect the amount of pesticides that will leave the area.

Soil, water and air or their combinations are major media for pesticide behavior (Jury *et al.*1987) (Ferenc, 2001).

Several reports suggest that a wide range of water and terrestrial ecosystems may be contaminated with organophosphorus compounds. Most distinctive phenomena of organic pesticide behaviour are metabolism and degradation (Katagi, 2002) (Kobara *et al,*. 2002). Pesticides undergo transformations and change their structures biotically (Kobara *et al.*, 2003) and abiotically in the environment (Katagi, 2004) and sometimes it will lead to the formation of more persistent and more toxic compounds.

The increased application of pesticides intentionally or accidentally pollute the soil in arable land. The effects of pesticide usage must be seen in the context of soil pollution and sustainability of the agro-ecosystem. Increasing pesticide usage in agriculture adds to the rise in concern for the environmental contamination (Zhu *et al.*, 2004).

2.3 PERSISTENCE OF PESTICIDE RESIDUES IN SOIL AND WATER

Pesticide residue means any specified substance which remains in or on a feed or food commodity, soil, air or water following use of a pesticide. For regulatory purposes it includes the parent compound and any specified derivative such as degradation and conversion product, metabolite and impurity considered to be of toxicological significance (FAO, 1986). Pesticide residues adversely affect human health and the natural environment (Basker *et* al., 1994).

2.3.1 Pesticide residues in soil

Soil is the ultimate sink for bulk of the pesticides applied either to the soil or to the foliage. It was estimated that more than 50 per cent of the applied pesticides and entire quantity of granular pesticides reaches the soil (Edwards, 1986). Several reports suggest that a wide range of water and terrestrial ecosystems may be contaminated with organophosphorus compounds. Direct or indirect application of pesticides may result in an accumulation of their residues in soil. The fate of a pesticide in the soil environment is governed by the retention, transformation and transport processes and their interaction. Cheng (1990) observed that factors, such as soil properties and conditions, the population dynamics of the micro organisms, weather patterns and soil management practices can affect the kinetics of the processes and the fate of a pesticide in soil.

Studies conducted on persistence and dissipation of organochlorine insecticides in different soils revealed that 86 per cent of the samples collected from agricultural lands of Punjab were contaminated with DDT, HCH, endrin and lindane (Pillai and Agarwal, 1989; Agnihotri *et al.*, 1995). In the first 180 days, the loss of lindane was found to be the highest (99%) followed by aldrin (98.7%), dieldrin (96.4%), DDT (94.8%) and heptachlor (86%) all over the world. The higher rate of dissipation in Indian soil was mainly attributed to its hot and humid climate.

Some pesticides become absorbed into clay and organic matter fractions in soil. As a result, they are not readily taken into plants, however, they may contaminate the groundwater supplies. Dissolved organic matter and suspended solid also account for pesticide contamination, since they are very mobile and most of the pesticides with hydrophobic moiety strongly adsorb to them (Krop *et al.*, 2001).

Organochlorine pesticide residues, particularly the oxidized form of heptachlor, remain in soils from South Korea, eventhough their use has been discontinued since 1980 (Kim and Smith, 2001). Residue of toxaphene, DDT, trifluralin and lindane have been detected in soils from cotton fields in South Carolina (Kannan *et al.*, 2003).

Ware and Whitacre (2004) reported that intensive agricultural practices often include the use of pesticides to enhance crop yields. However the improvement in yield is sometimes concomitant with the occurrence and persistence of pesticide residues in soil and water. Pesticide residues were determined in soils collected from four cotton producing areas of Mali, West Africa and 65 per cent of the samples were detected with endosulphan II with a maximum concentration of 37 ng g^{-1}. Residues detected in soil samples were below the quantification limit in the newer cotton producing region of Kita and intermediate region of San. Residues were detected at reportable levels in Koutiala (older) and Sikasso (intermediate) cotton producing areas. (Safiatou *et al.*, 2007)

2.3.2 Pesticide residues in water

Aquatic bodies act as sink of contaminated run-off water from treated field. The contaminated water due to toxic effects of residual pesticides adversely affects the aquatic flora and fauna. Indiscriminate sprays of chlorinated hydrocarbon insecticides have been found to cause many adverse side effects in the environment (Moulton, 1973).

The pesticides contaminate the aquatic body by run-off water from the surrounding fields especially with persistent chlorinated pesticides such as DDT, endosulphan, cyclodienes etc. The contamination of drinking water and ground water with organochlorine pesticides have been reported all over the world (Bakre *et al.*,1990; Jain *et al.*,1991)

Ritter (1990) reported that over 70 pesticides have been detected in ground water in USA. Aldicarb and atrazine along with the soil fumigants have been the pesticides most frequently detected in ground water. Atrazine concentrations have been correlated with high nitrate concentrations. The triazine herbicides, simazine and cyanazine, have also been detected in ground water. The annual amount of recharge, soil type, depth of aquifer from the surface and nitrate contamination are the important field parameters in determining ground-water contamination potential by pesticides.

Pesticides largely move with water in soil to ground water and on soil to surface water. The leaked water to ground water is used for irrigation or drinking water (Honeycutt and Schabacker, 1994). Dissolved organic matter and suspended solid should be taken into account on pesticide contamination in water. Factors that affect a pesticide's ability to contaminate water include its water solubility, the distance from an application site to a body of water, weather, soil type, presence of a growing crop and the method of applicaion of the chemical (Pedersen, 1997).

In the United states, pesticides were found to pollute every stream and over 90 per cent of wells sampled in a study by the US Geological Survey. Pesticide residues have also been found in groundwater also (Kellogg *et al.*, 2000). DDT was the main contaminant detected in soils and water from Banjul and Dakar in West Africa (Manirakiza *et al.*, 2003).

According to a recent study, practically 1 per cent loss of one pound pesticide applied in an acre can contaminate all of the drainage from a field in a normal rainfall year at 5 ppb level (Colborn, 2006).

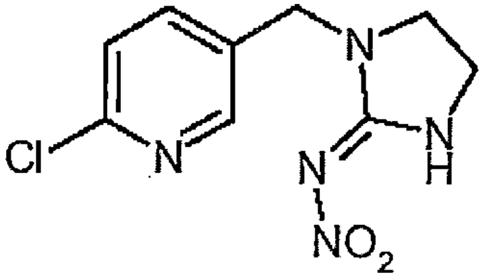
Safiatou *et al.* (2007) reported that eight pesticides were detected in water samples collected from four cotton producing areas of Mali, West Africa. The residues were detected below the quantification limit with endosulphan I and p,p' -DDE were detected in 75 per cent of the samples followed by endosulphan II (62%), endosulphan sulphate (50%), dieldrin (12%), p,p' -DDD (37%) atrazine (24%) and lindane (12%). All the pesticides detected in water had concentrations below quantification limit with exception of atrazine (1.4 μl^{-1}).

2.4 IMIDACLOPRID -THE NEW GENERATION INSECTICIDE

Imidacloprid is a systemic, chloro-nicotinyl insecticide introduced by Bayer crop science with a novel mode of action and it became the second biggest selling insecticide, close behind the organophosphate, chlorpyriphos. Imidacloprid shows excellent systemic activity and due to the relatively low rate of application it has been widely used in agricultural areas and drawn attention as a promising insecticide (Heijbrock and Huijbregts, 1995; McTier, *et al.*, 2003). Hence from the public health and environmental safety point of view, a field experiment was conducted to investigate the dissipation of imidacloprid in cardamom soils and the literature available in relation to this study was reviewed under the following heads. .

2.4.1 Salient features of imidacloprid

Common name	Imidacloprid
Chemical name	1-(6-chloro-3-pyridylmethyl)-N- nitroimidazolidin-2-ylideneamine
Alternate names	Gaucho, Admire, Confidor, Advantage, Merit, Provado, Imisol,Vision and Premise
Emperical formula	$C_9H_{10}ClN_5O_2$
Structural formula	



Molecular weight	255.7
Physical form	Colourless crystals, light yellow powder with a weak characteristic odour
Melting point	136.4 -143.8 ^{0} C
Water solubility	5.14 x 10^2 ppm (20° C at pH 7)
Vapour pressure	1.00 x 10^{-7} mm Hg (20^0 C)
Specific gravity/density	1.543 (20 ^{0} C)
Stability	Stable to hydrolysis at pH 5-11
Formulations	Dustable powder, Granular, Soluble concentrate, Suspension concentrate and Wettable powder
Toxicological data	Imidacloprid is moderately toxic. Rat acute oral LD_{50} is 450 ppm. Highly toxic to bees when used as foliar application. Honeybee LD_{50} (48 h) 0.008 µg per bee and the toxicity to fish is moderately low

Acceptable Daily Intake	0.06 mg kg^{-1} day^{-1}

2.4.1.1 *Solubility in other solvents@ 20^0 C:*

Dichloromethane	-	50.0 - 100.0 g l^{-1}
Isopropanol	-	1.0 - 2.0 g l^{-1}
Toluene	-	0.5 - 1.0 g l^{-1}
n-hexane	-	< 0.1 g l^{-1}

2.4.1.2 *Half-life of imidacloprid*

Hydrolysis half-life	>30 days (25^0 C at pH 7)	
Aqueous photolysis half-life	3.98 x10^{-2} days (24 ^{0} C at pH 7)	
Anaerobic half-life	27.1 days	
Aerobic half-life	9.97 x 10^2 days	
Soil photolysis half-life	38.9 days	
Field dissipation half-life	26.5 to 229 days	(Tomlin, 2000)

2.4.2 Uses of imidacloprid

Imidacloprid [1-(6-chloro-3-pyridylmethyl)-N-nitro-imidazolidin-2-ylideneamine], is a new systemic chloronicotinyl insecticide with both foliar and soil bioactivity. It is effective for controlling sucking insects, soil insects, termites and some species of biting insects. It is used as seed dressing, soil treatment and foliar treatment in different crops (Ishaaya and Degheele, 1998).

Imidacloprid is most commonly used on rice, maize, potatoes, vegetables, sugar beets, fruits, cotton, hops and turf and is especially systemic when used as a seed or soil treatment. (Nauen *et al.*, 1998; Farm Chemical Handbook, 2000).

2.4.2.1 Imidacloprid as crop protectant

Imidacloprid was found to be very effective in controlling sucking pests when applied as seed treatment in cotton (Graham, 1995). According to Xin and Xi (1995) imidacloprid caused significant mortality of Hemiptera.

Chandrasekaran (2001) reported that imidacloprid 0.004 per cent gave higher per cent reduction in aphid population on Bhindi.

Manjunatha and Shivanna (2001) reported that imidacloprid treated plots showed mortality of 65.12 per cent and 80.43 per cent of *Nephotettix* sp at 100 ml ha^{-1} and 400 ml ha^{-1} respectively. Ryeol *et al.* (2001) reported that residual effect of imidacloprid at 0.31 g a.i ha^{-1} granular formulation against *N. lugens* lasted for 40 days and for 30 and 20 days at half and quarter of the dose respectively.

Kumar *et al.* (2001) reported that the foliar application of imidacloprid (Confidor 200SL) @ 20 and 40 g a.i ha^{-1} resulted in faster dissipation and residues below detectable limit was recorded after 7 and 15 days.

Patil *et al.* (2002) reported that imidacloprid @ 12 and 150 ml ha^{-1} was highly effective against *A. gossypii* on chilli. Imidacloprid @ 25 g a.i ha^{-1} was superior in controlling aphid in okra (Misra, 2002). Michael Raj and Punnaiah (2003) observed that an overall efficacy of 98.92 per cent reduction in aphid population was recorded by sparying imidaclopid.

Imidacloprid was very effective against aphids (Chiranjeevi *et al.*, 2002; MichaelRaj and Punnaiahh 2003; Regupathy *et al.*, 2003) and the LC_{50} value of imidacloprid on cotton aphid was found 0.009 μ g ml^{-1} and the LC_{90} value of 0.048 μ g ml^{-1} (Dhawan *et al.*, 2008).

According to Rebek and Saief (2003) imidacloprid was used to control scale insects. Seed treatment of transgenic cotton with imidacloprid at 5 g kg^{-1} of seeds was more effective than other treatments (dimethoate and the untreated treatment) in controlling the populations of leafhoppers, *Amrasca biguttula biguttula* (Ishida) aphids, *A. gossypii,* thrips, (*S. dorsalis*) and whitefly, (*Bemisia tabaci*) and keeping them below economic threshold level up to 40 days after sowing (Kannan *et al.*, 2004).

Imidacloprid 17.8 SL (0.022 kg a.i. ha^{-1}) was the most effective in suppressing the thrips population and increasing the pod yield of chilli, followed by monocrotophos and acetamiprid (Mishra *et al.*, 2005). Field experiment conducted by Vikas Singh *et al.* (2005) at Chattisgarh, India, showed that imidacloprid 17.8 SL at 200 ml ha^{-1} was the most effective against *S. dorsalis* and *A. gossypii* in chilli.

Foliar application of imidacloprid 17.8 SL at 50 g a.i ha^{-1} showed toxicity for 29 and 31 days against aphids and leafhoppers. Imidacloprid 17.8 SL at the recommended dose of 25 g a.i. ha^{-1} was effective in controlling the population of aphids, *A. gossypii* up to 25 days in Bhindi (Preetha *et al.*, 2008). Imidacloprid 17.8 SL showed longer persistence and was superior to the conventional insecticides (Preetha, 2007).

A field trial was conducted in farmer's field in Kumily, Idukki district to evaluate the harvest time residues on cardamom with three sprays of imidacloprid 200 SL at 25 and 50 g a.i ha^{-1}. Samples were collected at random, on 30 days after last spraying for residue analysis. The results revealed that the harvest time residues were below detectable level both in green and cured cardamom capsules (Vinoth *et al.*, 2009). Naik *et al.* (2010) reported that imidacloprid 200 SL @ 0.5 ml per liter was found to be effective against shoot fly infestation in cardamom.

2.4.2.2 *Imidaclorid as a soil insecticide*

Imidacloprid is a systemic insecticide, introduced by Bayer India Ltd, in 1993, used as soil, seed and foliar insecticide effectively against soil insects, termites and has no effect on nematodes or spider mites (Gajbhiye *et al.*, 1997)

Imidacloprid spray applications generally provided good control of termites (Ramakrishnan *et al.*, 1999; Gahlhoff and Koehler., 1999). Baskaran *et al.* (1999) reported that imidacloprid was applied at 50 mg a.i as termiticde for termite control in Australia.

Imidacloprid can be used as a seed, soil, crop and structural treatment chemical. It controls sucking insects, soil insects, termites and some chewing insects. It is effective against adult and larval stages of insects. (Farm Chemical Handbook, 2000).

2.5 ENVIRONMENTAL FATE OF IMIDACLOPRID

2.5.1 Persistence of imidacloprid in soil

Persistence of imidacloprid in soil is affected by various factors, including temperature, organic matter content of the soil and whether the field is cropped or not. The time required for 50 per cent of the field-applied imidacloprid to dissipate (DT_{50}) range from approximately 80 days to 2 years. Assuming typical DT_{50} of 1 to 2 years, PMRA (Pest Management Regulatory Agency, 2001) has classified imidacloprid as persistent in soil based on the classification scheme of Goring *et al.* (1975).

The high water solubility of imidacloprid (514 ppm), suggests a potential to leach to ground water, although earlier field studies under normal weather conditions have found imidacloprid to be relatively immobile in silt loam soils (Miles Inc., 1993; Rouchaud *et al.*, 1994).

In the absence of light, the longest half-life of imidacloprid observed was 229 days in field studies and 997 days in laboratory studies (Miles Inc., 1993). Baskaran *et al.* (1999) reported that under laboratory conditions with 60 per cent water holding capacity, the half- life of imidacloprid in soil could be as high as 990 days.

Mulye (1996) conducted a two-year field lysimeter investigation in Germany using imidacloprid applied to seed potatoes and from the study results calculated a DT_{50} of approximately two years, indicating that the compound would persist in soil.

Rouchaud *et al.* (1996) reported that organic fertilizers, increased the pesticide adsorption to the organic matter and also increased its half-life. Half-lives ranged from 40 days when no organic fertilizers were used to 124 days when cow manure was used, similar to those not treated with organic fertilizers .

A laboratory experiment was performed to study the persistence of imidacloprid from two formulations (Confidor 200 g l^{-1} SL and Gaucho 700 g kg^{-1} WS) and its metabolism in three different soils (Gangetic alluvial soil of Kalyani, lateritic soil of Jhargram and coastal alkaline soil of Canning) of West Bengal following application at 0.5 kg and 1.0 kg a.i ha^{-1}. Dissipation of imidacloprid in soil followed first-order kinetics and DT_{50} values ranged from 28.7 to 47.8 days. In wettable powder formulations persistence increased by 3 to 6 days compared to liquid formulations (Sarkar *et al.*, 1999).

Studies determining dissipation time indicate that imidacloprid exhibits strong persistence in soil under standardized laboratory conditions and more variable persistence under a range of field conditions (Krohn and Hellpointner, 2002). The DT_{50} determined from 11 bare soil field trials in Northern and Southern Europe was 96 days at 20° C (Schad, 2001).

Field studies have shown that imidacloprid can persist in soil, with a half-life ranging from 27 to 229 days (Miles Inc., 1993). Sabbagh *et al.* (2002) observed that the calculated half-lives ranged from 83 days to greater than a year in a study on aerobic soil metabolism that examined loss of imidacloprid from eight different soil types.

Sanyal *et al.* (2006) conducted a field experiment at Kamalpur Tea Estate, Darjeeling, West Bengal, where imidacloprid (Confidor 200 SL) was applied on soil at the rate of 240 g a.i ha^{-1} (recommended dose) and 480 g a.i ha^{-1} (twice the recommended dose). The study revealed that the dissipation rate of imidacloprid was very fast and the residue concentration reached below detectable level on seventh day for recommended dose and tenth day for double the recommended dose. From the study it was found that the rate of dissipation was independant of initial deposits and the half life of imidacloprid ranged between 2.01 and 2.06 days irrespective of the application rate.

Singh *et al.* (2008) observed that imidacloprid persisted in soil upto 90 days with average half life of 40.9 days. The pesticides ability to move through soil has been tested and imidacloprid was found to be the quickest.

2.5.2 Sorption and desorption of imidacloprid

Sorption is one of the most important factors that affects the fate of pesticides in soil and determines their distribution in the environment which is widely used to describe the process of a pesticide partitioning between water solution and soil (Gawlik *et al.*, 1997) .

Baer and Calvet (1999) reported that adsorption is one of the most important processes which controls all other processes such as the pesticide movement, persistence and degradation and determines the fate of pesticides in soil systems. Sorption determines availability of pesticides for uptake by plants and the effectiveness of pesticides (Walker, 2000).

The sorption level of imidacloprid is also affected by soil properties such as organic carbon and minerals. As the organic carbon levels and laminar silicate clay content in the soil increases, the potential for imidacloprid to leach would decrease (Cox *et al.*, 1997,1998). Sorption intensity for imidacloprid and its metabolites is influenced by soil type and depends largely on organic carbon content (Cox *et al.*, 1998; Capri *et al.*, 2001). Imidacloprid has a medium to high sorption tendency for soil (Tomlin, 2000) (Krohn and Hellpointer, 2002).

Adsorption is the main fate process for imidacloprid in soil (Sabbagh *et al.*, 2002). Many soil factors influence pesticide adsorption. Soils high in organic matter or clay are more adsorptive than coarse sandy soils. Moisture also affects adsorption process, wet soils tend to adsorb less pesticides than dry soils.

Adsorption- desorption of imidacloprid on five different Indian soils of different origin was studied using batch equilibrium technique. Freundlich's constant K_f adsorption was highest for Alfisol soil having high organic carbon content and low pH (Agnihotri *et al.*, 2002).

Kalpana *et al.* (2002) reported that adsorption-desorpton influences mobility, persistence, degradation and volatility of a pesticide in soil. Sorption - desorption of a solute on soil depends on the properties of the compound as well as soil characteristics .

Imidacloprid sorption of the treated soils (Ferralsols) was studied at three pH levels (4.5, 6.0 and 7.5) and two temperatures (15^0 C and 25^0 C). Soil imidacloprid adsorption was related to pH and the type and quantity of added humic acids. Imidacloprid adsorption was usually higher under lower pH and temperature at same condition. Imidacloprid sorption fitted the Freundlich isotherm, indicating that exogenous humic substances influenced adsorption of imidacloprid, which in turn was affected by environmental conditions such as pH and temperature. When soil solution pH was 6, the amount of adsorbed imidacloprid was enhanced with increasing exogenous humic acids the amount adsorbed get decreased with increasing quantity of exogenous fulvic acids (Ping *et al.*, 2010).

Ping *et al.* (2010) reported that a pesticide held strongly to soil particless by adsorption is less likely to leach and soil factors that influence leaching include texture and organic matter content of soil because of their effect on pesticide adsorption.

2.5.3 Effect of vegetation on degradation of imidacloprid

There is evidence that dissipation time is reduced when imidacloprid is applied to cropped, rather than fallow fields (Scholz and Spiteller, 1992; Krohn and Hellpointer, 2002).

Scholz *et al.* (1992) reported that the half-life of imidacloprid in soil was 48-190 days, depending on the amount of ground cover and it breaks down faster in soils with plant ground cover than in fallow soils and it was observed that imidacloprid degraded more rapidly under vegetation with half life ($t_{1/2}$) of 48 days, versus 190 days without vegetation.

When imidacloprid was applied to bare soil at several sites in northern Europe, the mean DT_{50} was 174 days, while cropped conditions it reduced to 83 and 124 days (Krohn and Hellpointer, 2002). Half-life in soil varies depending on soil type, use of organic fertilizers and presence or absence of ground cover. The half life of imidacloprid in soil ranged between 7 to 146 days (Anonymous, 2002) and was less under cropped soil than under bare condition.

The persistence in vegetated areas is decreased through plant (Rouchaud *et al.*, 1994) and microbial (Capri *et al.*, 2001; Krohn and Hellpointner, 2002) uptake and metabolism.

Sanyal *et al.* (2006) reported that the dissipation of imidacloprid (Confidor 200 SL) in tea soils of West Bengal followed first order reaction kinetics and the half-life values ranged between 2.01-2.06 days .

2.5.4 Effect of organic matter on degradation of imidacloprid

Among the various factors responsible for the persistence of pesticides in soil, organic matter was the most important affecting the persistence of pesticides in soil, organic matter was the most important factor affecting the persistence of pesticides. (Chopra and Sree Ramulu, 1982). Organic material aging may also affect the breakdown rate of imidacloprid. Rouchard *et al.* (1994) reported that plots treated with cow manure which was more recently applied and not allowed to age showed longer persistence of imidacloprid in soils .

Application of dissolved organic carbon appears to reduce imidacloprid sorption by competing with the pesticide for sorption sites on the soil surface (Flores-Cespedes *et al.*, 2002). There is generally not a high risk of groundwater contamination with imidacloprid if used as directed. The chemical is moderately soluble and has moderate binding affinity to organic materials in soils. However, there is a potential for the compound to move through sensitive soil types including porous, gravelly, or cobbly soils, depending on irrigation practices.

Ahmad *et al.* (2009) reported that soil organic matter properties affect the sorption of organic molecules. A study showed that organic matter significantly affects the rate of biodegradation of imidacloprid.

2.5.5 Imidacloprid in plant system

Rouchaud *et al.* (1994) applied imidacloprid as a seed treatment to a sugar beet field and demonstrated that high imidacloprid concentrations were observed in the leaves of the plants.

In one study, at 97 days after sowing, the metabolites in sugar-beet leaves represented 44.5 per cent of the applied parent compound of imidacloprid. It shows that plants readily absorb imidacloprid through the roots and metabolize it (Westwood *et al.*, 1998).

In plants, imidacloprid is metabolized *via* loss of the nitro group, hydroxylation at the imidazolidine ring, hydrolysis to 6-chloronicotinic acid and formation of conjugates. The main metabolites detected in plants were imidacloprid-guanidine olefin and imidacloprid-guanidine (Tomlin, 2000).

In Bhindi fruits the harvest time residues of imidacloprid were at below detectable level for the samples collected during the first and second harvest in two season field trials (Sivaveerapandian ,2000; Suganthy, 2003) and it indicated the faster rate of degradation of imidacloprid in plant.

Absorption of pesticides by target and non-target organisms is influenced by environmental conditions and the chemical and physical properties of the pesticide and the soil. Imidacloprid is rapidly moved through plant tissues after applications and can be present in detectable concentration in tissues such as leaves, vascular fluids and pollen. In plants, pesticides may be broken down or may remain as such in the plant until tissue decay or harvest. Many non-target beneficial arthropods such as honeybees, parasitic wasps and predaceous ground beetles are sensitive to imidacloprid (Vishwakarma *et al.*, 2008).

Imidacloprid residues in the cotton lint, seed and oil from first and second picking were at below detectable level in the samples collected from the treated plots, 12 and 15 days after the last spray (Preetha *et al.*, 2008).

2.5.6 Degradation pattern of imidacloprid in soil

Biodegradation of pesticides is greatly influenced by the soil factors like moisture, temperature, pH and organic matter content, in addition to microbial population and pesticide solubility. Optimum temperature, moisture and organic matter in soil provide congenial environment for the break down or retention of any pesticide added to the soil. Metabolic activities of bacteria, fungi and actinomycetes have the significant role in the degradation of pesticides (Digrak and Ozcelik, 1998).

A first-order kinetic model described the degradation rate of pesticides. Degradation ends with complete mineralization to carbon dioxide, though binding of intermediate degradates to soil also occurs (Tomlin, 2000).

Experiments were also conducted to examine the effect of soil microorganisms on the degradation of imidacloprid in the silty loam soil. Pesticides degradation proceeded at a slower rate in sandy and sandy loam soil than that in silty loam soil. The half-lives were 9.90 weeks in silty loam soil; 12.16 weeks in sandy loam soil, and 12.60 weeks in sandy soil. Corresponding degradation half-lives was, 28.88 and 6.93 weeks for imidacloprid in sterilized and non-sterilized soils, respectively (Hafez and Thiemann, 2003).

Soil microorganisms had a major role in the acceleration of pesticide degradation. Amrit and Amarjeet (2005) observed that dehydrogenase activity is not impaired owing to imidacloprid application in treated mung field.

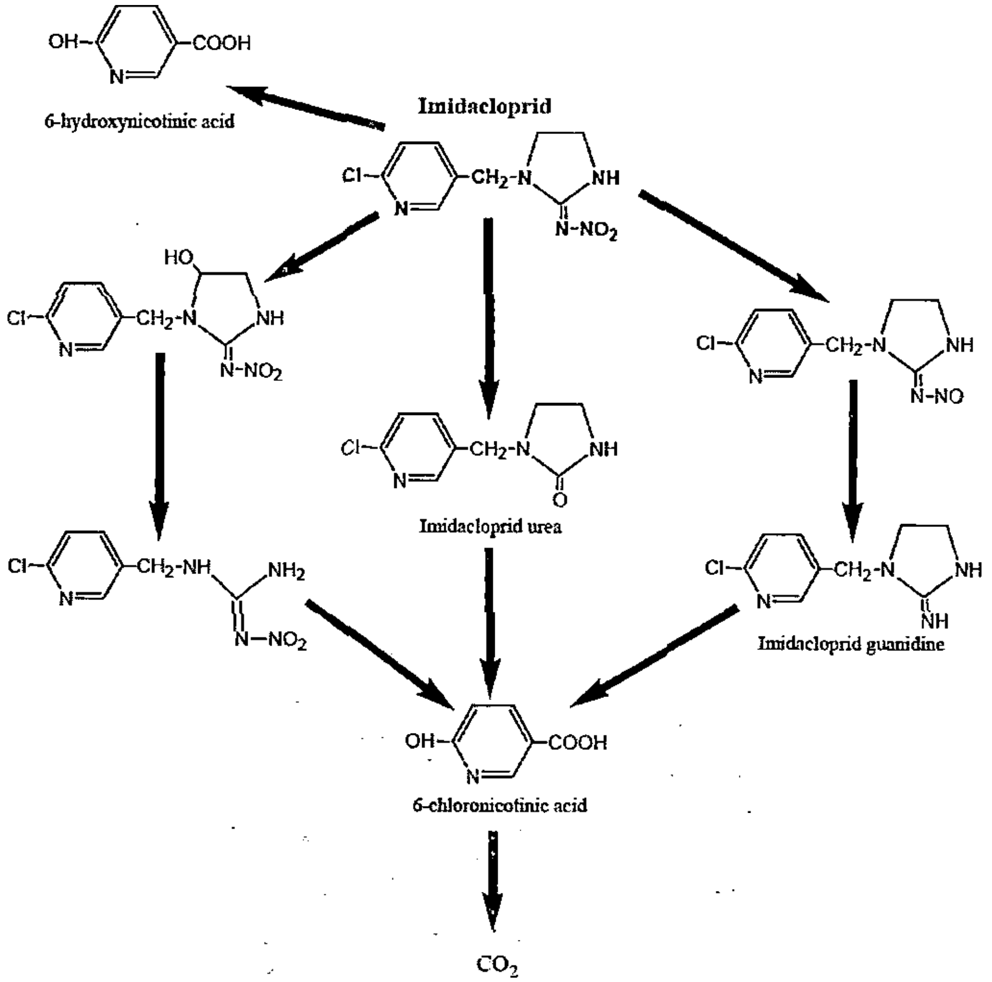


Fig. 1. Degradation pathway of imidacloprid in soil

Materials and methods

3. MATERIALS AND METHODS

The present study entitled "Dynamics of pesticide residues in cardamom growing soils of Idukki district" has been carried out to develop a database on pesticide use in cardamom growing plantations of Idukki district, to validate the method for estimation of multiple residues, to monitor the levels of pesticides and to study the dissipation kinetics of imidacloprid in soils of cardamom plantation

3.1 DEVELOPMENT OF A DATABASE ON PESTICIDE USE PATTERN IN CARDAMOM PLANTATIONS OF IDUKKI DISTRICT.

A purposive sampling survey was conducted in different cardamom plantations, five each in Pampadumpara, Kattappana and Nedumkandam Panchayaths adopting varying methods of pest control practices to assess the types of pesticides used, frequency of application and the amount of pesticides used. The survey proforma presented in Appendix I.

3.2 VALIDATION OF MULTIRESIDUE METHODS (MRM) FOR PESTICIDE RESIDUE ANALYSIS IN SOIL.

A mixture of the analytical standards of all commonly used pesticides in cardamom were fortified in soil at five different levels (0.01, 0.05, 0.1, 0.5, 1 µg g^{-1}). Extraction and clean up methods were performed by using different solvent systems.

Design : CRD
Treatments : 5
Replicates : 4

3.2.1 Preparation of mixture of standard insecticides

The analytical standard solution was prepared from the Certfied Reference Material (CRM) obtained from Sigma-Aldrich Chemicals Private Limited. 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 1000 ppm stock solution. From this, an aliquot of 10 ml was diluted to 100 ml with distilled n-hexane:toluene to get a 100 ppm stock solution of each insecticide. A working standard of 5 ppm of the mixture was prepared and stored in refregerator for further use. The individual standards of different insecticides were injected in Gas Liquid Chromatograph (ECD) and a calibration curve was prepared by plotting concentration *vs.* peak area.

Table 2. List of Certified Reference Materials (CRM) used in the preparation of insecticide mixture and their purity

CRMs	Pesticides	Purity(%)
Organochlorines	Gamma HCH	98.9
Organophosphorus compounds	Phorate	96.0
	Methyl parathion	99.8
	Malathion	97.2
	Quinalphos	99.2
	Ethion	97.8
	Profenophos	98.2
Synthetic pyrethroids	Fenpropathrin	98.7
	Lamda cyhalothrin	97.4

3.2.2 Fortification of soil with standard insecticide mixture

A 25 g each of air dried (2 mm sieved), soil samples were taken in five conical flasks and were spiked separately with 0.05 ml, 0.25 ml, 0.5 ml, 2.5 ml, 5 ml each of 5 ppm working standard mixture to get 0.01, 0.05, 0.1, 0.5 and 1 ppm levels, respectively.

3.2.3 Recovery experiment

A recovery experiment was conducted to standardise the procedure for extraction and clean up processes. The experiment was conducted by adding a known quantity of insecticide mixture to soil and trying the extraction process using different solvent systems. All the chemicals and solvents used in the study were analytical and of HPLC grade.

3.2.3.1 Extraction

The soil samples were extracted separately using acetone, acetonitrile and a combination of the two solvent system and the relative efficiencies of extraction were compared.

In acetone extraction, the fortified samples (25 g) were extracted sequentially twice with 50 and 25 ml each of acetone, combined and concentrated using rotary vacuum flash evaporator. The final volume was made upto 5 ml using n-hexane.

QuEChERS method was adopted for acetonitrile extraction of spiked pesticides from soil. For this purpose 10 g of air dried, sieved (2mm mesh) soil was weighed in a 50 ml centrifuge tube and spiked with the standard insecticide mixture and evaporated to release the solvent vapours. The soil samples were spiked with 20 µl, 0.1 ml, 0.2 ml, 1 ml and 2 ml of 5 ppm standard insecticide solution to get 0.01 ppm, 0.05 ppm, 0.1 ppm, 0.5 ppm and 1 ppm levels, respectively. To this, 4 g magnesium sulphate (hydrated), 1 g sodium chloride and 1 g sodium citrate tribasic dihydrate were added. Then, 20 ml of acetonitrile was added and the samples were shaken for one minute in a vortex and centrifuged for 4 minutes at 4,000 rpm. A dispersive soild phase extraction clean-up process was carried out by transferring the supernatant (10 ml) to a centrifuge tube (15 ml) containing 1.5 g magnesium sulphate (hydrated) and 0.250 g PSA (Primary Secondary Amine) and was shaken for a few seconds followed by centrifugation at 4,400 rpm for 10 minutes. The cleaned supernatant extract was evaporated to dryness at 40 ^{0}C using turbovap. The dry residue was redissolved in n-hexane and the volume was made upto 5 ml and analysed in Gas Liquid Chromatograph (Asensio-Ramos *et al.*, 2010).

In the third method, with slight modification of QuEChERS(Asensio-Ramos *et al.*, 2010) process of extraction was tried using acetonitrile and acetone (3:1) as extractant. A 10 g of air dried, sieved (2 mm) soil was transferred to a centrifuge tube (50 ml) and spiked with 20 µl, 0.1 ml, 0.2 ml, 1 ml and 2 ml of 5 ppm standard insecticide mixture so as to get 0.01 $\mu g\ g^{-1}$, 0.05 $\mu g\ g^{-1}$, 0.1 $\mu g\ g^{-1}$, 0.5 $\mu g\ g^{-1}$ and 1 $\mu g\ g^{-1}$ respectively. To this, 1 g sodium chloride and 1 g magnesium sulphate were added and extraction was carried out using 15 ml acetonitrile and 5 ml acetone and the mixture was shaken for 2 minutes. To this mixture, 2 g sodium sulphate and 1 g sodium chloride were added and shaken vigorously for 5 minutes, followed by centrifugation for 3 minutes at 3,000 rpm. The supernatant 10 ml of extract was collected, evaporated to dryness at 60^0 C using turbovap evaporator and the dry residue was made up to 2 ml using n-hexane:acetone (9:1) mixture for quantification of residues.

3.2.3.2 Estimation

The cleaned extracts were analysed on a Gas Liquid Chromatograph (Shimadzu-2010) equipped with ^{63} Ni 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 300^0 C, 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 1.06 ml min^{-1} and linear gas velocity of 26.0 cm sec^{-1}.

3.2.3.3 Residue quantification

$$\text{Residue} = \frac{\text{Peak area of sample} \times \text{Concentration of standard} \times \text{Finalvolume of extract}}{\text{Peak area of standard} \times \text{Weight of sample (g)} \times \text{Volume injected in } \mu\text{l}}$$

3.3 MONITORING OF PESTICIDE RESIDUES IN SOIL SAMPLES

3.3.1 Sample collection

Soil samples were collected randomly from different locations from each of the selected cardamom plantation at 0-15 cm and 15-30 cm depth before and after each spray for a period of six months (Dec-May). Samples were collected from ten locations from each plantation using an auger tube at depths 0-15 and 15-30 cm. A representative 1 kg soil was collected from each depth from every plantation. The extraction and clean-up procedures were performed as modified QuEChERS method detailed in section 3.2.3.1.

3.4 MONITORING OF PESTICIDE RESIDUES IN WATER SAMPLES

Water samples (2.5 l) were collected randomly from different water sources in the selected cardamom plantations before and after each spray for a period of six months from December to May. The residues were extracted by adopting standardised extaction and cleanup procedures and estimated in a GLC-ECD.

3.4.1 Extraction

A 750 ml of water sample collected from each of the selected plantation was taken in a separatory funnel (2 l) to which 150 g sodium chloride was added and shaken well until it get dissolved. Residues were extracted by partitioning with 75 ml of dichloromethane and shaken for about 1 minute and the organic layer was collected in a conical flask and extraction was repeated two more times with 40 ml each of dichloromethane. The partitioning was repeated using 50 ml hexane. The extracts were combined and passed through anhydrous sodium sulphate to remove excess water. The extracts were concentrated to dryness at low temperature (40 ^{0}C) in a rotary vacuum flash evaporator and the volume was made up to 2 ml using n-hexane (Mukherjee *et al.*, 2007).

3.4.2 Residue quantification

The residues were estimated in GC (ECD) as mentioned in section 3.2.3.3

3.5 DISSIPATION STUDY OF IMIACLOPRID IN SOIL

3.5.1 Experimental details

3.5.1.1 *Location and soil*

The experiment was conducted at the seventh block of Indian Cardamom Research Institute (ICRI), Myladumpara, Idukki district. The site is located at an altitude of 1,068 m above mean sea level at 9^0 53' N latitude, and 77^0 09' E longitude and enjoys humid tropical monsoon climate. The soil was forest loamy with pH of 5-6.

3.5.1.2 Selection of experimental plot

The site was selected in an area with no history of pesticide usage. Individual plots of one square meter were selected in bare soil for treatments T_1, T_2 and T_3 and one square meter area was selected between four cardamom plants for treatments T_4, T_5 and T_6.

Design : Randomized Block Design

Treatments : 7

Replications : 4

3.5.2 Treatments

The commercial formulation of imidacloprid (Confidor 200SL) manufactured by Bayer crop science was purchased from local market and applied at three different levels *viz.* half the recommended dose (0.05 ml l^{-1}), recommended dose (0.10 ml l^{-1}) and double the recommended dose (0.20 ml l^{-1}) with an untreated control in cropped and non-cropped situations, in four replicates.

T_1 - half the recommended dose 0.05 ml l^{-1} in bare soil

T_2 - recommended dose 0.10 ml l^{-1} in bare soil

T_3 - double the recommended dose 0.20 ml l^{-1} in bare soil

T_4 - half the recommended dose 0.05 ml l^{-1} in cropped soil

T_5 - recommended dose 0.10 ml l^{-1} in cropped soil

T_6 - double the recommended dose 0.20 ml l^{-1} in cropped soil

T_7 - untreated control

3.5.2.1 Standardisation of treatment volume

Quantity of spray volume needed to wet 15 cm soil depth was determined by drenching 30 cm × 30 cm area with known quantity of water. It was found that 600 ml of water was required to wet 15 cm soil when applied in an area of 30× 30 cm. Accordingly, the volume of pesticide solution required per plot in an area of 1 m^2 was estimated as 6.6 l.

200 ml - 5 cm

600 ml - 15 cm

ie., 0.09 m^2 - 600 ml

for 1 m^2 - 6.6 ml

3.5.3 Sampling

Soil samples were taken at 0 (2 hours after spraying), 1, 3, 5, 7, 10, 15, 20 and 25 days after treatment of insecticide at 0-15 cm soil depth. A 10 g of the sample was drawn from each replication and transfered to a 50 ml centrifuge tube by adding 10 ml of solvent. It was stored in a deep freezer at sub-zero temperature (-18 ^{0}C).

3.5.4 Recovery experiment

A recovery experiment was carried out to determine the efficiency of the analytical procedure adopted during the experiment and to standardise the procedure for extraction and clean up process. The experiment was conducted by adding a known quantity of standard imidacloprid to soil samples and trying the extraction process using different solvent systems.

3.5.4.1 Preparation of Standard solution

The standard solution of imidacloprid was prepared from the Certified Reference Material (CRM) procured from Sigma-Aldrich Chemicals Private Limited. A weighed amount of the analytical grade material (99.9% purity) was dissolved in acetonitrile (HPLC grade) to obtain 1000 ppm stock solution. From the stock solution an aliquot of 10 ml was diluted to 100 ml with acetonitrile (HPLC grade) to get a 100 ppm stock solution. From this working standard of 5 ppm was prepared and stored in refrigerator for further use. The working standards of different concentration were injected in High Performance Liquid Chromatograph (HPLC) and a calibration curve was prepared by plotting concentration *vs.* peak area.

3.5.4.2 Fortification of soil with imidacloprid

A 25 g air dry soil was taken in a conical flask and spiked with 0.05 ml of 5 ppm standard solution to obtain 0.01 μg g^{-1} in triplicates. Similarly 0.25 ml, 0.5 ml, 2.5 ml, 5 ml of 5 ppm solution were spiked to get five different levels 0.05, 0.1, 0.5, 1 μg g^{-1} respectively. The spiked samples were homogenised for few minutes, extracted using different solvents and analysed. Among the selected procedures the best one was choosen for the estimation of imidacloprid in the study.

3.5.4.3 Extraction

The samples were extracted using acetone as solvent. The samples were extracted sequentially thrice with 50 ml of acetone, the extracts were combined, concentrated using vacuum flash evaporator and the dry residue was made up to 5 ml using acetnitrile.

In acetonitrile extraction the fortified samples (25g) were extracted sequentially twice with 50 and 25 ml each of acetonitrile, the extracts were combined and concentrated using rotary vacuum flash evaporator. The final volume was made upto 5 ml using acetnitrile (Bhaskaran *et al.*, 1997).

In QuEChERS method a 10 g of soil sample was taken in a centrifuge tube (50 ml) and spiked with 0.02 ml of 5 ppm standard solution to obtain 0.01 $\mu g\ g^{-1}$ in triplicates. Similarly 0.1 ml, 0.2 ml, 1 ml, 2 ml of 5 ppm solution were spiked to get 0.05, 0.1, 0.5, 1 $\mu g\ g^{-1}$ levels respectively. The spiked samples were extracted with 10 ml of acetonitrile (HPLC grade) and shaken for 10 minutes. The acetonitrile layer was drained to another centrifuge tube and 2 ml of saturated NaCl solution was added. The supernatant 5 ml acetonitrile layer was transfered for clean up into another centrifuge tube by adding 25 mg PSA and 0.5 g magnesium sulphate. It was mixed in a vortex mixer and centrifuged for 2 minutes. The supernatant 2.5 ml was taken for estimation of residues.

3.5.5 Estimation

The residues of imidacloprid were estimated by high performance liquid chromatography (HPLC), Model Schimadzu LC 20AT, reverse phase (RP) with Phenomenex C-18 column and PDA detector. The mobile phase was acetonitrile: water (35:65v/v) with a flow rate of 1ml min^{-1}. Detection was at a wavelength of 270 nm with an injection volume of 20 µl (fixed loop). The retention time of imidacloprid was 6.10 minutes.

3.5.6 Residue quantification

$$\text{Residue}=\frac{\text{Peak area of sample}\times\text{Concentration of standard}\times\text{Finalvolume of extract}}{\text{Peak area of standard }\times\text{Weight of sample (g)}\times\text{ Volume injected in }\mu\text{l}}$$

3.6. Calculation of half-life

Theoretically, the residues on a treated substrate should decrease logarithmically with time since the amount lost per unit time should be proportional to the total present at any time, provided all were equally exposed to weathering, degradation reaction etc. (Hoskins, 1981). When log of residue was plotted against time elapsed, a linear trend could be observed. This means that log D can be represented as a linear function of 't' where D is the residue in ppm at time 't', 't' being expressed in week or days. Thus, the model is log $D=K_1E+\log K_2$, which means that D=k2. Thus k_2 esimates the initial deposits. The time taken to reduce the deposit to D/2, which is defined as the time required for half of the given quantity of material to react or dissipate is calculated as $t_{1/2}= \log 2/k_1$.

3.7 SOIL ANALYSIS

Soil samples collected from the three different locations and the experimental soil of imidacloprid were analysed for physico-chemical properties like pH, electrical conductivity, cation exchange capacity and soil nutrients such as organic carbon, nitrogen, phosphorus, potassium, calcium and magnesium following standard analytical procedures.

3.7.1 Assessment of dehydrogenase activity in soil

A 20 g of air dried soil and 0.2 g of $CaCO_3$ were throughly mixed and 6 g of this mixture was transferred to a test tube. To each tube, 1 ml of 3 per cent aqueous solution of Triphenyl Tetrazolium Chloride (TTC) and 2.5 ml of distilled water were added. The contents were mixed throughly using a glass rod, stoppered and was kept for incubation at 37 ° C in a BOD incubator for 24 hours. After 24 hours of incubation, 10 ml of methanol was added and shaken for 1 min. The tube was opened and the suspension was filtered through a glass funnel plugged with absorbent cotton to a 100 ml volumetric flask. The intensity of red colour obtained was measured using a spectrophotometer at a wavelength of 485 nm with methanol as blank.

3.8 STATISTICAL ANALYSIS

The data generated was statistically analysed using analysis of covariance technique (Gomez and Gomez, 1984) and from the dissipation data half life of the insecticide in soil was worked out using Hoskins formula (Hoskins, 1981).

Table 3. Analytical methods followed for soil analysis

Sl No:	Parameters	Method	Reference
1	Texture	International pipette method	Piper (1966)
2	Water holding capacity	Undisturbed core sample	Black *et al.* (1965)
3	pH (soil:water)1:2.5	p H meter with glass electrode	Jackson (1973)
4	EC (soil:water)1:2.5	Conductivity meter	Jackson (1973)
5	CEC	Ammonium acetate method	Jackson (1973)
6	Percentage base saturation	Ammonium acetate method	Jackson (1973)
7	Organic carbon	Walkley and Black method	Jackson (1973)
8	Available N ($KMnO_4$-N)	Alkaline permanganate method	Subbiah and Asija (1956)
9	Available P	Bray No:1 extraction and spectrophotometry	Jackson (1973)
10	Available K	Neutral normal ammonium acetate extraction and flame photometry	Jackson (1973)
11	Exchangeable Ca	Neutral normal ammonium acetate extraction and titration with EDTA	Hesse (1971)
12	Exchangeable Mg	Neutral normal ammonium acetate extraction and titration with EDTA	Hesse (1971)
13	Available S	Turbidimetry	Chesnin and Yein (1951)
14	Dehydrogenase activity	Extraction with methanol	Casida *et al.* (1964)

Results&Discussion

4 & 5. RESULTS AND DISCUSSION

The salient results of the study entitled "Dynamics of pesticide residues in cardamom growing soils of Idukki district" are presented and discussed below under the following heads.

4.1 Database on pesticide use pattern in cardamom plantations of Idukki district.

4.2. Multiresidue method validation in soil

4.3 Physico-chemical parameters of the soil

4.4. Monitoring of pesticide residues in soil samples

4.5. Monitoring of pesticide residues in water samples

4.6 Dissipation study of imidacloprid in soil

4.1 DATABASE ON PESTICIDE USE PATTERN IN CARDAMOM PLANTATIONS OF IDUKKI DISTRICT

Adoption of modern farming techniques in India involving improved irrigation, high-yielding varieties, agrochemicals and farm mechanisation has made significant contributions towards raising food production. At the same time, intensive cultivation of high yielding varieties, monoculture of commercially important crops, overlapping of cropping seasons and excessive application of agro-chemicals have resulted in high incidence of pests and diseases. Crop protection is an integral part of modern agriculture with pesticide application as a major component.

The liberal and continued use of pesticides has disturbing consequences on the farming system, particularly due to the development of resistance, resurgence of insect pest and decline in population of the natural enemies of pests. Farmers are using high doses of chemicals to manage resistant pests which are resulting in high pesticide residue accumulation in plant as well as soil posing threat to human health as well as soil ecosystem. Most of the pesticides are organic or inorganic chemicals, which have longer persistence in the environment

4.1.1 Pesticide use pattern in cardamom plantations of Idukki district

Cardamom the "Queen of spices", is the fruit of *Elettaria cardamom* L. Maton which has high export potential and fetches high monetary return in international market. The crop is regularly affected by several pests and diseases and for their timely management, farmers resort to continuous and inappropriate application of pesticides. In the light of the above, a detailed field investigation was carried out to obtain information on the use of pesticides and their consequent residues in different cardamom plantations of Idukki district.

4.1.1.1 *Sampling and methodology*

Based on area wise pesticide consumption pattern, intensive pesticide use hot spots were selected and a field survey was carried out with the help of pretested schedules. The total sample size was 15 cardamom growing plantations randomly selected in three Panchayaths of Idukki district. Apart from the use schedules for farmers, individual schedules for pesticide dealers were also utilized to collect specific information on pesticide use.

A purposive sampling survey was conducted in cardamom growing plantations of Idukki district to assess the amount of pesticides used, frequency of application and extent of pollution due to the usage of these toxic chemicals. The survey was conducted mainly in Pampadumpara, Kattappana and Nedumkandam Panchayaths in Idukki district. Majority (95 %) of the respondents in the hot spots were adopting prophylactic and remedial use of pesticides and preferring the use of synthetic pesticides because of their easy availability in the local market and also due to their immediate knock-down effect on crop pests. The farmers are mainly concerned about the control of thrips attack, which they consider as the most important pest to be controlled.

4.1.2 Frequency of pesticide application

Most of the farmers are in their old age and are adopting the management practices based on their own experience. It was observed that a majority of the farmers follow their own spraying schedules and doses of insecticides to control insect pests and diseases. The traditionally used organophosphorous compounds are being preferred by most of the farmers for pest control. The farmers in general were not aware of the chemical nature, persistence and properties of the applied pesticides and are mainly concerned with the production of capsules with good appearance.

In rainfed 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. Contrary to this, farmers apply up to 22 sprays per year, usually at 15 days interval in the peak period of bearing. The export potential and higher monetary return from the produce promotes the planters in protecting the plants from pest and disease incidence by applying pesticides from 15 days interval to once in a month.

The dosage of the various pesticides used by the farmers of the surveyed plantations is presented in Table 4. Regarding the dosage of pesticides, most of the farmers are of the opinion that the recommended doses of pesticides in the package are ineffective in controlling the pests and diseases. Majority of the respondents are using 50 per cent higher dose than recommended during application. It was observed during the survey that the spraying schedule has gone upto more than twenty four rounds of spraying with various chemicals in rotation. 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.

Most of the chemicals are applied in foliar form and soil application was also practised to manage root grub and nematode infestation. Chlorpyriphos and phorate are mainly applied as soil insecticides in cardamom. 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).

4.1.3 Types of pesticides used

Cardamom enjoys a unique position in the international spice market and due to the higher monetary return from the produce, farmers are more concerned about the plant protection measures. The major pests infesting cardamom include thrips, capsule borer and root grub and for their timely management farmers were adopting plant protection measures with conventional insecticides. Eventhough the package of practice recommendations prescribe the kind of pesticides to be used for controlling insect pests at various stages of their lifecycle, about 30 per cent of the respondents are using several chemicals and following the recommendations of company representatives.

Among the conventional insecticides, organophosphorus compounds like phorate, chlorpyriphos, quinalphos, methyl parathion, triazophos, profenophos and ethion are contributing the lionshare (60-65 %) and the synthetic pyrethroids cypermethrin, cyfluthrin, fenvalerate and lamda cyhalothrin are widely used in plant protection (20-25 %). Some progressive farmers are adopting the usage of newer insecticides available in the market (10 %). Several insecticides were used in rotation and among fungicides, bavistin and bordeaux mixture are widely used.

The progressive farmers among the respondents are concerned about the quality of the ecosystem and are adopting the new generation insecticide as a component in plant protection. The newer insecticides fame (Flubendiamide) and coragen are used by them.

The proactive approach and extensive network of pesticide companies help in popularising and promoting pesticides in rural areas. The dealers promote the products of those companies which give maximum incentives and they are not completely aware of the active ingredient and toxicity level of the chemical sold by them. Most pesticide dealers are found, trying to hide the facts regarding the purchase of pesticides from within or outside their locality. In addition, the banned pesticide endosulfan is still being used for agricultural purpose.

The results also revealed that most of the respondents are relatively ignorant about the insecticide formulations, dosage and guidelines of application given on the insecticide labels or directions of usage in the leaflets. Some respondents were not aware about the time needed for a chemical to dissipate in the environment. More than 50 per cent of the respondents in the selected locations were depending on company representatives for technical information regarding plant protection. About 60 per cent of the respondents take their own decisions regarding the type of chemicals to be used in controlling pests and diseases.

The respondents in the hot spots were concerned about increasing crop loss due to pests and diseases. The farmers resort to improper usage of toxic chemicals and it may lead to a great impact on human health and environment and will result in adverse effect on non-target organisms. A majority of the respondents do not follow any of the recommended safety measures while handling and applying pesticides, such as wearing gloves, shoes, face masks and other protective clothing (Plate. 1). It was observed that 40 per cent of the respondents personally undertake spraying operations and the farmers or agricultural labourers are unaware of the significance of warning symbols on the label and are often subjected to the risk of poisoning. Moreover, persons who handle pesticides during application, transportation and storage are susceptible to health hazards. 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).

Synthetic insecticides controlled the pests effectively during the early green revolution period. However, the indiscriminate use of these chemicals resulted in the elimination of the natural enemies of pests, leading to increased outbreak and resurgence of insect pests (Shetty, 2000).

The respondents were of the opinion that chemical methods of pest control are very effective in combating serious pest infestation and pesticides take up 8 per cent share of the total cost of cardamom cultivation (Murugan, 2008). The dosage of pesticide ranged from 2-3 ml l^{-1} with more than 24 rounds of spraying with different chemicals in a year is being practised by most of the farmers.

From the survey it could be presumed that due to the over dose and over usage of insecticides, the soil and water of the ecosystem are likely to be polluted with residues of the applied pesticides (Shetty, 2004). The socio-ecological balance of the ecosystem could be affected with the continued use of these pesticides in the same field over a prolonged period, irrespective of the type of pesticide.

a) Preparation of spray solution

b) Foliar spraying of pesticides

c) Foliar spraying of pesticides

Plate1. Field application of pesticides

Table 4. Pesticide use pattern in cardamom plantations vis a vis recommendations

Pesticides used	Frequency of application (interval in days)	Farmer's practice (dosage in ml l^{-1})	Recommended dosage (ml l^{-1})
Phorate	At the time of planting	8.3 kg ha^{-1}	60-80 g per plant
Curacron (Profenophos)	15-20	1.5-3	1.5 - 2
Hilban (Chlorpyriphos)	20-25	1.5 - 3	2
Ekalux, Hilquin (Quinalphos)	25	2	1.5 - 2
Hostathion,Josh (Triazohos)	25	2.5-3	2
Monocil, Nuvacron (Monocrotophos)	25	2 - 2.5	2
Metacid(Methyl parathion)	15-20	2	1
Viraat(Cypermethrin +Quinalphos)	15-20	3	-
Avaunt (Indoxacarb)	30	1	-
Spark(Deltamethrin+ Triazophos)	22	1 - 3	-
Karate(Lamda cyhalothrin)	15-20	3	-
Shakti (Cypermethrin)	20-22	3	-
Coragen (Chloranthraniliprole)	30	0.3	-

4.2. MULTIRESIDUE METHOD VALIDATION IN SOIL

Validation of multiresidue methods for pesticide residue analysis in soil was done to standardise a procedure for the extraction of pesticides from soil using different solvents/solvent systems. The various parameters for assessing the efficiency of extraction process have been evaluated from the different methods tried and the results are presented below.

4.2.1 Extraction using acetone as solvent

A 25 g each of soil sample was spiked at five different levels (0.01, 0.05, 0.1, 0.5, 1 µg g^{-1}) in three replicates and extraction was carried out individually using 50 ml acetone (AR grade) as the solvent. The recovery obtained for each level is presented in Table 5.

The mean recovery percentage of various compounds spiked at the highest level of 1 µg g^{-1}, ranged from 25.81 to 79.20 per cent and was unsatisfactory. The percent recovery for profenophos (25.81- 35.32%) was very low at all the five different levels. The percent recovery never exceeded 80 per cent for any of the compounds fortified. More than 50 per cent recovery was obtained for quinalphos (79.20 %), malathion (78.70 %), methyl parathion (65.62 %), ethion (55.09 %), Gamma HCH (57.78 %), fenpropathrin (62.83 %) and lamda cyhalothrin (70.54 %). Profenophos (25.81 %) was found to be the least recovered compound. At 0.5 µg g^{-1} level of fortification, the recovery percentage was above 80 per cent for phorate (87.97 %), quinalphos (89.21 %), malathion (93.16 %), while for other compounds, the recovery ranged from 74.55 - 35.32 per cent. The recovery percentages of all the compounds were very low at 0.1 and 0.05 µg g^{-1}. At 0.1µg g^{-1} level of fortification, the percentage recovery of organophosphorus compounds ranged from 26.66 to 161.39 per cent and were highly variable. Among the synthetic pyrethroids fenpropathrin (47.82 %) and lamda cyhalothrin (43.10 %) recovered. The average recovery percentage at 0.05 µg g^{-1} level of fortification ranged from 31.93 to 125.81 per cent for the organophosphorus compounds and the synthetic pyrethroids fenpropathrin (37.77 %) per cent and lamda cyhalothrin (47.97%) recovered. The number of pesticides detected was limited to only two (Gamma HCH and Phorate) at 0.01 µg g^{-1} level of fortification.

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 multiresidue estimation of pesticides form soil. In addition, several compounds were not at all recovered at the lowest level. Hence this method was rejected for the residue estimation from soil.

Similar reports were available on the poor recovery of clay loam soil spiked with organochlorine pesticides and polycyclic aromatic hydrocarbons at 0.4 µg g^{-1} level. The spiked samples were extracted with (1:1) mixture of dichloromethane and acetone as extractant and percentage recovery obtained was only 50-60 per cent (Scarlett *et al*., 1997).

Table 5. Percentage recoveries of pesticides at different levels of fortification using acetone as solvent (%)

Pesticides	% Recovery (1µg g^{-1})	% Recovery (0.5 µg g^{-1})	% Recovery (0.1 µg g^{-1})	% Recovery (0.05 µg g^{-1})	% Recovery (0.01 µg g^{-1})
Gamma HCH	57.78	53.11	33.89	31.93	24.28
Phorate	70.20	87.97	35.09	125.81	33.62
Methyl parathion	65.62	74.55	30.39	47.17	-
Malathion	78.70	93.16	161.39	-	-
Quinalphos	79.20	89.21	45.93	98.49	-
Profenophos	25.81	35.32	30.55	-	-
Ethion	55.09	53.11	26.66	-	-
Fenpropathrin	62.83	67.83	47.82	37.77	-
Lamda cyhalothrin	70.54	70.95	43.10	47.97	-

4.2.2 Extraction using acetonitrile as solvent

The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe) method using acetonitrile as the extractant was tried at five different levels. The percentage recovery obtained when soil samples fortified at five different levels (0.01, 0.05, 0.1, 0.5 and 1 $\mu g\ g^{-1}$) were presented in Table 6-10.

The mean recovery percentage of various compounds spiked at 1 $\mu g\ g^{-1}$ ranged from 84 to 98 per cent for all the compounds except for profenophos (24.22 %) and presented in Table 6. The recovery percentage of organophosphorus compounds ranged from 98.43 to 24.22, with acceptable RSD (12.48 - 2.06). The synthetic pyrethroids showed more than 90 per cent efficiency with fenpropathrin (93.51 %) and lamda cyhalothrin (98.09 %) recovery with calculated RSD value of 5.11 and 2.95, respectively. The mean recovery percentage of Gamma HCH was 84.33 per cent and the RSD worked out was 9.09.

The mean recovery percentage at 0.5 $\mu g\ g^{-1}$ level of fortification for various compounds ranged from 32.82 to 114.22 per cent (Table 7). When fortified at 0.5 $\mu g\ g^{-1}$ level, the mean recovery percentage for Gamma HCH was 43.99 per cent with RSD of 4.09. Among the pesticides fortified recovery of organophosphorus compounds were in the range of 32.82 to 114.22 per cent, with acceptable RSD (8.68 - 11.99). Among the synthetic pyrethroids, 101.09 per cent of fenpropathrin got recovered with RSD 5.80 and lamda cyhalothrin with 88.95 percentage recovery while the relative standard deviation worked out was 8.77.

The mean recovery percentage at 0.1 $\mu g\ g^{-1}$ level of fortification for various compounds ranged from 25.54 to 126.06 per cent (Table 8). When fortified at 0.1 $\mu g\ g^{-1}$ level, the mean recovery percentage for Gamma HCH was lowest 25.54 per cent with RSD of 12.86. The percentage recovery of organophosphorus compounds ranged from 35.54 to 126.06 per cent and profenophos with lowest recovery (35.54%). The calculated RSD was in the acceptable range (1.07 to 11.13%). Among the synthetic pyrethroids, 126.06 per cent of fenpropathrin and 99.05 per cent of lamda cyhalothrin recovered with RSD of 9.74 and 17.81 respectively.

The mean recovery percentage of various compounds spiked at 0.05 μg g^{-1} ranged from 13.44 to 83.73 per cent (Table 9). When fortified at 0.05μg g^{-1} level, the mean recovery percentage for Gamma HCH was lowest 13.44 per cent with RSD of 11.83. The recovery percentage of organophosphorus compounds ranged from 61.54 to 79.48 per cent and the lowest recovery was obtained for profenophos (24.04 %). The RSD calculated ranged from 1.33 to 13.37. Among the synthetic pyrethroids, fenpropathrin (83.73 %) and lamda cyhalothrin 34.46 per cent recovered with RSD values of 9.13 and 8.90, respectively.

The mean recovery percentage of various compounds spiked at 0.01μg g^{-1} ranged from 2.62 to 118.91 per cent (Table 10). When fortified at 0.01 μg g^{-1} level, the mean recovery percentage for Gamma HCH was lowest 2.62 per cent with RSD of 15.31. The recovery percentage of organophosphorus compounds ranged from 4.66 to 118.91 per cent with RSD of 5.09 to 26.29. Among the organophosphorus compounds, profenophos showed lowest percentage recovery 4.66 per cent and the calculated RSD was 26.29. Among the synthetic pyrethroids, 33.76 per cent of fenpropathrin and 15.32 per cent lamda cyhalothrin recovered with the relative standard deviation worked out as 8.04 and 16.31, respectively.

The method eventhough, effective in extracting all the compounds, the percentage recovery of several of the compounds are very low, especially at the lower levels of fortification. In this method satisfactory recovery percentage was obtained for all the compounds except for profenophos which showed the lowest recovery percentage. 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. Eventhough a satisfactory RSD value has been obtained for all the levels tried, this method was not effective in offering a satisfactory recovery of all the compounds fortified. Hence this was not adopted for multiresidue extraction of pesticides from soil.

Similar reports were available on poor recovery percentages of the insecticides spiked at 0.05 ppm and 0.01 ppm level in soil and extraction was carried out using acetonitrile as solvent.

Asensio-Ramos *et al.* (2010) tried this method for the determination of ten organophosphorus pesticides in different types of soils (forestal, ornamental and agricultural) and acceptable recovery values were obtained between 45 and 96 per cent for all the pesticides, except for malathion and malaoxon in ornamental and forest soil.

Table 6. Percentage recoveries in acetonitrile extraction at 1 μg g^{-1} level of fortification

Pesticides	Recovery (%)	SD	RSD (%)
Gamma HCH	84.33	7.67	9.09
Phorate	88.05	1.81	2.06
Methyl parathion	94.53	11.79	12.48
Malathion	98.43	4.92	5.00
Quinalphos	97.75	6.72	6.88
Profenophos	24.22	2.26	9.33
Ethion	92.48	5.00	5.41
Fenpropathrin	93.51	4.78	5.11
Lamda cyhalothrin	98.09	2.90	2.95

Table 7. Percentage recoveries in acetonitrile extraction at 0.5 μg g^{-1} level of fortification

Pesticides	Recovery (%)	SD	RSD (%)
Gamma HCH	43.99	1.80	4.09
Phorate	53.27	6.40	11.99
Methyl parathion	92.05	0.88	0.95
Malathion	92.05	9.72	10.56
Quinalphos	114.22	13.58	11.88
Profenophos	32.82	3.66	11.15
Ethion	98.81	8.58	8.68
Fenpropathrin	101.09	5.87	5.80
Lamda cyhalothrin	88.95	7.80	8.77

Table 8. Percentage recoveries in acetonitrile extraction at 0.1 µg g^{-1} level of fortification

Pesticides	Recovery (%)	SD	RSD (%)
Gamma HCH	25.54	3.28	12.86
Phorate	61.06	6.79	11.13
Methyl parathion	85.64	3.40	3.97
Malathion	64.66	4.04	6.25
Quinalphos	110.66	5.50	4.98
Profenophos	35.54	2.76	7.78
Ethion	118.72	1.27	1.07
Fenpropathrin	126.06	12.27	9.74
Lamda cyhalothrin	99.05	17.64	17.81

Table 9. Percentage recoveries in acetonitrile extraction at 0.05 µg g^{-1} level of fortification

Pesticides	Recovery (%)	SD	RSD (%)
Gamma HCH	13.44	1.60	11.83
Phorate	71.81	9.60	13.37
Methyl parathion	65.79	3.54	5.37
Malathion	61.54	0.82	1.33
Quinalphos	74.25	3.35	4.52
Profenophos	24.04	2.51	10.43
Ethion	79.48	6.60	8.30
Fenpropathrin	83.73	7.64	9.13
Lamda cyhalothrin	34.46	3.07	8.90

Table 10. Percentage recoveries in acetonitrile extraction at 0.01 µg g^{-1} level of fortification

Pesticides	Recovery (%)	SD	RSD (%)
Gamma HCH	2.62	0.40	15.31
Phorate	111.3	12.75	11.46
Methyl parathion	21.66	1.10	5.09
Malathion	118.91	9.19	7.73
Quinalphos	34.46	3.19	9.25
Profenophos	4.66	1.23	26.29
Ethion	27.28	1.87	6.85
Fenpropathrin	33.76	2.71	8.04
Lamda cyhalothrin	15.32	2.52	16.31

4.2.3 Extraction using acetonitrile acetone mixture as solvent

In this modified QuEChERS method, extraction was carried out using mixture of two solvents *viz.* acetonitrile and acetone (3:1) and the recovery percentage ranged between 80 and 110 per cent. The percentage recovery of each compound at different levels of fortification by this method is presented in Tables 11 to 15.

The mean recovery percentage of various compounds spiked at 1 µg g^{-1}, ranged from 85.77 to 128.28 per cent (Table 11). When fortified at 1 µg g^{-1} level, the mean recovery percentage for Gamma HCH was the highest 128.28 per cent with RSD of 2.55. The recovery percentage of organophosphorus compounds ranged from 85.77 to 108.35 per cent and the calculated RSD ranged from 0.62 to 11.32. Among the synthetic pyrethroids, 109.61 per cent of fenpropathrin and 104.63 per cent of lamda cyhalothrin were recovered with RSD of 9.07 and 2.36 respectively.

The mean recovery percentage of various compounds spiked at 0.5 µg g^{-1} level of fortification ranged from 63.72 to 114.90 per cent (Table 12). When fortified at 0.5 µg g^{-1} level, the mean recovery percentage for Gamma HCH was 90.76 per cent with RSD of 5.84. The recovery percentage of organophosphorus compounds ranged from 63.72 to 114.90 per cent with RSD of 5.03 to 13.28. Among the synthetic pyrethroids, fenpropathrin 97.15 per cent and lamda cyhalothrin 107.73 per cent recovered with RSD of 7.88 and 9.67 respectively.

The recovery percentage of various compounds spiked at 0.1 µg g^{-1} level of fortification ranged from 63.84 to 111.11 per cent (Table 13). When fortified at 0.1 µg g^{-1} level, the mean recovery percentage for Gamma HCH was 83.92 per cent with RSD of 9.04. The recovery percentage of organophosphorus compounds ranged from 63.84 to 111.11 per cent with RSD 1.67 to 13.61. Among the synthetic pyrethroids, 104.38 per cent of fenpropathrin and 110.81 per cent of lamda cyhalothrin were recovered with RSD of 4.55 and 4.28 respectively.

The mean recovery percentage of various compounds spiked at 0.05 µg g^{-1} ranged from 60.34 to 106.45 per cent (Table 14). When fortified at 0.05 µg g^{-1} level, the mean recovery percentage for Gamma HCH was 67.13 per cent with

RSD of 4.78. The recovery percentage of organophosphorus compounds ranged from (60.34 to 116.30 %) with RSD 0.82 to 5.79. Among the synthetic pyrethroids, 99.78 per cent of fenpropathrin and 106.75 per cent of lamda cyhalothrin recovered with RSD 1.14 and 6.0 respectively.

The mean recovery percentage at 0.01 $\mu g\ g^{-1}$ level of fortification for various compounds ranged from 47.05 to 106.73 per cent (Table 15). When fortified at 0.01 $\mu g\ g^{-1}$ level, the mean recovery percentage for Gamma HCH was 47.05 per cent with RSD of 11.10. The recovery percentage of organophosphorus compounds ranged from 34.60 to 101.70 with RSD of 2.32 to 18.23. Among the synthetic pyrethroids, fenpropathrin 94.87 per cent and lamda cyhalothrin 106.73 per cent recovered with RSD 4.01 and 2.25 respectively.

A satisfactory recovery has been obtained for almost all the compounds fortified. In addition, the reasonably 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 the method. All these clearly demonstrate the superiority of the method over other two methods tried. The method is cheap and less time consuming and hence was recommended for all the analytical procedures for the estimation of pesticide residues from soil (Asensio-Ramos *et al.*, 2010).

Similar study was reported for multiresidue method validation for the detection of 37 pesticides in soil matrix and samples were fortified with a known quantity of pesticides at two different levels(0.1 and 0.01$\mu g\ g^{-1}$). Method validation was accomplished with good linearity and satisfactory recoveries (70.5–110.4%) were obtained with 32 pesticides at both spiking levels. The developed method could be employed as a simple and cost-effective method for the routine detection and analysis of pesticides in soil samples (Park *et al.*, 2010).

Calibration curve

A calibration curve was prepared by the analysis of each of the pure standard solution of the pesticides at five different concentrations (0.01 $\mu g\ g^{-1}$, 0.05 $\mu g\ g^{-1}$ 0.1 $\mu g\ g^{-1}$, 0.5 $\mu g\ g^{-1}$, 1 $\mu g\ g^{-1}$) (Fig. 2-10). The calibration curves were best fitted to a linear curve with good linearity.

Table 11. Percentage recoveries in modified QuEChERS method at 1 $\mu g\ g^{-1}$ level of fortification

Pesticides	% Recovery	SD	% RSD
Gamma HCH	128.28	2.2	2.55
Phorate	85.77	0.79	0.62
Methyl parathion	105.92	11.99	11.32
Malathion	99.92	5.58	5.58
Quinalphos	95.47	8.36	8.76
Profenophos	107.69	7.29	6.77
Ethion	108.35	7.19	6.6
Fenpropathrin	109.61	9.94	9.07
Lamda cyhalothrin	104.63	2.47	2.36

Table 12. Percentage recoveries in modified QuEChERS method at 0.5 $\mu g\ g^{-1}$ level of fortification

Pesticides	% Recovery	SD	% RSD
Gamma HCH	90.76	5.28	5.84
Phorate	63.72	3.20	5.03
Methyl parathion	106.13	11.04	10.40
Malathion	80.47	5.77	7.18
Quinalphos	106.56	12.36	11.60
Profenophos	114.90	2.48	2.16
Ethion	90.17	11.97	13.28
Fenpropathrin	97.15	7.65	7.88
Lamda cyhalothrin	107.73	10.41	9.67

Table13. Percentage recoveries in modified QuEChERS method at 0.1 μg g^{-1} level of fortification

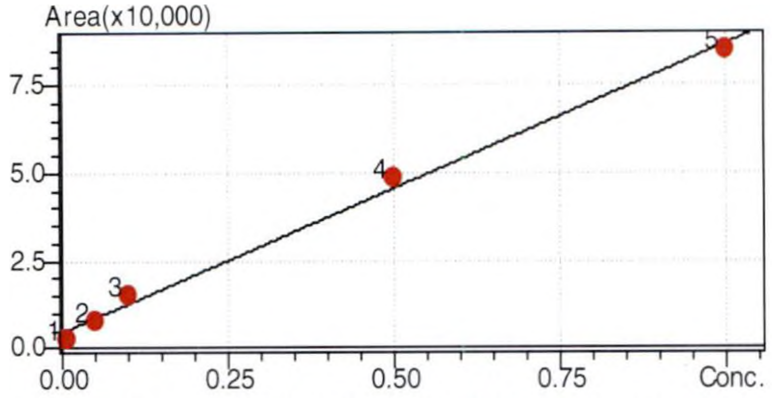
Pesticides	% Recovery	SD	% RSD
Gamma HCH	83.92	7.78	9.04
Phorate	63.84	1.06	1.67
Methyl parathion	109.68	6.32	5.77
Malathion	76.02	6.73	8.85
Quinalphos	104.68	14.25	13.61
Profenophos	111.11	5.65	5.09
Ethion	101.19	9.64	9.53
Fenpropathrin	104.38	4.75	4.55
Lamda cyhalothrin	110.81	4.75	4.28

Table 14. Percentage recoveries in modified QuEChERS method at 0.05 μg g^{-1} level of fortification

Pesticides	% Recovery	SD	%RSD
Gamma HCH	67.13	2.88	4.78
Phorate	60.34	1.18	1.77
Methyl parathion	94.85	5.27	5.56
Malathion	62.12	1.42	2.28
Quinalphos	116.30	0.95	0.82
Profenophos	106.45	6.17	5.79
Ethion	84.66	0.04	0.04
Fenpropathrin	99.78	1.14	1.14
Lamda cyhalothrin	106.75	6.49	6.0

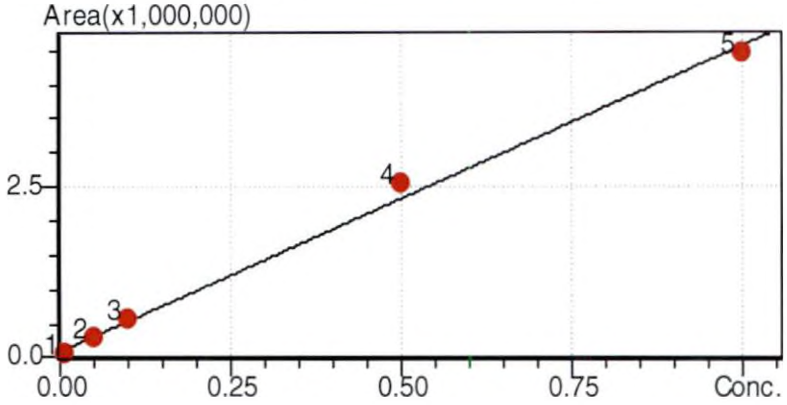
Table 15. Percentage recoveries in modified QuEChERS method at 0.01 μg g^{-1} level of fortification

Pesticides	% Recovery	SD	% RSD
Gamma HCH	47.05	5.22	11.10
Phorate	34.60	6.31	18.23
Methyl parathion	99.80	4.34	4.34
Malathion	101.71	71.49	17.80
Quinalphos	80.50	0.08	1.0
Profenophos	68.28	7.44	10.89
Ethion	82.20	2.82	2.32
Fenpropathrin	94.87	3.83	4.01
Lamda cyhalothrin	106.73	2.41	2.25



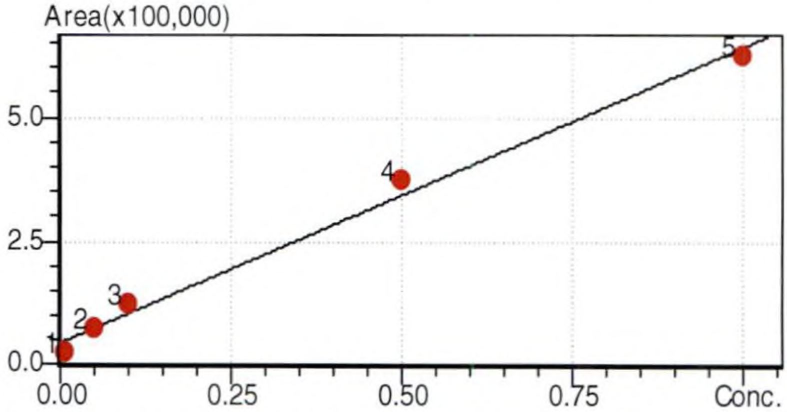
Y = aX + b, a = 82018.77, b = 4649.329, R^2 = 0.995, R = 0.997

Fig. 2. Calibration curve of Phorate



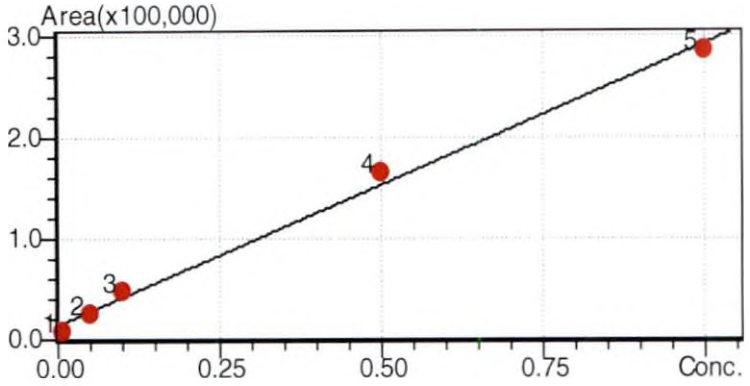
Y = aX + b, a = 4471387, b = 93196.42, R^2 = 0.995, R = 0.997

Fig. 3. Calibration curve of Gamma HCH



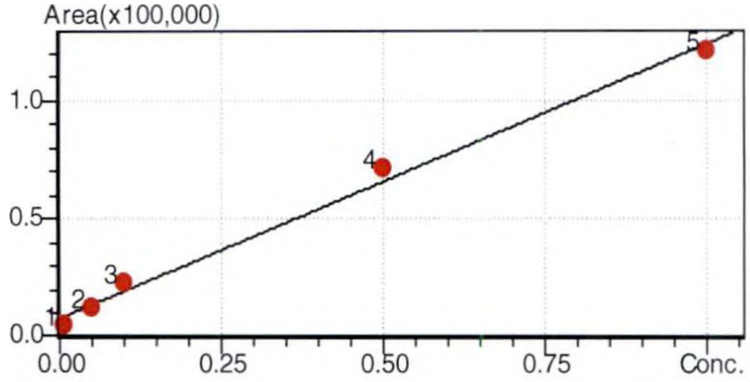
Y = aX + b, a = 595405.7, b = 45196.04, R^2 = 0.991, R = 0.995

Fig. 4. Calibration curve of Methyl parathion



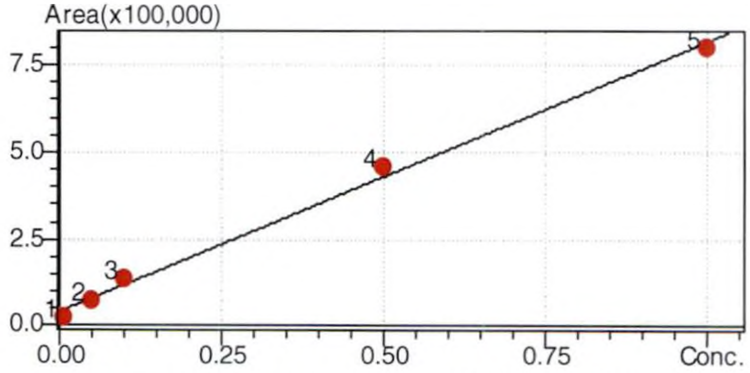
$Y = aX + b,\ a = 277349.8,\ b = 15425.69,\ R^2 = 0.994,\ R = 0.997$

Fig. 5. Calibration curve of Malathion



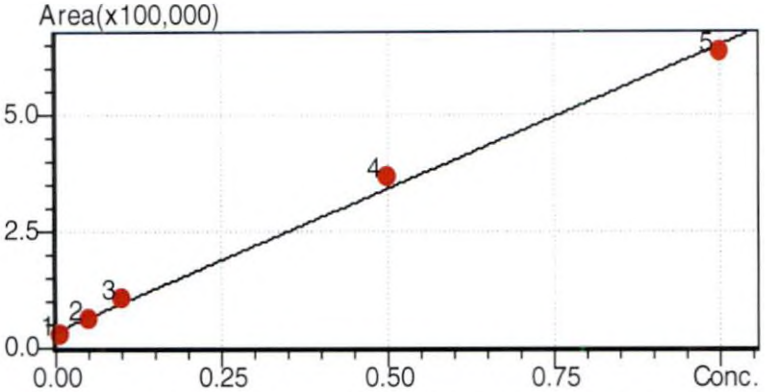
$Y = aX + b,\ a = 116217.0,\ b = 7739.979,\ R^2 = 0.994,\ R = 0.997$

Fig. 6. Calibration curve of Quinalphos



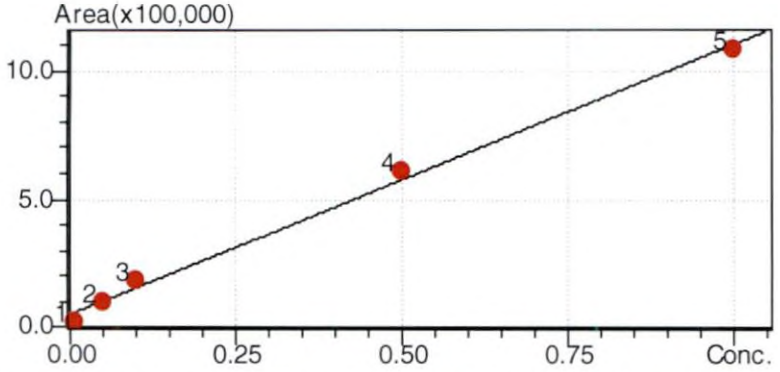
$Y = aX + b,\ a = 775107.5,\ b = 42856.62,\ R^2 = 0.995,\ R = 0.997$

Fig. 7. Calibration curve of Profenophos



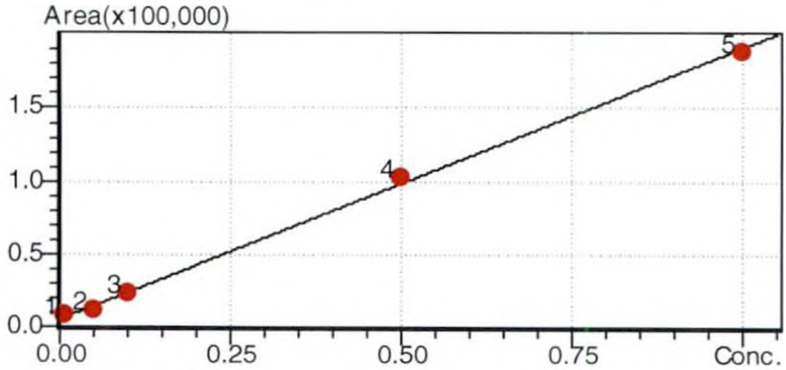
Y = aX + b, a = 613759.1, b = 38153.36, R^2 = 0.995, R = 0.997

Fig.8.Calibration curve of Ethion



Y = aX + b, a = 1051908, b = 51492.75, R^2 = 0.995, R = 0.997

Fig.9.Calibration curve of Fenpropathrin



Y = aX + b, a = 185188.8, b = 6151.639, R^2 = 0.998, R = 0.999

Fig.10.Calibration curve of Lamda cyhalothrin

4.3 PHYSICO-CHEMICAL PARAMETERS OF SOIL

The physico chemical properties of the control samples from the three locations were analysed and it was observed that the soils were rich in organic carbon (2.11-2.20 %) and organic matter content (3.63 - 3.79 %) (Table 16). Kattappana and Nedumkandam soils have near neutral pH (6.04-6.94) and Pampadaumpara soils were acidic (5.72). The nutrient status revealed that the soils were high in nitrogen (366.91 - 702.46 kg ha^{-1}) content. The phosphorus status varied in the three locations and the lowest amount was reported in Kattappana soils. More than 40 per cent water holding capacity was observed in soils from the three locations and the dehydrogenase enzyme activity was highest in Pampadumpara soils followed by Kattappana and the lowest was reported in Nedumkandam.

4.3 MONITORING OF PESTICIDE RESIDUES IN SOIL SAMPLES

In the present study, pesticide residues in soil samples from cardamom plantations were analysed to assess the extent of pollution due to the usage of pesticides at levels above LOQ (0.01 ppm). Cardamom plantations, five each in Kattappana, Pampadumpara and Nedumkandam Panchayats, from which soil samples were collected before and after spraying at two different depths (0-15 cm and 15-30 cm) for a period of six months (December-May) (Plate. 2).

Calibration curve

Pesticide standards were purchased from Sigma -Aldrich and stock solutions were prepared using pesticide grade solvents. From the stock solutions, working standards were prepared. Calibration curves of standards were prepared from the working standards and were used to evaluate the linearity of the Gas Liquid Chromatograph and were used for calculation of residues in the samples.

The samples were estimated for the presence organochlorine pesticides like alpha endosulphan, beta endosulphan, endosulphan sulphate, p, p'- DDT, p, p'-DDE, lindane, alpha HCH, beta HCH, delta HCH and organophosphorus compounds like phorate, methyl parathion, malathion, chlorpyriphos, quinalphos, ethion, profenophos and synthetic pyrethroids like fenpropathrin, lamda cyhalothrin, cyfluthrin, cypermethrin, bifenthrin and fenvalerate.

Table 16. Physico-chemical properties of the soil

Parameters	Kattappana	Pampadumpara	Nedumkandam
Coarse sand (%)	33.74	36.09	38.43
Fine sand (%)	10.05	9.62	9.18
Silt (%)	11.09	11.21	11.32
Clay (%)	41.91	40.35	38.29
pH	6.04	5.72	6.94
EC (dS m^{-1})	0.198	0.142	0.263
CEC (c mol (+) kg^{-1})	9.3	9.0	9.8
Percentage base saturation (%)	38.39	35.61	40.15
Available N (kg ha^{-1})	366.91	589.56	702.46
Available P (kg ha^{-1})	34.98	113.75	72.79
Available K (kg ha^{-1})	769.80	769.06	751.20
Available S (kg ha^{-1})	18.66	41.06	114.8
Organic C (%)	2.11	2.20	2.11
Organic matter (%)	3.63	3.79	3.63
Exchangeable Ca (c mol kg^{-1})	1.66	1.82	1.98
Exchangeable Mg (c mol kg^{-1})	0.93	1.07	1.22
Water holding capacity (%)	41.74	45.40	41.06
Dehydrogenase (μg g^{-1}) activity	0.15	0.64	0.30

a) Soil sample collection from Pampadumpara

b) Soil sample collection from Nedumkandam

Plate 2. Soil sample collection from cardamom plantations

The data on residues of insecticides persisting at 0-15 cm and 15-30 cm depth for six months starting from December 2010 to May 2011 in the three locations are presented in Tables 17 to 40.

The data on the residues present in soil before and after spraying during the month December are presented in Tables 17-20. The residues detected in samples collected from Kattappana, at 0-15 cm depth before spraying were phorate (0.01 ppm) and endosulphan sulphate (0.05 ppm). Methyl parathion (0.05 ppm) and phorate (0.03 ppm) were detected in samples collected after spraying from the above location. At the lower depth, samples before spraying were found to contain residues of phorate (0.01 ppm) and endosulphan sulphate (0.01 ppm). Methyl parathion (0.03 ppm) was found in samples collected after spraying.

In the case of samples collected from Pampadumpara, residues of ethion (0.01 ppm) and p, p'- DDT (0.03 ppm) were found at 0-15 cm depth before spraying, while the samples collected after spraying were found contaminated with residues of quinalphos (0.12 ppm), ethion (0.07 ppm), profenophos (0.05 ppm), methyl parathion (0.08 ppm), fenpropathrin (0.46 ppm), cyfluthrin (0.03 ppm), fenvalerate (0.02 ppm) in addition to the residues found before spraying. At the lower depth before spraying samples were detected with residues of p, p'-DDT (0.01 ppm) and after spraying the samples were detected with residues of quinalphos (0.06 ppm), profenophos and methyl parathion (0.02 ppm), ethion (0.05 ppm), p, p'- DDT (0.03 ppm) and fenpropathrin (0.21 ppm) during December month. The data throws suspect on the wide use of quinalphos, fenpropathrin and methyl parathion for plant protection by the selected farmers in the location.

The samples collected from the Nedumkandam Panchayat at 0-15 cm depth before spraying were found contaminated with residues of phorate (0.01 ppm), quinalphos (0.01 ppm) and after spraying the samples were found with residues of methyl parathion (0.02 ppm) and fenpropathrin (0.06 ppm). At the lower depth before spraying no residues were found and the samples collected after spraying were found with residues of methyl parathion (0.02 ppm). The data shows the wide usage of methyl parathion and fenpropathrin by the farmers in the location.

The data on the residues present in soil before and after spraying during January month are presented in Tables 21-24. The residues detected in the samples collected from Kattappana, before spraying at 0-15 cm depth were phorate (0.01 ppm), chlorpyriphos (0.03 ppm), beta endosulphan (0.007 ppm), endosulphan sulphate (0.014 ppm), p, p'-DDT (0.01 ppm) while residues of phorate and chlorpyriphos (0.03 ppm), quinalphos and methyl parathion (0.07 ppm), endosulphan sulphate (0.08 ppm) and profenophos (0.004 ppm) were detected after spraying. At the lower depth the samples were found to contain residues of chlorpyriphos and phorate (0.01 ppm) before spraying while samples collected after spraying were found with residues of quinalphos (0.02 ppm), methyl parathion (0.03 ppm), p, p' -DDT (0.01 ppm) in addition to the residues detected before spraying and from the data it can be suspected that the insecticide phoate, quinalphos and methyl parathion were applied for plant protection by the selected farmers during the month January.

In the case of Pampadumpara, samples collected before spraying were found with residues of chlorpyriphos, ethion and alpha endosulphan at 0.01 ppm level, endosulphan sulphate (0.03 ppm), cypermethrin and fenvalerate (0.02 ppm) at 0-15cm depth and the samples collected after spraying were found contaminated with residues of quinalphos (0.10 ppm) and fenvalerate (0.14 ppm) in addition to the residues found before spraying. At 15-30 cm depth before spraying residues of phorate (0.01 ppm) were detected and samples after spraying were found to contain residues of quinalphos (0.05ppm). The data supports the suspect of the wide use of quinalphos and fenpropathrin for plant protection by the selected farmers in the location.

The samples collected from Nedumkandam, before spraying were found contaminated with residues of chlorpyriphos, profenophos, cypermethrin and fenvalerate (0.01 ppm), quinalphos (0.02 ppm), p, p'-DDT(0.05 ppm), fenpropathrin (0.03 ppm), while the samples after spraying were found with residues of chlorpyriphos (0.05 ppm), quinalphos (0.08 ppm), profenophos (0.21

ppm), p, p' -DDT (0.05 ppm), fenpropathrin (0.02 ppm), cypermethrin (0.01 ppm) and lamda cyhalothrin (0.01 ppm). At 15- 30 cm depth before spraying the samples were found with residues of phorate (0.01 ppm), while residues of chlorpyriphos (0.01 ppm), quinalphos (0.04 ppm), profenophos (0.02 ppm) were detected in samples after spraying. From the data on residues it can be suspected that the insecticides chlorpyriphos, quinalphos, profenophos, fenpropathrin, cypermethrin and lamda cyhalothrin were used for plant protection by the selected farmers during the month January.

The data on the residues present in soil before and after spraying during February month are presented in (Table 25-28). The samples collected from Kattappana at 0-15cm depth before spraying detected with residues of chlorpyriphos (0.01 ppm), profenophos (0.04 ppm), beta endosulphan (0.01 ppm), p, p' –DDT (0.01 ppm), while residues of phorate (0.07 ppm), chlorpyriphos (0.07 ppm), profenophos (0.08 ppm), fenvalerate (0.15 ppm) were found in the samples after spraying. At the lower depth, the samples before spraying were found contaminated with residues of chlorpyriphos (0.01 ppm) and profenophos (0.02 ppm), while the samples after spraying were detected with residues of phorate (0.04 ppm), chlorpyriphos (0.02 ppm) and profenophos (0.05 ppm). From the level of residues present in samples before and after spraying it can be suspected that farmers were using phorate, chlorpyriphos, profenophos and fenvalerate for plant protection during February month.

The samples collected from Pampadumpara before spraying at 0-15 cm depth were detected with residues of phorate and chlorpyriphos (0.02 ppm), fenvalerate (0.01 ppm), while the samples after spraying were found contaminated with residues of phorate (0.08 ppm), chlorpyriphos (0.06 ppm) and fenvalerate (0.05 ppm). At the lower depth, 15-30 cm before spraying the samples were found with residues of phorate (0.02 ppm) and fenvalerate (0.01 ppm), while residues of phorate (0.07 ppm) and chlorpyriphos (0.05 ppm) were detected in samples after spraying . From the residue data during the month February it can be suspected that farmers were using phorate, chlorpyriphos and fenvalerate for plant protection in the selected location.

The samples collected from Nedumkandam at 0-15 cm depth before spraying were found with residues of phorate (0.02 ppm) and fenvalerate (0.02 ppm), while the samples after spraying were contaminated with residues chlorpyriphos (0.07 ppm) in addition to the residues detected before spraying. At the lower depth, samples were found with residues of phorate (0.02 ppm) and fenvalerate (0.01 ppm) before and after spraying. From the higher level of residues of chlorpyriphos found in the samples after spraying it can suspect that farmers were widely using chlorpyriphos in the selected location during February month.

The data on the residues present in soil before and after spraying during March are presented in Table 29-32. The samples collected from Kattappana before spraying at 0-15cm, were found with residues of chlorpyriphos, endosulphan sulphate and quinalphos (0.02 ppm), profenophos (0.01 ppm), methyl parathion (0.04 ppm), while the samples after spraying were contaminated with residues of phorate (1.30 ppm), quinalphos (0.15 ppm), profenophos (0.20 ppm), ethion (0.11 ppm), alpha endosulphan (1.50 ppm), beta endosulphan (1.71 ppm), endosulphan sulphate (0.78 ppm). At 15-30 cm depth before spraying the samples were found contaminated with residues of chlorpyriphos, profenophos and quinalphos (0.01 ppm), endosulphan sulphate and methyl parathion (0.02 ppm), while residues of phorate (0.70 ppm), quinalphos and ethion (0.03 ppm), profenophos (0.07 ppm), alpha endosulphan (0.60 ppm), beta endosulphan (0.50 ppm), endosulphan sulphate (0.05 ppm) were detected in samples after spraying. From the residue data it can be suspected that farmers are widely using phorate, quinalphos, profenophos, ethion and endosulphan for plant protection during the month March.

The samples collected from Pampadumpara, before spraying were found with residues of phorate (0.05 ppm), quinalphos, p, p' -DDT and profenophos (0.02 ppm), ethion (0.03 ppm), endosulphan sulphate (0.05 ppm), while the samples collected after spraying were detected with residues of phorate (1.0 ppm), quinalphos (0.15 ppm), profenophos (0.21 ppm), alpha endosulphan (1.08 ppm), beta endosulphan (1.60 ppm), endosulphan sulphate (1.23 ppm). At the lower depth, samples were found contaminated with residues of quinalphos, phorate, p, p' -DDT and profenophos (0.01 ppm) and endosulphan sulphate (0.03 ppm), ethion (0.02 ppm), while the samples collected after spraying detected with residues of phorate (0.50 ppm), quinalphos (0.05 ppm), profenophos (0.08 ppm), alpha endosulphan (0.10 ppm), beta endosulphan (0.06 ppm), endosulphan sulphate (0.10 ppm). From the data on residue it can suspected that phorate, quinalphos, profenophos and endosulphan are being widely used by the selected farmers during the month March.

The samples collected from Nedumkandam, before spraying at 0-15 cm was found with residues of chlorpyriphos and alpha endosulphan (0.01 ppm), cyfluthrin (0.02 ppm), quinalphos (0.03 ppm), p,p –DDT, methyl parathion and beta endosulphan (0.04 ppm) fenpropathrin (0.08 ppm) and endosulphan sulphate (1.26 ppm), while the samples after spraying were found contaminated with residues of phorate (2.27 ppm), quinalphos (0.02 ppm), profenophos (0.28 ppm), alpha endosulphan (0.20 ppm), beta endosulphan (0.50 ppm), endosulphan sulphate (018 ppm). At the lower depth, before spraying residues of quinalphos and alpha enddosulphan (0.01 ppm), methyl parathion, beta endosulphan, p, p-DDT (0.02 ppm), fenpropathrin (0.04 ppm), endosulphan sulphate (0.05 ppm) were found while the samples after spraying were found with residues of phorate (1.94 ppm), profenophos and endosulphan sulphate (0.05 ppm), methyl parathion (0.01 ppm), alpha endosulphan (0.20 ppm), beta endosulphan (0.10 ppm). From the residue data it can be suspected that the wide usage of phorate, profenophos and endosulphan in plant protection by the selected farmers during the month March.

The data on the residues present in soil before and after spraying during the month April are presented in Table 33-36. The samples collected from Kattappana, before spraying at 0-15 cm depth were detected with residues of phorate and methyl parathion (0.05 ppm), quinalphos (0.03 ppm), profenophos (0.01 ppm), beta endosulphan (0.04 ppm) while residues of chlorpyriphos (0.90 ppm), quinalphos (0.08 ppm), profenophos (0.17 ppm), beta endosulphan (0.10

ppm), endosulphan sulphate (0.51 ppm), cypermethrin (0.24 ppm) were found in samples after spraying. The residues of phorate, quinalphos, beta endosulphan (0.02 ppm), profenophos (0.01 ppm), methyl parathion (0.03 ppm) were detected at 15-30 cm depth before spraying, while the samples after spraying were found contaminated with residues of quinalphos and profenophos (0.05 ppm), beta endosulphan (0.07 ppm) during the month March. The residue data showed that the selected farmers were used chlorpyriphos, profenophos, quinalphos, cypermethrin and endosulphan for plant protection during the month April.

In the case of samples collected from Pampadumpara before spraying at 0-15cm depth were detected with residues of chlorpyriphos and alpha endosulphan (0.02 ppm), ethion, profenophos, methyl parathion, beta endosulphan (0.01 ppm), endosulphan sulphate and cypermethrin (0.03 ppm) while the samples after spraying were found contaminated with residues of chlorpyriphos (0.17 ppm), quinalphos (0.11 ppm), profenophos (1.22 ppm), methyl parathion (0.02 ppm), beta endosulphan (0.30 ppm), endosulphan sulphate (0.45 ppm). At the lower depth 15-30 cm before spaying the samples were found with residues of chlorpyriphos and endosulphan sulphate (0.02 ppm), profenophos, methyl parathion, alpha endosulphan and cypermethrin (0.01 ppm), while residues of chlorpyriphos (0.50 ppm), quinalphos (0.01 ppm), profenophos (0.26 ppm), methyl parathion (0.01 ppm), beta endosulphan (0.02 ppm), endosulphan sulphate (0.08 ppm) were detected in samples after spraying and from the data it can be suspected that farmers were widely using of chlorpyriphos, quinalphos, profenophos and endosulphan for plant protection.

The samples collected from Nedumkandam at 0-15 cm before spraying were found with residues of phorate and quinalphos (0.05 ppm), chlorpyriphos and methyl parathion (0.02 ppm), endosulphan sulphate (0.01 ppm), cyfluthrin (0.06 ppm), fenvalerate (0.10 ppm) while the samples after spraying were found contaminated with residues of chlorpyriphos (1.38 ppm), quinalphos (0.07 ppm), profenophos and methyl parathion (0.06 ppm). At the lower depth before spraying, the samples were found with residues of phorate (0.02 ppm), quinalphos (0.03 ppm), chlorpyriphos, methyl parathion, endosulphan sulphate (0.01 ppm), cyfluthrin (0.04 ppm), fenvalerate (0.05 ppm), while the samples after spraying were detected with residues of chlorpyriphos (0.70 ppm), quinalphos, profenophos and methyl parathion (0.05 ppm). From the residue data it can be suspected that farmers were widely using chlorpyriphos, quinalphos, profenophos and methyl parathion for plant protection during April month.

The data on the residues present in soil before and after spraying during the month May are presented in Table 37-40. The samples collected from Kattapana, before spraying at 0-15 cm depth was detected with residues of methyl parathion (0.05 ppm), alpha endosulphan (0.02 ppm), beta endosulphan (0.13 ppm), endosulphan sulphate (0.42 ppm), while the samples after spraying were found to contain residues of phorate (0.86 ppm), chlorpyriphos (0.13 ppm), quinalphos (0.23 ppm), endosulphan sulphate (0.85 ppm) and cypermethrin (0.22 ppm). At 15-30 cm depth before spraying the samples were detected with residues of methyl parathion (0.03 ppm), alpha endosulphan (0.02 ppm), beta endosulphan (0.05 ppm), endosulphan sulphate (0.10 ppm), while the samples after spraying were found contaminated with residues of chlorpyriphos (0.74 ppm), profenophos (0.05 ppm), quinalphos (0.07 ppm), endosulphan sulphate (0.10 ppm), cypermethrin (0.15 ppm). From the residue data it can be suspected that the selected farmers were widely using phorate, chlorpyriphos, quinalphos and endosulphan for plant protection during the month May.

The samples collected from Pampadumpara before spraying at 0-15 cm depth were found contaminated with residues of chlorpyriphos, quinalphos, ethion, endosulphan sulphate (0.02 ppm) profenophos, methyl parathion, alpha endosulphan, beta endosulphan (0.01 ppm), while the samples after spraying were found contaminated with residues of chlorpyriphos (0.07 ppm), quinalphos (0.49 ppm), profenophos (1.22 ppm), methyl parathion (0.02 ppm), beta endosulphan (0.30 ppm), endosulphan sulphate (0.64 ppm). At the lower depth before spraying residues of chlorpyriphos, quinalphos and endosulphan sulphate (0.02 ppm) profenophos, ethion, methyl parathion, alpha endosulphan (0.01 ppm) were detected while the residues detected after spraying were chlorpyriphos (0.03 ppm), quinalphos and methyl parathion (0.01 ppm), profenophos and ethion (0.33

ppm), endosulphan sulphate (0.09 ppm). From the residue data it can be suspected that the selected farmers were widely using chlorpyriphos, quinalphos, profenophos and endosulphan for plant protection in the location.

In the case of samples collected from Nedumkandam, at 0-15 cm depth before spraying residues of phorate and quinalphos (0.03 ppm), profenophos (0.05 ppm), methyl parathion (0.02 ppm) were detected while the samples after spraying were found contaminated with residues of chlorpyriphos (1.43 ppm), profenophos (0.05 ppm), ethion (0.33 ppm), methyl parathion (0.10 ppm). At the lower depth residues of phorate and quinalphos (0.02 ppm), profenophos (0.03 ppm) and methyl parathion (0.01 ppm) were found before spraying while the samples after spraying maximum contamination was found with residues of chlorpyriphos (0.92 ppm), quinalphos (0.05 ppm), methyl parathion (0.06 ppm). From the residue data it can be suspected that the farmers are widely using chlorpyriphos, ethion, methyl parathion for plant protection during the month May.

Table 17: Pesticide residues in soil (ppm) at 0-15cm depth before spraying for the month December

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.01	BDL	0.01
Chlorpyriphos	BDL	BDL	BDL
Quinalphos	BDL	BDL	0.01
Profenophos	BDL	BDL	BDL
Ethion	BDL	0.01	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	0.05	BDL	BDL
p, p'- DDT	BDL	0.03	ND
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

Table 18. Pesticide residues in soil (ppm) at 0-15 cm depth after spraying for the month December

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.03	BDL	BDL
Chlorpyriphos	BDL	BDL	BDL
Quinalphos	BDL	0.12	BDL
Profenophos	BDL	0.05	BDL
Ethion	BDL	0.07	BDL
Methyl parathion	0.05	0.08	0.02
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	0.05	BDL	BDL
p,p'- DDT	BDL	0.04	BDL
Fenpropathrin	BDL	0.46	0.06
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	0.03	0.004
Fenvalerate	BDL	0.02	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 19. Pesticide residues in soil (ppm) at 15-30cm depth before spraying for the month December

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.01	BDL	BDL
Chlorpyriphos	BDL	BDL	BDL
Quinalphos	BDL	BDL	BDL
Profenophos	BDL	BDL	BDL
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	0.01	BDL	BDL
p,p'- DDT	BDL	0.01	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

Table 20. Pesticide residues in soil (ppm) at 15-30 cm depth after spraying for the month December

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.01	BDL	BDL
Chlorpyriphos	BDL	BDL	BDL
Quinalphos	BDL	0.06	BDL
Profenophos	BDL	0.02	BDL
Ethion	BDL	0.05	BDL
Methyl parathion	0.03	0.02	0.02
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	BDL	BDL	BDL
p,p'- DDT	BDL	0.03	BDL
Fenpropathrin	BDL	0.21	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	0.02	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 21. Pesticide residues in soil(ppm) before spraying at 0-15 cm depth for the month January

Pesticides detected	Kattappana	Pampadumpara	Nedumkandm
Phorate	0.01	BDL	BDL
Chlorpyriphos	0.03	0.01	0.01
Quinalphos	BDL	BDL	0.02
Profenophos	BDL	BDL	0.01
Ethion	BDL	0.01	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	0.01	BDL
Beta endosulphan	0.007	BDL	BDL
Endosulphan sulphate	0.014	0.03	BDL
p,p'- DDT	0.01	BDL	0.05
Fenpropathrin	BDL	BDL	0.03
Cypermethrin	BDL	0.02	0.01
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	0.02	0.01

Table 22. Pesticide residues in soil (ppm) after spraying at 0-15 cm depth for the month January

Pesticides detected	Kattappana	Pampadumpara	Nedunkandam
Phorate	0.03	BDL	BDL
Chlorpyriphos	0.03	0.01	0.05
Quinalphos	0.07	0.10	0.08
Profenophos	0.004	BDL	0.21
Ethion	BDL	0.01	BDL
Methyl parathion	0.07	BDL	BDL
Alpha endosulphan	BDL	0.01	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	0.08	0.03	BDL
p, p'- DDT	0.01	BDL	0.05
Fenpropathrin	BDL	BDL	0.02
Cypermethrin	BDL	0.02	0.01
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	0.14	BDL
Lamda cyhalothrin	BDL	BDL	0.01

*BDL - Below Detectable Level

Table 23. Pesticide residues in soil (ppm) before spraying at 15-30cm depth for the month January

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.01	0.01	0.01
Chlorpyriphos	0.01	BDL	BDL
Quinalphos	BDL	BDL	BDL
Profenophos	BDL	BDL	BDL
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	BDL	BDL	BDL
p,p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

Table 24. Pesticide residues in soil (ppm) after spraying at 15-30 cm depth for the month January

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.01	BDL	BDL
Chlorpyriphos	BDL	BDL	0.01
Quinalphos	0.02	0.05	0.04
Profenophos	BDL	BDL	0.02
Ethion	BDL	BDL	BDL
Methyl parathion	0.03	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	BDL	BDL	BDL
p,p'- DDT	0.01	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 25. Pesticide residues in soil (ppm) before spraying at 0-15 cm depth for the month February

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	0.02	0.02
Chlorpyriphos	0.01	0.02	BDL
Quinalphos	BDL	BDL	BDL
Profenophos	0.04	BDL	BDL
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	0.01	BDL	BDL
Endosulphan sulphate	BDL	BDL	BDL
p, p'- DDT	0.01	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	0.01	0.02
Lamda cyhalothrin	BDL	BDL	BDL

Table 26. Pesticide residues in soil (ppm) after spraying at 0-15 depth cm for the month February

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.07	0.08	0.02
Chlorpyriphos	0.07	0.06	0.07
Quinalphos	BDL	BDL	BDL
Profenophos	0.08	BDL	BDL
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	BDL	BDL	BDL
p, p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	0.15	0.05	0.02
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 27. Pesticide residues in soil(ppm) before spraying at 15-30cm depth for the month February

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	0.02	0.02
Chlorpyriphos	0.01	BDL	BDL
Quinalphos	BDL	BDL	BDL
Profenophos	0.02	BDL	BDL
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	BDL	BDL	BDL
p, p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	0.01	0.01
Lamda cyhalothrin	BDL	BDL	BDL

Table 28. Pesticide residues in soil (ppm) after spraying at 15-30 cm depth for the month February

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.04	0.07	0.02
Chlorpyriphos	0.02	0.05	BDL
Quinalphos	BDL	BDL	BDL
Profenophos	0.05	BDL	BDL
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	BDL	BDL	BDL
p, p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	0.02
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 29. Pesticide residues in soil (ppm) before spraying at 0-15 cm depth for the month March

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	0.05	BDL
Chlorpyriphos	0.02	BDL	0.01
Quinalphos	0.02	0.02	0.03
Profenophos	0.01	0.02	BDL
Ethion	BDL	0.03	BDL
Methyl parathion	0.04	BDL	0.04
Alpha endosulphan	BDL	BDL	0.01
Beta endosulphan	BDL	BDL	0.04
Endosulphan sulphate	0.02	0.05	1.26
p, p'- DDT	BDL	0.02	0.04
Fenpropathrin	BDL	BDL	0.08
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	0.02
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

Table 30. Pesticide residues in soil (ppm) after spraying at 0-15 cm depth for the month March

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	1.30	1.0	2.27
Chlorpyriphos	BDL	BDL	BDL
Quinalphos	0.15	0.15	0.02
Profenophos	0.20	0.21	0.28
Ethion	0.11	BDL	BDL
Methyl parathion	0.01	BDL	BDL
Alpha endosulphan	1.50	1.08	0.20
Beta endosulphan	1.71	1.60	0.50
Endosulphan sulphate	0.78	1.23	0.18
p, p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 31. Pesticide residues in soil (ppm) before spraying at 15-30 cm depth for the month March

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	0.01	BDL
Chlorpyriphos	0.01	BDL	BDL
Quinalphos	0.01	0.01	0.01
Profenophos	0.01	0.01	BDL
Ethion	BDL	0.02	BDL
Methyl parathion	0.02	BDL	0.02
Alpha endosulphan	BDL	BDL	0.01
Beta endosulphan	BDL	BDL	0.02
Endosulphan sulphate	0.02	0.03	0.05
p, p'- DDT	BDL	0.01	0.02
Fenpropathrin	BDL	BDL	0.04
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

Table 32. Pesticide residues in soil (ppm) after spraying at 15-30 depth cm for the month March

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.70	0.50	1.94
Chlorpyriphos	BDL	BDL	BDL
Quinalphos	0.03	0.05	BDL
Profenophos	0.07	0.08	0.05
Ethion	0.03	BDL	BDL
Methyl parathion	BDL	BDL	0.01
Alpha endosulphan	0.60	0.10	0.20
Beta endosulphan	0.50	0.06	0.10
Endosulphan sulphate	0.05	0.10	0.05
p, p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 33. Pesticide residues in soil (ppm) before spraying at 0-15 cm depth for the month April

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.05	BDL	0.05
Chlorpyriphos	BDL	0.02	0.02
Quinalphos	0.03	BDL	0.05
Profenophos	0.01	0.01	BDL
Ethion	BDL	0.01	BDL
Methyl parathion	0.05	0.01	0.02
Alpha endosulphan	BDL	0.02	BDL
Beta endosulphan	0.04	0.01	BDL
Endosulphan sulphate	BDL	0.03	0.01
p, p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	0.03	BDL
Cyfluthrin	BDL	BDL	0.06
Fenvalerate	BDL	BDL	0.10
Lamda cyhalothrin	BDL	BDL	BDL

Table 34. Pesticide residues in soil (ppm) after spraying at 0-15 cm depth for the month April

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	BDL	BDL
Chlorpyriphos	0.90	0.17	1.38
Quinalphos	0.08	0.11	0.07
Profenophos	0.17	1.22	0.06
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	0.02	0.06
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	0.10	0.30	BDL
Endosulphan sulphate	0.51	0.45	BDL
p, p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	0.24	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 35. Pesticide residues in soil (ppm) before spraying at 15-30 cm depth for the month April

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.02	BDL	0.02
Chlorpyriphos	BDL	0.02	0.01
Quinalphos	0.02	BDL	0.03
Profenophos	0.01	0.01	BDL
Ethion	BDL	BDL	BDL
Methyl parathion	0.03	0.01	0.01
Alpha endosulphan	BDL	0.01	BDL
Beta endosulphan	0.02	BDL	BDL
Endosulphan sulphate	BDL	0.02	0.01
p,p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	0.01	BDL
Cyfluthrin	BDL	BDL	0.04
Fenvalerate	BDL	BDL	0.05
Lamda cyhalothrin	BDL	BDL	BDL

Table 36. Pesticide residues in soil (ppm) after spraying at 15-30 cm depth for the month April

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	BDL	BDL
Chlorpyriphos	BDL	0.50	0.70
Quinalphos	0.05	0.01	0.05
Profenophos	0.05	0.26	0.05
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	0.01	0.05
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	0.07	0.02	BDL
Endosulphan sulphate	BDL	0.08	BDL
p,p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 37. Pesticide residues in soil (ppm) before spraying at 0-15 depth cm for the month May

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	BDL	0.03
Chlorpyriphos	BDL	0.02	BDL
Quinalphos	BDL	0.02	0.03
Profenophos	BDL	0.01	0.05
Ethion	BDL	0.02	ND
Methyl parathion	0.05	0.01	0.02
Alpha endosulphan	0.02	0.01	BDL
Beta endosulphan	0.13	0.01	BDL
Endosulphan sulphate	0.42	0.02	BDL
p, p'- DDT	ND	BDL	BDL
Fenpropathrin	ND	BDL	BDL
Cypermethrin	ND	BDL	BDL
Cyfluthrin	ND	BDL	BDL
Fenvalerate	ND	BDL	BDL
Lamda cyhalothrin	ND	BDL	BDL

Table 38. Pesticide residues in soil (ppm) after spraying at 0-15 cm depth for the month May

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	0.86	BDL	BDL
Chlorpyriphos	0.13	0.07	1.43
Quinalphos	0.23	0.49	BDL
Profenophos	BDL	1.22	0.05
Ethion	BDL	BDL	0.33
Methyl parathion	BDL	0.02	0.10
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	0.30	BDL
Endosulphan sulphate	0.85	0.64	BDL
p,p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	0.22	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

Table 39. Pesticide residues in soil (ppm) before spraying at 15-30 cm depth for the month May

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	BDL	0.02
Chlorpyriphos	BDL	0.02	BDL
Quinalphos	BDL	0.02	0.02
Profenophos	BDL	0.01	0.03
Ethion	BDL	0.01	BDL
Methyl parathion	0.03	0.01	0.01
Alpha endosulphan	0.02	0.01	BDL
Beta endosulphan	0.05	BDL	BDL
Endosulphan sulphate	0.10	0.02	BDL
p,p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

Table 40. Pesticide residues in soil (ppm) after spraying at 15 -30 cm depth for the month May

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	BDL	BDL
Chlorpyriphos	0.74	0.03	0.92
Quinalphos	0.07	0.01	0.05
Profenophos	0.05	0.33	BDL
Ethion	BDL	0.33	BDL
Methyl parathion	BDL	0.01	0.06
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	0.10	0.09	BDL
p,p'- DDT	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	0.15	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level

4.3.1 Monthwise mean residues of pesticides in soil at 0-15 cm depth

The pesticides most frequently detected were phorate, chlorpyriphos, quinalphos, profenophos, ethion and methyl parathion and the monthwise mean residue levels presented in Table 41 (Fig.11).

The monthwise mean residue level of phorate revealed that the highest amount of residue was observed during March and it was significantly different from all other months. It may be due to the fact that for the timely management of root grub, one of the major pest of cardamom, farmers are applying the insecticide during the starting of first generation of life cycle of the insect. On an average small cardamom consumes 100 kg $ha^{-1}year^{-1}$ of phorate in Kerala (Usha, 2007).

Chlorpyriphos, the organophosphorus insecticide widely used in pest management in cardamom. The highest mean residue level of chlorpyriphos was recorded during April and it was significantly different from the residue level present at all other months. No residues of chlorpyriphos detected during the months December and January. The residue level was lowest during the months February and March. The higher rate of adsorption may be the reason for higher residue level of the insecticide eventhough higher rainfall (268 mm) was reported during the month April. The residues of chlorpyriphos persist for a longer period in the lower layers of soil with half lives ranging from 53.75 to 235.77 days (Rekha, 2005). Due to higher persistence of the insecticide in soil ecosystem residues were detected in samples collected before and after spraying.

Quinalphos residues were most frequently detected and the highest level was observed during the month December and there was no significant difference between the residue level present in various months. No residues were detected during January and February.

Among the organophosphorus insecticides, highest level of residues were found with profenophos which account for 0.200 $\mu g\ g^{-1}$ and it was detected during the month April and was significantly different from the all other months. The critical examination of mean residue data revealed that the residue level present in each month was significantly different. Profenophos residues were detected during the period of five months, with the exception during January.

The highest level of ethion was found during the month December and the amount of residue was comparatively lower and it was significantly different from the residue level recorded during the month April. It was observed that the mean residue level of ethion was minimum during the other months.

In the case of methyl parathion mean residue level persisting at various months did not show any significant difference and the highest level was reported during April. The mean residue levels at various months were on par.

The mean residue level of alpha endosulphan revealed that highest level of residues was observed during the month May and it was significantly different from the other months (Fig.12) Table 42. Beta endosulphan mean residue was detected during the month of December at a higher amount of 0.003 $\mu g\ g^{-1}$. Endosulphan sulphate was detected at the highest level in May and the mean residue level was significantly different from the mean residue detected during the month March and December.

4.3.2 Locationwise mean residues of pesticides in soil at 0-15 cm depth

In location wise comparison, (Fig.13) (Table 43) the mean residue level of phorate was highest in Nedumkandam and it accounted for 0.195 $\mu g\ g^{-1}$. It was observed that the mean residue level of phorate in Nedumkandam was significantly different from Pampadumpara and it was on par with Kattappana. Phorate residues were detected at a lower level (0.034 $\mu g\ g^{-1}$) in Pampadumpara.

Statistical analysis of the data shows that the mean residue level of chlorpyriphos was highest in Pampadumpara (0.990 $\mu g\ g^{-1}$) which was significantly different from the mean residue level of the other two locations. It was obvious from the data that the mean residue level of chlorpyriphos in Nedumkandam and Kattappana are on par.

Analysis of the data shows that there was no significant difference in the use pattern of quinalphos in the selected three locations. The maximum mean residue level was found in Pampadumpara (0.053 $\mu g\ g^{-1}$) followed by Kattappana and Nedumkandam. Similarly no significant difference was observed in the use pattern of profenophos, with highest amount of mean residue was observed in Pampadumpara (0.117 $\mu g\ g^{-1}$) followed by Kattappana and lowest amount of residues were found in Nedumkandam.

Statistical analysis of the data revealed that the mean residue level of ethion was found at a lower level compared to other compounds. Highest amount of residue was detected in Nedumkandam (0.022 $\mu g\ g^{-1}$) which was significantly different from the mean residue observed in Pampadumpara and it was on par with mean residue level in Kattappana. The mean residue level recorded in Kattappana and Pampadumpara are on par.

There was no significant difference in the usage of the insecticide methyl parathion and mean residue level in the three locations were on par.

There was no significant difference in the use pattern of organochlorine insecticides in the selected locations (Fig. 14). Alpha endosulphan was found at a higher level in Kattappana (0.076 $\mu g\ g^{-1}$) which was on par with mean residue level observed in Pampadumpara and it was significantly different from that of Nedumkandam.

In the case of beta endosulphan the highest level of residue was detected in Kattappana (0.130 $\mu g\ g^{-1}$). The mean residue level at Pampadumpara was found significantly different from the residues found in Nedumkandam. Endosulphan sulphate was detected at a higher amount in Kattappana (0.528 $\mu g\ g^{-1}$) and was significantly different from Pampadumpara location (0.184 $\mu g\ g^{-1}$). Similarly the mean residue level found in Pampadumpara was significantly different from that of Nedumkandam.

In most of the samples maximum residue level was found with residues of organophosphorus insecticides like chlorpyriphos, quinalphos, phorate, profenophos, ethion and methyl parathion. Among organochlorine insecticides alpha endosulphan, beta endosulphan and endosulphan sulphate were found with a lower relative occurance in the samples. The number of samples contaminated with synthetic pyrethroids was also relatively less. The presence of multiresidues in soil samples indicates that farmers are following the application of mixtures of insecticides or spraying at frequent interval of 15-22 days. The pesticide load was maximum in surface soil. From the residue data it was found that the relative overall contamination was more in the surface soil compared to sub surface soil in the selected locations.

In small cardamom, twelve insecticide and six fungicide sprays per year are required (Shetty *et al.*, 2008). The organophosphorus compounds were widely used by the farmers because of their easy availability in the local market and are less expensive. Among these compounds phorate and chlorpyriphos are directly applied to soil in order to manage root grub infestation in cardamom.

It is evident that eventhough endosulphan was banned, it's easy availability in the local market and effectiveness in plant protection drive farmers to use the chemical in pest management widely. Synthetic pyrethroids like cypermethrin, cyfluthrin and lamda cyhalothrin residues were reported at a very lower level. Synthetic pesticides, because of their immediate knock-down effect on crop pests and shorter period of persistence in the environment leave, residues are detected at a lower level in soil (Mueller *et al.*, 1990).

The half lives for cypermethrin was 5.6-7.6 days. It was found that the dissipation half lives in top soil were linearly correlated with rain, sunshine and vapour pressure and soil properties such as sorption and microbial activity may have a stronger influence on degradation rate of cypermethrin in soil. Compared to other pesticides due to its faster degradation rate the amount of residue detected was at a minimum level (ETN, 1996).

Table 41. Monthwise mean residues (μg g^{-1}) of organophosphorus pesticides in soil at 0-15 cm depth

Month	Phorate	Chlorpyriphos	Quinalphos	Profenophos	Ethion	Methyl parathion
M1 (Dec)	0.070	0.000	0.045	0.005	0.009	0.020
M2 (Jan)	0.000	0.000	0.000	0.000	0.000	0.000
M3 (Feb)	0.010	0.010	0.000	0.010	0.000	0.010
M4 (Mar)	0.170	0.019	0.040	0.050	0.000	0.010
M5 (April)	0.050	0.090	0.031	0.200	0.001	0.020
M6 (May)	0.001	0.023	0.040	0.003	0.000	0.002
CD	0.34	0.31	0.04	0.13	0.03	0.01

Table 42. Monthwise mean residues of organochlorine pesticides (μg g^{-1}) in soil at 0-15 cm depth

Month	Alpha endosulphan	Beta endosulphan	Endosulphan sulphate
M1(Dec)	0.000	0.003	0.014
M2(Jan)	0.000	0.000	0.000
M3(Feb)	0.000	0.000	0.000
M4(Mar)	0.000	0.000	0.020
M5(April)	0.000	0.000	0.000
M6(May)	0.006	0.000	0.040
CD	0.17	0.21	0.39

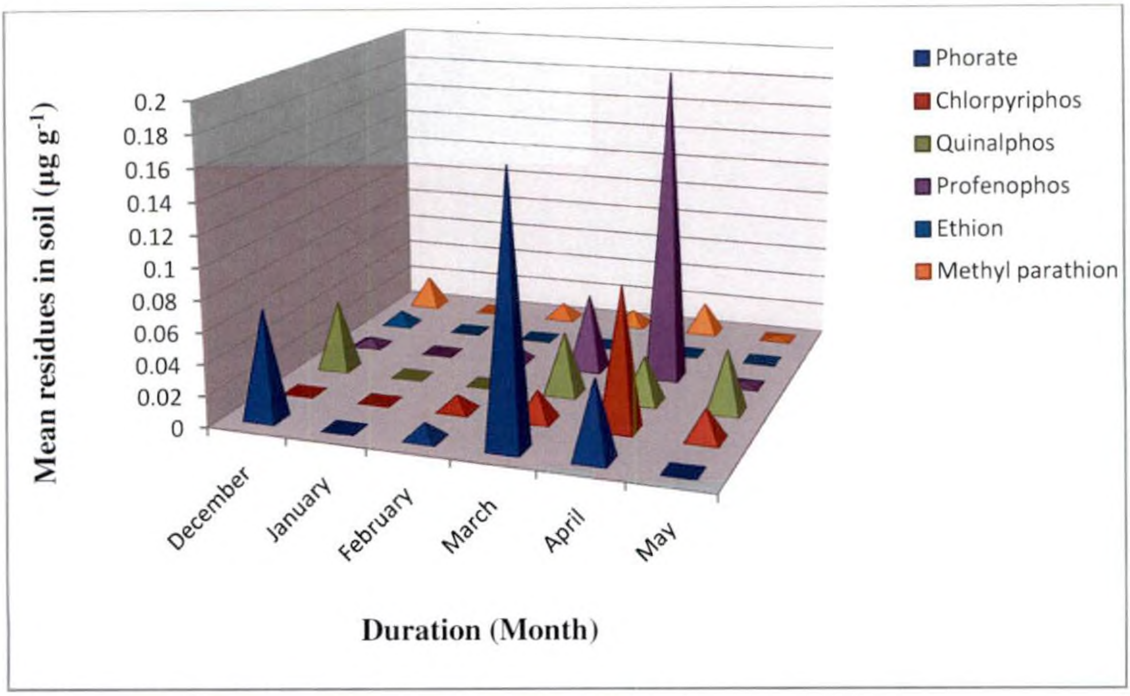


Fig. 11. Month wise mean residues of organophosphorus insecticides in soil at 0-15 cm depth

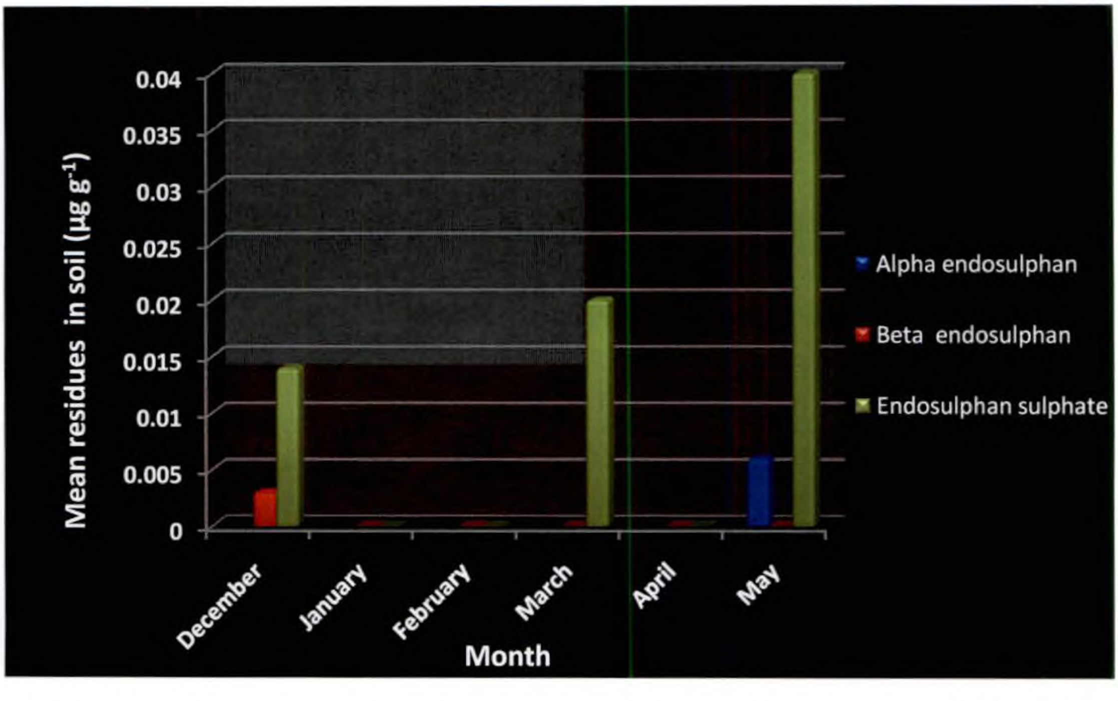


Fig. 12. Month wise mean residues of organochlorine insecticides in soil at 0-15 cm depth

Table 43. Locationwise mean residues of organophosphorus pesticides (μg g^{-1}) in soil at 0-15 cm depth

Location	Phorate	Chlorpyriphos	Quinalphos	Profenophos	Ethion	Methyl parathion
LI	0.110	0.079	0.034	0.065	0.005	0.013
L2	0.034	0.990	0.053	0.117	0.007	0.009
L3	0.195	0.195	0.018	0.037	0.022	0.013
CD	0.24	0.22	0.03	0.09	0.02	0.01

(L1 – Kattappana, L2- Pampadumpara, L3 – Nedumkandam)

Table 44. Locationwise mean residues of organochlorine pesticides (μg g^{-1}) in soil at 0-15 cm depth

Location	Alpha endosulphan	Beta endosulphan	Endosulphan sulphate
LI	0.076	0.130	0.528
L2	0.040	0.078	0.184
L3	0.014	0.035	0.093
CD	0.12	0.14	0.28

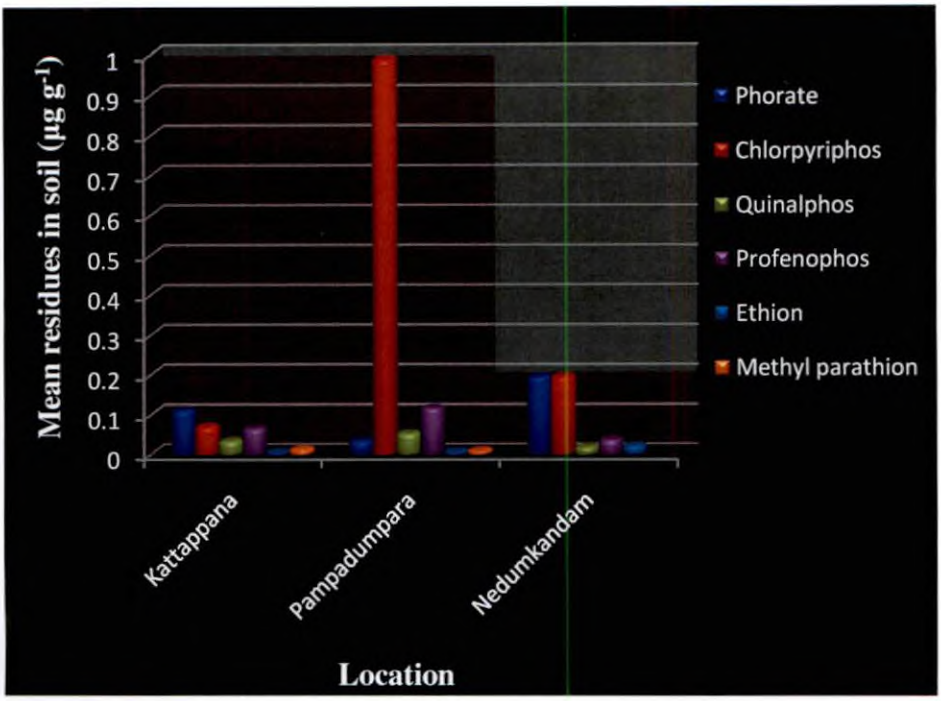


Fig.13.. Location wise mean residues of organophosphorus insecticides in soil at 0-15 cm depth

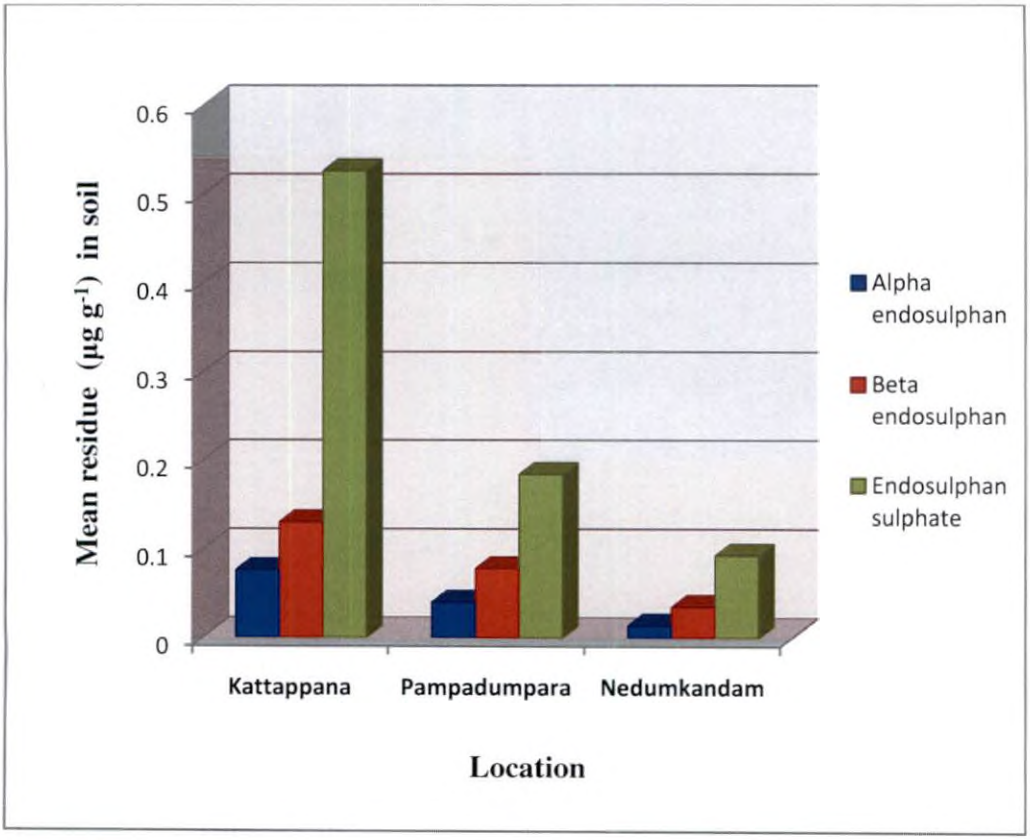


Fig.14. Location wise mean residues of organochlorine insecticides in soil at 0-15 cm depth

4. 4. Monitoring of pesticide residues in water samples

Water samples were collected from water resources in the cardamom plantations like pond, streams, well and rivers. 2.5 l of water samples were collected from the selected cardamom plantations before and after spraying of insecticides for a period of six months. The water samples were analysed for the presence of a total 23 pesticides and none of the samples were contaminated with pesticide residues (Chromatogram of standard insecticide mixture 0.5 ppm Appendix II).

Pesticide residue limits in water for monitoring or regulatory purposes should be established at a level not lower than the LOQ (Limit of Quantification) of a practical analytical method (EPA, 2002). The limits of pesticides in drinking water prescribed by Indian Government are 0.5 $\mu g\ l^{-1}$ for total pesticides and 0.1 $\mu g\ l^{-1}$ for individual pesticide (GOI, 2002).

Dissolved organic matter and suspended solid should be taken into account on pesticide contamination in water. Factors that affect a pesticide's ability to contaminate water include its water solubility, the distance from an application site to a body of water, weather, soil type, presence of a growing crop and the method of application of the chemical (Pedersen, 1997).

From the results it can be concluded that the water bodies are not polluted due to pesticide spraying presumably due to a higher adsorption on to sediments or colloids, high organic carbon status of soil, poor leaching from soil or due to a high degradation rate of pesticides in aquatic ecosystem system. So the hazard due to aquatic pollution by pesticides usage is not a matter of concern in the cardamom ecosystem.

Table 45. Pesticide residues in water samples for the period December 2010- May 2011(ppm)

Pesticides detected	Kattappana	Pampadumpara	Nedumkandam
Phorate	BDL	BDL	BDL
Chlorpyriphos	BDL	BDL	BDL
Quinalphos	BDL	BDL	BDL
Profenophos	BDL	BDL	BDL
Ethion	BDL	BDL	BDL
Methyl parathion	BDL	BDL	BDL
Alpha endosulphan	BDL	BDL	BDL
Beta endosulphan	BDL	BDL	BDL
Endosulphan sulphate	BDL	BDL	BDL
Alpha HCH	BDL	BDL	BDL
Beta HCH	BDL	BDL	BDL
Delta HCH	BDL	BDL	BDL
Lindane	BDL	BDL	BDL
Malathion	BDL	BDL	BDL
p, p'- DDE	BDL	BDL	BDL
p, p' -DDT	BDL	BDL	BDL
p, p'- DDD	BDL	BDL	BDL
Fenpropathrin	BDL	BDL	BDL
Cypermethrin	BDL	BDL	BDL
Cyfluthrin	BDL	BDL	BDL
Fenvalerate	BDL	BDL	BDL
Lamda cyhalothrin	BDL	BDL	BDL

*BDL - Below Detectable Level (0.5 ppb)

4.5 DISSIPATION STUDY OF IMIDACLOPRID IN SOIL

A field experiment was conducted to study the dissipation kinetics of imidacloprid in the loamy forest soils in cardamom plantation (Plate. 3). The experiment was conducted at the plantations of Indian Caradmom Research Institute, Myladumpara. The study also envisaged the effect of cropping and dosage on dissipation of imidacloprid. The persistence was studied under cropped and non-cropped situations at three different doses of imidacloprid. The results and observations of the study are presented under the following heads.

4.5.1. Pre-treatment analysis

Physical and chemical characteristics of soil used for the study were determined as per standard procedures and are presented in Table 46. The soil was forest loam with 2.5 per cent organic carbon content. The soil pH and EC values were found to be 4.85 and EC 0.231 d S m^{-1}, respectively

4.5.2 *Recovery of imidacloprid in soil*

The percentage recovery of imidacloprid with different extractants was tried and extraction using acetonitrile was found superior. The percent recovery obtained in acetone extraction was only 60 per cent while in the acetonitrile extraction (QuEChERS method) higher percentage recovery (84-92%) was obtained and this method was adopted for the estimation of imidacloprid in soil.

4.5.2.1 *Extraction efficiency of imidacloprid using acetonitrile*

The recovery percentage of imidacloprid at various fortification levels ranged from 48.39 to 95.59 (Table 47). When spiked at the lowest level of 0.01 $\mu g\ g^{-1}$, the mean recovery percentage was 54.52 with RSD of 1.16. At 0.05 $\mu g\ g^{-1}$ level the mean recovery percentage was found to be 48.39 and the relative standard deviation worked out was 2.76. At 0.1 $\mu g\ g^{-1}$ level, an average of 73.08 per cent residue recovered with RSD of 1.04. At 0.5 $\mu g\ g^{-1}$, the mean recovery percentage was 76.22 per cent with RSD of 2.03. At higher level of fortification, 1 $\mu g\ g^{-1}$, 95.59 per cent of the residue recovered with RSD of 0.46.

Table 46. Physico chemical properties of the experimental soil

Parameters	
Coarse sand (%)	33.24
Fine sand (%)	10.46
Silt (%)	11.12
Clay (%)	42.06
CEC (c mol (+) kg^{-1})	9.86
Percentage base saturation (%)	46.38
pH	4.85
EC (dS m^{-1})	0.231
Available N (kg ha^{-1})	1204.92
Available P (kg ha^{-1})	384.09
Available K (kg ha^{-1})	746
Available S (kg ha^{-1})	75.60
Organic C (%)	3.85
Organic matter (%)	6.64
Exchangeable Ca (c mol kg^{-1})	2.06
Exchangeable Mg (c mol kg^{-1})	1.71
Water holding capacity (%)	54.96
Dehydrogenase activity in control plot (µg g^{-1})	0.10
Dehydrogenase activity in imidacloprid treated soil (µg g^{-1})	0.18

Plate 3. General view of the experimental field

The recovery of imidacloprid was much better when the QuEChERS method of extraction and clean up was adopted. The recovery percentage ranged from 84.44 to 92.63 per cent (Table 48). At 0.01 μg g^{-1} fortification level, the mean recovery of imidacloprid was 84.44 per cent with an RSD of 2.01. At 0.05 μg g^{-1}, the mean recovery was 86.80 per cent with a relative standard deviation of 1.32. At 0.1 μg g^{-1} level fortification, 83.64 per cent of the residue recovered with an RSD of 0.77. At 0.5 μg g^{-1} and 1 μg g^{-1} level of fortification the mean recovery percentage was 89.76 and 92.63 with RSD of 1.18 and 0.72 respectively. Due to the satisfactory recovery, RSD value and easiness, this method was selected for the estimation of imidacloprid in soil.

Calibration curve

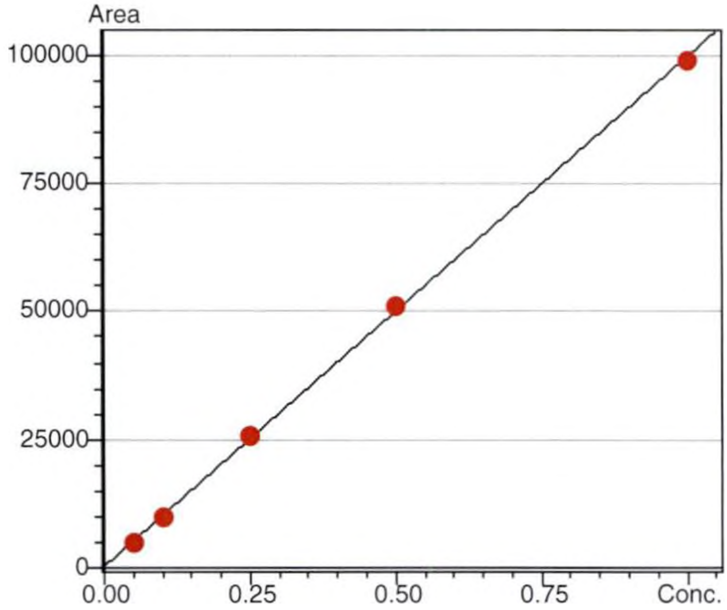
A calibration curve was prepared by plotting different concentration (0.01 μg g^{-1} , 0.05 μg g^{-1} , 0.1μg g^{-1} , 0.5 μg g^{-1} and 1μg g^{-1}) against peak area. Good linearity was found within the range of 0.01-1.0 μg g^{-1} concentration Fig.15.

Table 47. Percentage recoveries of imidacloprid in acetonitrile extraction

Level of fortification	Recovery (%)	SD	RSD (%)
1 μg g^{-1}	95.59	0.44	0.46
0.5 μg g^{-1}	76.22	1.55	2.03
0.1 μg g^{-1}	73.08	0.76	1.04
0.05 μg g^{-1}	48.39	1.34	2.76
0.01 μg g^{-1}	54.52	0.63	1.16

Table 48. Percentage recoveries of imidacloprid in QuEChERS method

Level of fortification	Recovery (%)	SD	RSD (%)
1 μg g^{-1}	92.63	0.67	0.72
0.5 μg g^{-1}	89.76	1.07	1.18
0.1 μg g^{-1}	83.64	0.65	0.77
0.05 μg g^{-1}	86.80	1.04	1.32
0.01 μg g^{-1}	84.44	1.73	2.01



Y = aX + b, a = 99278.58, b = 413.9816, R^2 = 0.999, R = 0.999

Fig.15 .Calibration curve of Imidacloprid

4.5.3 Residues of imidacloprid in 0-15 cm soil depth

The data on residues of imidacloprid persisting in soil at 0-15 cm depth in different treatments are presented in Table 49.

In T_1 the lower dose (0.05 ml l^{-1}) applied in non-cropped situation, samples collected at 2 hours after spraying recorded an average initial deposit of 0.130 $\mu g\ g^{-1}$. After one day, 23.85 per centage of the residues got dissipated and the level reached 0.099 $\mu g\ g^{-1}$. On the fifth day, 62.88 per centage of the residues got degraded and the residue level became 0.048 $\mu g\ g^{-1}$. On seventh day onwards the residue reached below detectable level with a calculated half life of 4.09 days.

In T_2 (recommended dose 0.10 ml l^{-1}) in non-cropped situation the initial residue (2 hours after spraying) was found to be 0.351 $\mu g\ g^{-1}$. On the first day 23.93 per centage of residues got dissipated and the level reached to 0.267 $\mu g\ g^{-1}$. Samples collected on fifth day after insecticide application reported a residue level of 0.125 $\mu g\ g^{-1}$ with 64.39 per centage of residues getting dissipated. On tenth day 82.45 per centage of residues got dissipated and the residue level reached 0.061 $\mu g\ g^{-1}$ and from fifteenth day onwards residues reached below detectable level with half life of 3.98 days.

In T_3 (double the recommended dose of 0.20 ml l^{-1}) in non-cropped situation, the mean initial residue at 2 hours after spraying was 1.02 $\mu g\ g^{-1}$. On the first day the residue level got reduced to 0.932 $\mu g\ g^{-1}$ with 8.62 per centage getting dissipated. On fifth day 57.45 per centage of residues got dissipated and the residue level reached 0.434 $\mu g\ g^{-1}$. When samples were collected on tenth day, 86.27 per centage of residues got dissipated and the residue level became 0.140 $\mu g\ g^{-1}$ and on 20th day, 95.09 per centage of residues got dissipated and the mean residue level obtained was 0.050 $\mu g\ g^{-1}$ with a half life of 4.25 days.

In T_4, the lowest dose (0.05 ml l^{-1}) applied in cropped situation, the mean initial residue was found to be 0.121 $\mu g\ g^{-1}$. On first day the residue level got dissipated to 0.101 $\mu g\ g^{-1}$ with dissipation per centage of 16.53. On the fifth day 74.38 percentage of the residues got dissipated and the mean residue level got reduced to 0.031 $\mu g\ g^{-1}$ and from seventh day onwards the residue level reached below detectable level. The half life of the treatment was 2.55 days.

In T_5, Imidacloprid was applied at the rate of (0.10 ml l^{-1}) in cropped situation resulted in an average initial deposit of 0.336 µg g^{-1}. On the first day, the residue level got dissipated to 0.204 µg g^{-1} with 39.28 per cent dissipation. The residues degraded further to 67.26 per cent on the fifth day resulting in a mean residue level of 0.11 µg g^{-1}. On seventh day, 83.63 per centage of the initial deposit got dissipated with average residue level of 0.05 µg g^{-1}. No residue were detected from the tenth day after spraying. The half life of the treatment was 2.95 days.

In T_6, when samples collected two hours after application of imidacloprid at 0.20 ml l^{-1} in cropped situation, an initial deposit of 0.944 µg g^{-1} was observed. On the first day, the residue level was found to be 0.854 µg g^{-1}, with 9.53 per centage of dissipation. On fifth day, the residue level was 0.343 µg g^{-1} whereby 63.67 per cent of the initial deposit got dissipated. On tenth day, the residue level was 0.082 µg g^{-1} whereby 91.31 per cent of the initial deposit got dissipated. On fifteenth day, 93.54 per cent of the residue got dissipated with a mean residue level of 0.061 µg g^{-1}. No residue was detected from the 20th day after insecticide application. The half life of the treatment was 3.34 days.

The samples of control plots *ie*, soil without the application of insecticide showed no residues and were totally free of co-extractives also, when analysed in HPLC. The data on residues of imidacloprid persisting in top 15 cm layer under different treatments showed that the persistence was maximum in non cropped condition with half life of 4.25 days, when double the recommended dose was applied. The degradation rate of imidacloprid in cropped situation was faster with half life of 2.95 days when the recommended dose was applied. Thus the half life of imidacloprid in soil was short and can be considered safe from the point of environmental contamination .

The degradation of imidacloprid was reported to be mediated mainly by biotic agents and this could be the reason for faster degradation in cropped condition. The higher persistence in non-cropped situation could presumably be due to the low pH of soil, relatively high proportion of clay and absence of rhizosphere effect.

As the organic carbon levels and laminar silicate clay content in the soil increases, the potential for imidacloprid to leach would decrease (Cox *et al.*, 1998). The lower half life observed in soil under cropped condition might be due to the biotic and or abiotic factors of the soil. The higher organic matter status of the soil might have provided a more favourable environment for proliferation of the soil micro-organisms or aeration of the soil and these factors would have contributed to a still faster degradation in cropped situation.

The enhanced degradation observed in the present study under cropped situation could be the combined effect of crop root system, high enzyme activity and higher microbial activity of the soil. Scholz *et al.* (1992) observed that imidacloprid degraded more rapidly under vegetation with half life of 48 days, versus 190 days without vegetation. The persistence in vegetated areas is decreased through plant (Rouchaud *et al.*, 1994) and microbial uptake and metabolism (Krohn and Hellpointner, 2002).

In the present study it was found that the dissipation was independent of initial deposit of imidacloprid and the half life obtained was much less compared to the previous reports and fits well with the time required for the knock-down effect of imidacloprid which is 24-48 hours (Sanyal *et al.*, 2006). The dissipation of imidacloprid in soil followed first order dissipation, wherein the residues dissipated proportionately with time. Imidacloprid has a medium to high sorption tendency for soil (Krohn and Hellpointner, 2002). The half life obtained in the present study corroborates well with the previous report when imidcloprid was applied in Northeastern India in tea soil at termiticidal rate at 240 g a.i ha^{-1} and the half life of imidacloprid ranged between 2.01-2.06 days irrespective of application rates (Sanyal *et al.*, 2006). Soils with highest organic matter and clay content exhibited the strongest affinity for imidacloprid and least kinetic behaviour (Jenog *et al.*, 2006).

From the forgoing discussion it can be summarised that the presence of crop can significantly enhance the degradation of imidacloprid in soil. The lowest dose shown faster degradation and presence of organic matter coupled with a low pH of the soil hastens the process of degradation. Application of dissolved organic carbon appears to reduce imidacloprid sorption by competing with the pesticide for sorption sites on the soil surface (Flores-Cespedes *et al.*, 2002*)*. Ping *et al*. (2010) reported that imidacloprid adsorption was usually higher under lower pH and temperature at same condition.

Table 49. Mean residue of imidacloprid (ppm) in soil at 0-15 cm depth

Days	Imidacloprid residue (ppm)								
	0	1	3	5	7	10	15	20	$t_{1/2}$
T_1(0.05ml l^{-1} in bare soil)	0.130	0.099 (23.85)	0.070 (46.15)	0.048 (62.88)	BDL	BDL	BDL	BDL	4.09
T_2(0.10ml l^{-1} in bare soil)	0.351	0.267 (23.93)	0.180 (48.72)	0.125 (64.39)	0.090 (74.36)	0.061 (82.45)	BDL	BDL	3.98
T_3(0.20ml l^{-1} in bare soil)	1.02	0.932 (8.62)	0.697 (31.67)	0.434 (57.45)	0.260 (74.51)	0.140 (86.27)	0.080 (92.16)	0.050 (95.09)	4.25
T_4 (0.05ml l^{-1} in cropped soil)	0.121	0.101 (16.53)	0.073 (39.67)	0.031 (74.38)	BDL	BDL	BDL	BDL	2.55
T_5(0.10 ml l^{-1} in cropped soil)	0.336	0.204 (39.28)	0.147 (56.25)	0.110 (67.26)	0.055 (83.63)	BDL	BDL	BDL	2.95
T_6(0.20ml l^{-1} in cropped soil)	0.944	0.854 (9.53)	0.592 (37.29)	0.343 (63.67)	0.180 (80.93)	0.082 (91.31)	0.061 (93.54)	BDL	3.34
T_7(Control)	-	-	-	-	-	-	-	-	-

- Figures in parenthesis represent percentage decrease in residues

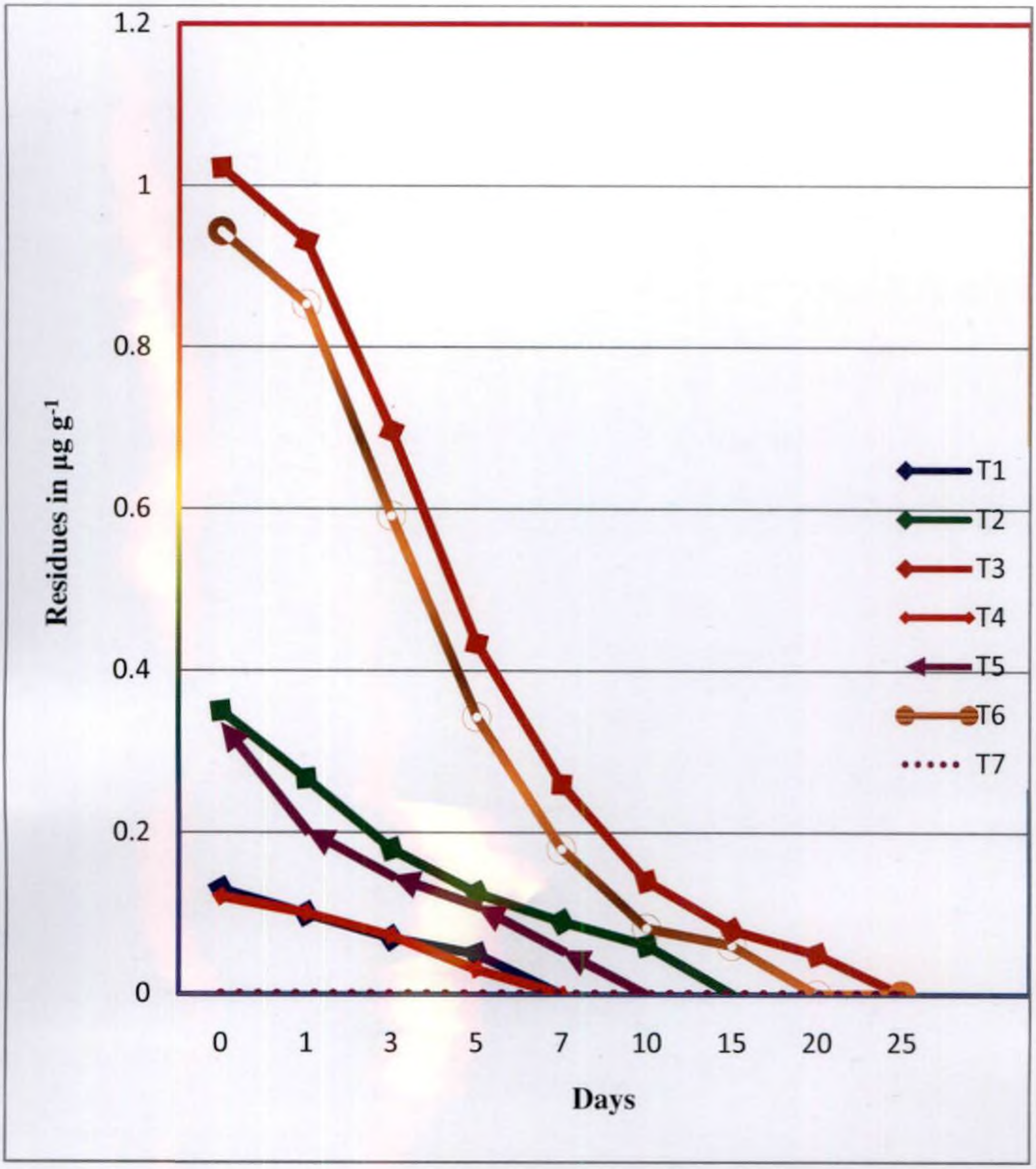


Fig. 16 . Dissipation of imidacloprid in soil at 0-15 cm depth

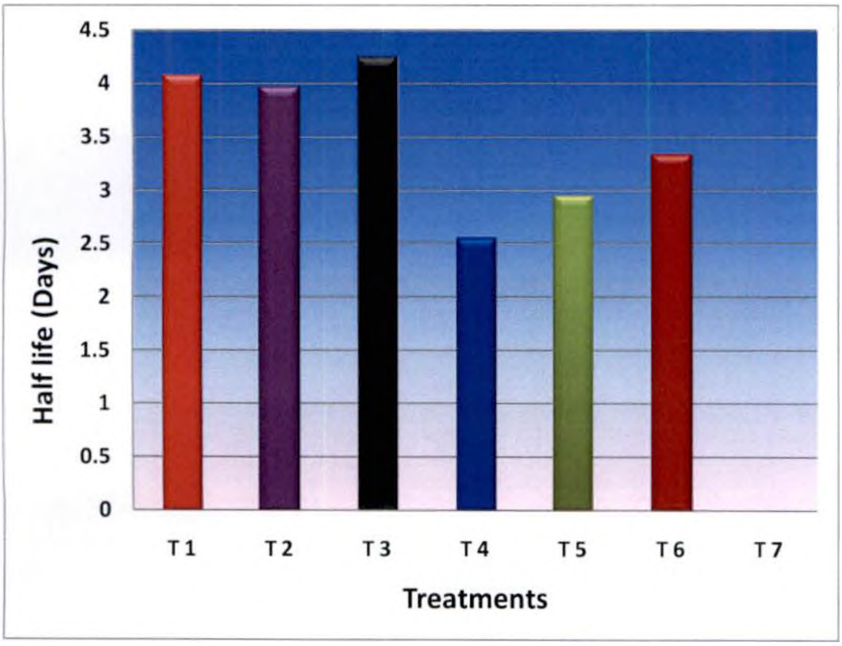


Fig. 17. Half life of various treatments

Summary

6. SUMMARY

Pesticides are indispensable in modern agriculture, using high yielding varieties of crops, which get infested by a variety of pests. This is also true with regard to the control of various soil inhabiting pests. Among the different methods of pest control, farmers resort to the use of chemicals for their timely management. A chemical used in agriculture or public health purposes should disappear from the environment after the desired period of pesticidal action and should not cause any adverse side effect on environment.

Cardamom is the most important export oriented spice commodity of Kerala, which is often infested by various pests and diseases. Plant protection have an important role in cultivation practices of cardamom. In order to minimise crop loss, farmers aggressively adopt plant protection measures such as either increasing dosage or frequency of pesticide application, regardless of its effects on environment, health and socio-economic conditions of the community. The farmers resort to prophylactic and remedial plant protection measures and the usage of these toxic chemicals in inappropriate manner made a great impact on human health and environmental pollution and it will leads to adverse effect on non-target organisms. Literature on pesticide pollution in forest loamy soils of Idukki is scanty inspite of its wide use in the district. In this context an investigation was carried out to study the dynamics of pesticide residues in cardamom growing soils of Idukki district.

A field survey was conducted in cardamom plantations of Idukki district to assess the pesticide use pattern. A suitable method was selected for the estimation of multiple residues in soil by trying different procedures using various solvents. Soil and water samples were collected randomly from the selected farmers field for monitoring of pesticide residues for a period of December to May. The samples were analysed and the residues persisting at various time period were estimated using GC-ECD.

A field experiment was conducted at Indian Cardamom Reasrch Institute, Myladumpara to study the dissipation kinetics of Imidacloprid

(Confidor 200SL). The insecticide was applied at three different levels in cropped and non-cropped situation in four replicates. Soil samples were drawn at 0, 1, 3, 5, 7, 10, 15, 20 days after treatment. The samples were analysed and insecticide residues were estimated using HPLC. The data were statistically analysed and results were summarized below.

1. The major pest infesting cardamom were thrips, capsule borer, root grub, whitefly and nematode for their timely management farmers are following strict plant protection measures at an interval of 15 to 20 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.
2. The efficiency of extraction of multiresidues of pesticides from soil was standardised through recovery experiment. The modified QuEChERS method with extraction using acetonitrile and acetone (3:1) was found to be the best method. The analytical procedure gave good recovery for mutiresidues, 76- 110 per cent from soil when spiked at 0.01- 1 μg g^{-1}. A calibration curve was prepared by plotting different concentrations (0.01 μg g^{-1}, 0.05 μg g^{-1} , 0.1 μg g^{-1} 0.5 μg g^{-1} , 1 μg g^{-1}) *vs*. peak area. Good linearity was found within the range of 0.01-1 μg g^{-1} concentration
3. For monitoring of pesticide residues in soil, samples were collected before and after spraying of insecticides at 0-15 cm and 15-30 cm depth and it was observed that higher residue level was found in surface soil and relatively lower residue level was detected in lower depth.
4. The maximum contamination was found with organophosphorus insecticides like phorate, chlorpyriphos, quinalphos, profenophos and methyl parathion. Due to the faster degradation rate of synthetic pyrethroids relatively lower level of residue was detected in surface soil.
5. The physico chemical parameters of the soil indicates that the higher persistence of insecticides may be due to higher organic matter content, and acidic pH of soil which leads to higher rate of adsorption of these xenobiotics.

6. The moisture content of the soil and weather parameters also plays an important role in the persistence of these chemicals.
7. The level of residues in water samples collected from the cardamom plantation was minimum and no residues were found in samples collected before and after spraying of the insecticide. The data revealed that water bodies are not polluted due to pesticide spraying or the degradation rate of pesticides in aquatic ecosystem system was faster. So the hazard due to aquatic pollution by pesticides usage is not a matter of concern in the cardamom ecosystem.
8. The dissipation study was conducted in forest loamy soils of Myladumpara, the pH of the soil was acidic with higher organic carbon and nitrogen . The fertility status of the experimental soil was high.
9. The treatments were applied both in cropped and non cropped condition with the application of recommended dose (0.10 ml l^{-1}) half the recommended dose (0.05 ml l^{-1}) and double the recommended dose (0.20 ml l^{-1}) of imidaloprid. The lowest half life was found, when half the recommended dose of imidacloprid applied in cropped situation. It is mainly by the activity of soil micro organisms and the rhizosphere effect.
10. The highest half life was obtained when double the recommended dose was applied in non cropped condition. The higher persistence of the insecticide might be due to higher organic matter content and acidic pH of the soil. In addition absence of rhizosphere effect or biotic agents for degradation was also increased the half life of the chemical in non-cropped situation.

Future line of work

If the pesticide use pattern in cardamom will be continued with liberal and continued usage of conventional insecticides it will create severe environmental impact in the future. Instead of the conventional insecticides the new generation insecticides which have lower dosage of application and faster degradation rate should be tried for pest management in cardamom. The effectiveness of these chemicals for protection of cardamom crop from pests and their environmental safety should be assessed by conducting field dissipation studies and it should be included as a component in plant protection programme, recommended by the concerned agencies. This can hopefully minimize the environmental load as well as residues of toxic pesticides in cardamom capsules, thereby offering a certain level of safety to consumers and environment. The use 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.

References

7. REFERENCES

Agnihotri, N. P., Gajbhiye, V. T., Kulshrestha, G. and Mahapatra, S. P. 1995. Monitoring of pesticides in Ganga river water and agricultural fields on its bank at Farrukhabad using multiple residue methods. In: Pesticides crop protection and environment (Eds., Walia, S. and Parmar, B.S.). Society of Pesticide Science India, and Oxford & IBH Publishers, New Delhi.

560 p.

Agnihotri, N. P., Kalpana. and Gajbhiye, V. T. 2002. Effect of organic matter on adsorption of imidacloprid on soil. *Pest. Res. J.* **14**(2):281-285.

Ahmad, G. A., Ronald, J. S., Rai. S. K. David, J. C. 2009. The effect of solvent- conditioning on soil organic matter sorption affinity for diuron and phenanthrene. Chemosphere **76**(8):1062-1066.

AICRP (PR), 2001. Annual progress report of the All India Coordinated Research Project on Pesticide Residues, Indian Council of Agricultural Research, New Delhi. 46p.

Amrit, K. and Amarjeet, K. 2005. Impact of imidacloprid on soil fertility and nodulation in mung bean (*Vigna radiata*). *Asian J. Water Environ. Pollution*, 2(2): 63-67.

* Anonymous, 2002. Environmental fate of imidacloprid. Pflanzenschutz-Nachrichten Bayer 55, Special Edition. Bayer Crop Science AG. 80 p.

Asensio-Ramos, M., Hernandez-Borges, J., Ravelo-Perez, L. M. Rodriguez-Delgado, M. A. 2010. Evaluation of a modified QuEChERS method for the extraction of pesticides from agricultural, ornamental and forestall soils. Anal Bioanal Chem. **396**: 2307-2319.

Baer, U., Calvet, R. 1999. Fate of soil applied herbicides:Experimental data and prediction of dissipation kinetics. *J. Environ. Qual* **28**:1765-1777.

Basker, P. P., Mishra. V. and Bhatnagar, P. 1994. Organochlorine residues in water from the Mahala water reservoir, Jaipur, India. *Environ Pollut* **63**:275-281.

Baskaran, S., Kookana, R. S. and Naidu, R. 1997. Determination of the insecticide imidacloprid in water and soil using high-performance liquid chromatography. *J. chromatography A*: 271-275.

Baskaran, S., Kookana, R. S. and Naidu, R. 1999. Degradation of bifenthrin, chlorpyriphos and imidacloprid in soil and bedding materials at termiticidal application rates. *Pestic Sci.* **55**:1222-1228.

Beevi, S. N., Thomas, B. M., Thomas, G. and Josephrajkumar, A. 2007. Pesticide residues in cardamom in Kerala. In *Proceedings of the 8th Agricultural Science Congress*; 15-17 February 2007; TNAU, Coimbatore, pp 104-105.

Bhattacharyya, B., Baruah, A., Bhuyan, U., Das, P. 2007. Management of termites in preserved setts of sugarcane in Assam. *Pestic. Res. J.* **19** (1):45-46.

Black, C. A., Evans, D. D., Ensminger, L. E., White, J. L. and Clark, F. E. 1965. Methods of Soil Analysis. Part 1. Am. Soc. Agron. Inc., Madison, Wisconsin, USA. 1569p.

Capri, E., Camisa, M. G., Flores-Céspedes, F. Glass, C. R., Gonzalez-Pradas, E. and Trevisan, M. 2001. Imidacloprid and pyrimethanil soil sorption. Agronomie **21**:57-64.

Casida, Jr L. E., Klein, D. and Santoro, T. 1964. Soil dehydrogenase activity. *Soil Sci.* **98**:371-376.

Chadha, K. L. and Swaminathan, M. S. 2006. Pesticide residues. Environment and Agriculture, Chandha Publishers, New Delhi, India. 670p.

Chandrasekaran, M. 2001. Development of integrated pest management on Bhindi. Ph.D Thesis,Tamil Nadu Agricultural University, Coimbatore. 175p.

*Cheng, H. H. 1990. Pesticides in the soil environment- An overview In "Pesticides in soil environment:Process, impact and modelling." HH Cheng (ed), SSSA Book Series 2, SSSA, Madison, WI. pp 1-5.

Chesnin, I. and Yien, C. H. 1951. Turbidimetric determination of available sulphur. *Proc. Soil Sci. Soc. Am.* **15** :149-151.

Chiranjeevi, C., Reddy, I. P., Neeraja, G. and Narayanamma, M. 2002. Management of sucking pests in chilli *Capsicum annum* L. *Veg. Sci.* **29**(2):197p.

Chozen, K. and Regupathy, A. 1994. Gas chromatographic method for determination of multiresidues of OP insecticides in cardamom. *Pestic. Res. J.* **6**(2): 180-188.

Chopra, S. L. and Sree Ramulu, U. S. 1982. Soil Pesticide interactions. Review of Soil Reserch in India. ISSS, New Delhi. P199.

*Colborn, T., 2006. A case for revisiting the safety of pesticides: A closer look at neurodevelopment, *J. Environ. Health Perspect.* **114** :10-17.

Cox, L., Koskinen, W. C. and Yen, P. Y. 1997. Sorption-desorption of imidacloprid and its metabolites in soils. *J. Agric. Food Chem.* **45**(4):1468-1472.

Cox, L., Koskinen, W. C. and Yen, P. Y. 1998. Influence of soil properties on sorption-desorption of imidacloprid. *J. Environ. Sci. Health* B. **33**(2): 123-134.

Dhawan, A. K., Saini, S. and Aneja, A. 2008. Relative toxicity of different insecticides against cotton aphid *Aphis gossypii* Glover. *Environ. Ecol.* **26**(4B): 2067-2069.

Digrak, M., Ozcelik., 1998. Effect of some pesticides on soil microorganisms. *Bull. Environ. Contam. Toxicol.* **60**:916-922.

Edwards, C. A. 1986. Inorganic chemicals in the soil environment, Marcel Dekker Inc, New York. 513 p.

EPA. 2002. EPA: Drinking water standards and health advisories, US Environmental Protection agency office of water 4304 EPA 8828-00-001.

Extension Toxicology Network (ETN). 1996. Cypermethrin. Pesticide information proflles. University of California-Davis, Oregon State University.

FAO, 1986. Regional overview, pesticide poicy and monitoring guidelines. In *Proceedigs of the Asia regional workshop on implementation, monitoring and observance of International code of conduct on the distribution and use of pesticides*, Bangkok, Thailand. pp 26-28.

Farm Chemical Handbook. 2000. Meister Publishing Company. 83:208p.

Ferenc, S. A. 2001. "Impact of low-dose, high-potency herbicides on non target and unintended plant species", SETAC Press, Florida. 177p.

*Flores-Cespedes, F., Gonzalez-Pradas, E., Fernandez-Perez, M.,Villafranca-Sanchez, M., Socias- Viciana, M. and Urena-Amate, M. D. 2002. Effects of dissolved organic carbon on sorption and mobility of imidacloprid in soil. *J. Environ. Qual.* **31**:880-888.

Gahlhoff, J. E. and Koehler, P. G. 2001. Penetration of the eastern subterranean termite into soil treated at various thicknesses and and concentrations of Dursban TC and Premise 75. *J. Econ. Ento.* **94**:486-491.

Gajbhiye, V. T., Singh, A., Agnitori, N. P. and Sreevastava, K. P. 1997. Efficacy of imidacloprid against termites in sugarcane. *Pestology* **21**(1):41-46.

Gawlik, B. M., Sotiriou, N., Feicht, E. A., Schulte-Hostede, S., Kettrup, A. 1997. Alternatives for the determination of the soil adsorption coeffcient Koc, of non-ionic organic compounds-a review. Chemosphere, **34** (12): 2525-2551.

Government of India (GOI), 2002. Government of India notification-GSR No. 759 E and 760 E dated 29.09. Ministry of Health and family welfare.

Gomez, K. A., Gomez, A. A. 1984. Statistical proceedings for agricultural research (2 nd Ed.). John Wiley and sons, Inc. Singapore. 262p.

Goring, C. A. I., Laskowski, D. A., Hamaker, J. H. and Meikle, R. W. 1975. Principles of pesticide degradation in soil. *In*: Haque, R. and Freed, V. H. eds. *Environmental dynamics of pesticides*. Plenum Press, New York. pp 135 -172.

Graham, C. T., Jenkins, J. N. and Mc Carty, J. C . 1995. Performance of Gaucho as seed treatment insecticide against early season cotton insect pests. *Proc. Beltneide cotton conf;*4- 7 January, 1995, San Antonio Texas, USA, pp.917-918.

Hafez, H. F. H. and Thiemann, W. H. P. 2003. Persistence and biodegradation of diazinon and imidacloprid in soil. Pesticide in air, plant, soil and water system. In: *Proceedingds XII Symposium Pesticide on chemistry,* Congress centre Universita Cattolica, Via Emilia Parmense, Italy 84-6, Piacenza. pp 35-42.

Harvey, J. 1983. A simple method for evaluating soil breakdown of 14 C-pesticides under field conditions. Residue Review **85**:149-158.

Heijbrock, W., Huijbregts, A. W. H. 1995. Fungicides and insecticides applied to pelleted sugar-beet seeds-III. Control of insects in soil. *Crop Prot.* **14**:367-373.

Hesse, P. R. 1971. A Textbook of Soil Chemical Analysis. William Clowes and Sons, London. 513p.

Honeycutt, R. C. and Schabacker, D. J. (eds.), 1994. Mechanisms of pesticide movement into ground water. 2nd eds. Lewis Publishers, Boca Raton. 189p.

*Horwood, M. A. 2007. Rapid degradation of termiticides under field conditions. *Australian J. Ento.* **46**: 75–78.

Hoskins, M. L. 1981. Mathematical treatment of loss of pesticide residue. Pl. Prot. Bull. FAO 9:163-169.

Hundal, B. S., Singh, A. R. 2006. Pesticide marketing: The Indian scenario, *Icfai J. Manage. Econ.* **4**: 32-37.

Ishaaya, I., Degheele, D. 1998. Insecticides with ovel modes of action: Mechanism and application.-Springer Verlag, Berlin Heidelberg, Germany. pp160-178.

Jackson, M. L. 1973. Soil Chemical Analysis. Second edition. Prentice Hall of India (Pvt.) Ltd., New Delhi. 498 p.

Jain, J. P., Raiyanine, V. C., Mistry, J. S., Patel, S. J., Desai, N. M. and Kashyap, S. K. 1991. Residue of organochlorine pesticide and polycyclic hydrocarbons in drinking water at Ahmedabad city of India. *Bull. Environ. Contam. Toxicol* **47**:381-385.

Jeong, Chang Yoon; Selim, H. M. 2006. Modeling Adsorption-Desorption Kinetics of Imidacloprid in Soils. Soil Science. **175**(5):214-222.

Jury, W. A. and Winer, A. M. Spencer W. F. and Focht, D. D. 1987. Transport and transformations of organic chemicals I the soil-air-water ecosystem. Residue Reviews, Springer-Verlag, New York. **99:**119-164.

Kalpana, Agnihotri, N. P. and Gajbhiye, V. T. 2002. Adsorption-desorption of imidacloprid on five tropical Indian soils. *Pest. Res. J.* 14 (**1**): 63-68.

Kannan, K., Battula, S., Loganathan, B. G., Hong, C. S., Villeneuve, D. L., Sajwan, K., Giesy, J. P., Aldous, K. M. 2003. Trace organics contaminants, including toxaphene and trifluralin, in cotton field soils from Georgia and South Carolina, USA. Arch. Environ. Contam. Toxicol. **45**: 30-36.

Kannan, M., Uthamasamy, S. and Mohan, S. 2004. Impact of insecticides on sucking pests and natural enemy complex of transgenic cotton. Current Sci. **86** (5): 726-729.

Katagi, K., 2002. Abiotic hydrolysis of pesticides in the aquatic environment. Reviews of Environ. Contam. Toxicol. Springer-Verlag, New York. **175.** pp 79-261.

Katagi, K., 2004. Photodegradation of pesticides on plant and soil surfaces. Reviews of Environ. Contam. Toxicol. Springer-Verlag, New York. **182:** pp 1-195.

Kathpal, T. S. and Beena Kumari. 1993. Pesticide contamination of non-fatty food in developing countries. In:Dhaliwal, G. S, Balwinder Singh., Ed., Pesticides-their Ecological Impact in developing countries:Commonwealth Publishers, New Delhi. pp162-189.

Kellogg, R. L., Nehring, R., Grube, A., Goss, D. W. and Plotkin, S. 2000. Environmental indicators of pesticide leaching and runoff from farm fields. United States Department of Agriculture Natural Resources Conservation Service. pp 165-178.

Kim, J. H., Smith, A. 2001. Distribution of organochlorine pesticides in soils from South Korea. *Chemosphere* **43**: 137-140.

Kobara, Y. S., Endo, Ishihara, S. Horio, T. and Ohtsu, K. 2002. Preliminary studies on photolysis of polychlorinated dibenzo-p-dioxins on soils surface. A Organohalogen Compounds. **56** :429-432.

Kobara, Y., Endo, S. Horio, T. Ishihara, S. and Ohtsu, K. 2003. Photolysis of polychlorinated dibenzo-p-dioxins and enhanced detoxication by titanium dioxide photocatalyst on the soils surface. Organohalogen Compounds. **63**:369-372.

Kovacs, M. F. 1986. Regulatory aspects of bound residues (chemistry). Residue Reviews, Springer-Verlag, New York. **97**: 1-17.

Krohn, J. and E. Hellpointner. 2002. Environmental fate of imidacloprid. Pflanzenschutz Nachrichten Bayer. 55, Special Edition. 498p.

Krop, H. B., Paul, C. M . van Noort and Govers, H. A. J. 2001. Determination and theoretical aspects of the equilibrium between dissolved organic matter and hydrophobic organic micropollutants in water (Kdoc). Reviews of Environ. Contam. Toxicol, Springer-Verlag, New York. **169**:1-122.

Kumar, R. and Dikshit, A. K. 2001. Assessment of imidacloprid in brassica envmt. *J. Envision, Sci, Hlth* Part B pesticides, Food Contaminants and Agrl. Wastes. **36**:619-629.

Kumaresan, D. and George, K. V. 1999. Pests and diseases of cardamom- A Review. Proc. Second Annu. Symp. Plant Crops, PlacrosymII: 412-433.

Liu, W., Zheng, W., Ma, Y., Liu, K. K. 2006. Sorption and degradation of imidacloprid in soil and water. *J Environ Sci. Health.* **41** (5):623-634.

Manirakiza, P., Akinbamijo, O., Covaci, A., Pitonzo, R., Schepens, P. 2003. Assessment of organochlorine pesticide residues in West African city farms: Banjul and Dakar case study. *Arch. Environ. Contam. Toxicol.* **44**: 171-179.

Manjunatha, M. and Shivanna, B. K. 2001. Field evaluation of RIL 1820 SL (Imidacloprid)against brown plant hopper and green leaf hopper. *Insect Environ.* **6**:177-178.

Mc Tier, T. L., Evans, N. A., Martin-Short M., Gration, K. 2003. Comparison of the activity of selamectin, fipronil and imidacloprid against flea larvae (*Ctenocephalides felis felis*) in vitro. *Vet. Parasitol.* **116**:45-50.

McEwen, F. L. and Stephenson, G. R. 1979. The use and significance of pesticides in the environment. John Wiley & Sons, New York. pp. 538

Michael Raj, S. and Punnaiah, K. C. 2003. Efficacy of insecticides by stem application against *A. gossypii* on okra. In: Subrahmanyam, B. and Ramamurthy, V. V(eds.), *Proceedings of the national symposium on frontier areas of entomological research*; 5-7 November, 2003; Division of Entomology IARI, New Delhi and Entomological society of India. 67 p.

Miles Inc., 1993. Imidacloprid: Pesticide leaching potential model. Report No. 105008. 540p.

Mishra, H. P. 1999. Efficacy of chlorpyriphos against termites in groundnut. *Indian. J. Ent.* **61**(4):326-329.

Misra~~, H~~. P. 2002. Field evaluation of some newer insecticides against aphids (*A. gossypii*) and jassids (*Amrasca biguttula biguttula*) on okra. *Indian J. Ent.* **64**(1):80-84.

Mishra, N. C., Ram, S., Swain, S. C. and Rath, S. 2005. Effect of some new insecticides on the thrips (*Scirtothrips dorsalis* Hood) and yield of chilli crop in the Eastern Ghat Highland Zone of *Orissa. Hort. J.* **18**(1): 32-34.

Moorman, J. B. 1995. A review of pesticide effects on micro-organisms and microbial processes related to soil fertility. *J. Prod Agric.* **2**(1):14-23.

Moulton, T. P. 1973. The effect of various insecticides (specially Thiodan and BHC) on fish in the paddy fields of west Malaysia. *Mal Agric J.* **49**:224-253.

Mueller, Beilschmidt, Doria. 1990. Toxicology and environmental fate of synthetic pyrethroids. *J. Pesticide Reform.* **10** (3):32-37.

Mukherjee, I., Gupta, S., Kulshrestha, A., Pant, S., Singh, A., Kumar, A., Gajbhiye, V. T. 2007. Simultaneous Estimation of aldicarb, carbofuran and carbaryl in water by HPLC. *Pestic. Res. J.* **19** (1):128-130.

Mulye, H. S. 1996. Supplementary review of imidacloprid technical and the end-use product, Admire 240F insecticide. Submission Numbers: 94-1706 and 94-1705. Environmental Evaluation Division, Pest Management Regulatory Agency, Health Canada.

Shetty, P. K., Murugan, M., Sreeja, K. G. 2008. Crop protection stewardship in India: wanted or unwanted. Current Sci. **95**(4) :457-464.

Naik, J. D., Thippesha, D., Chandra Naik, S. and Devaraju, K. M. 2010. Bio-efficacy of insecticides against hairy caterpillars, *Eupterote canarica* Moore, (Eupterotidae:Lepidoptera) in small cardamom and its correlation of weather factors with incidence. *Karnataka J. Agric. Sci.* **23**(1) : 176-177.

Naik, J. D., Thippesha, D., Devaraju, K. M., Lakshmana, D., Venkatesha, J. 2010. Ecology and management of shoot fly, *Formosina flavipes* Mall. (Chloropidae: Diptera) in small cardamom. *Karnataka J. Agric. Sci.* **23**(1) : 76-78.

Nauen, R., Hungenberg, H., Tollo, B., Tietjen, K., Elbert, A. 1998. Antifeedant effect, biological efficacy and high affinity binding of imidacloprid to acetylcholine receptors in *Myzus persicae* and *Myzus nicotianae. Pest Mgmt Sci.* **53**:133–140.

Nybe, E.N. and Miniraj, N. 2007. Spices. New India publishing agency, New Delhi. 680p.

Pal, R., Chakrabarti, K., Chakraborty, A., Chowdhury, A. 2000. Degradation and effects of pesticides on soil microbiological parameters-a review. *Int. J. Ag. Res.* **19**(3):240-258.

Park, J. H., Iqbal Rouf Mamun, M., Abd El-Aty, A. M., Na, T. W., Choi, J. H., Ghafar, M. W., Kim, K. S., Kim, S. D. and Shim, J. H. 2010. Development and validation of a multiresidue method for determination of 37 pesticides in soil using GC-NPD. Biomedical Chromatography. 1556p.

Patil, A. S., Patil, P. D. and Patil, R. S. 2002. Efficacy of different schedule doses of imidacloprid against sucking pest complex of chilli (*Capsicum annum L.*) *Pestology*, **26**(12): 31-34.

Pedersen, T. L. 1997. Pesticide residues in drinking water. extoxnet.orst.edu. 68 p.

Pillai, M. K. K. and Agarwal, H. C. 1989. In: DDT residues and its degradation in soil, water and few aquatic animals of Jamuna in New Delhi. Directorate of Science and Technology, New Delhi, India. 540 p.

Pimental, D. 1995. Amounts of pesticides reaching target pests:Environmental impacts and their ethics: *J. Agric Environ Ethics* **8**:17-29.

Ping, L., Zhang, C., Zhu, Y.,Wu, M., Dai, F., Hu, X., Zhao, H., and Li, Z. 2010. Imidacloprid adsorption by soils treated with humic substances under different pH and temperature conditions. *African J Biotechnology* **9**(13):1935-1940.

Piper, C. S. 1966. Soil and Plant Analysis. Asija Publishing House, Bombay, 368p.

PMRA (Pest Management Regulatory Agency). 2001. Imidacloprid. Regulatory Note. REG2001-1. Ottawa: Health Canada, Pest Management Regulatory Agency.

Preetha, G. 2007. Impact assessment of chloronicotinyls on the management of sucking pests in cotton and bhendi ecosystem. Ph. D. Thesis, Tamil Nadu Agricultural University, Coimbatore, India, 197p.

Preetha, G., Manoharan, T., Kuttalam, S., Stanley, J. 2008. Pesistent toxicity of imidacloprid against aphid, *Aphis gossypii* and leaf hopper, *Amrasca biguttula biguttula* in cotton. *Pestic. Res. J.* **20**(2):197-200.

Rajabaskar, D. 2003. Studies on the evaluation of IPM modules against *Conogethes punctiferalis* Guenee and *Sciothrips cardamomi* Ramk. On cardamom. Ph. D. Thesis, Tamil Nadu Agricultural University, Coimbatore, India. 198p.

Rajagopal, D. 2002. Economically important termite species in India. Sociobiol. **40**:33-46.

Ramakrishnan, R., Suiter, D. R. Nakatsu, C. H., Humber, R. A. and Bennett, G. W. 1999. Imidacloprid enhanced *Reticulitermes flavipes*(Isoptera:Rhinotermitidae) susceptibility to the entomopathogen *Metarhizium anisopliae*. *J. Econ. Ent.* **92**:1125-1132.

* Rebek, E. J. and Saief, C. S. 2003. Effect of pesticide application on the euonymes scale (Hemiptera: Diaspididae) and its parasitoid *Encarsia citrina* (Hymenoptera: Aphilinidae). *J. Econ. Ent.* **96** (2): 446-452.

Regupathy, A., Palaniswamy, S., Chandramohan, N. and Gunathilagaraj, K. 2003. A guide on crop pests. Fourth edition. Soorya Desktop Publishers, Coimbatore. 264 p.

Rekha, P. R. 2005. Dissipation of chlorpyriphos in red loam soil and its effect on soil organisms. M.Sc (Ag) thesis, Kerala Agricultural University, Thrissur. 71 p.

Renuka, S. 2001. Studies on the bioefficacy and dissipation of profenophos (Curacron 50 EC) applied to cardamom and cashew. Ph. D. Thesis, Tamil Nadu Agricultural University, Coimbatore, India. 132 p.

Roonwal, M. L. 1999. Termite injurious crops plantation and fruits and forest trees and their control. In "Termite life and termite control in tropical South Asia."Scientific publsher Jodhpur. pp 27-30.

Rouchaud, J., Gustin, F., Wauters, A. 1994. Soil biodegradation and leaf transfer of insecticide imidacloprid applied in seed dressing in sugar beet crops. *Bull. Environ. Contam. Toxicol.* **53**(3) :344-350.

Rouchaud, J., Thirion, A., Wauters, A., Van de Steene, F., Benoit, F. Ceustermans, N. Gillet, J., Marchand, S., Vanparys, L. 1996. Effects of fertilizer on insecticides adsorption and biodegradation in crop soils. *Arch. Environ. Contam. Toxicol.* **31**(1):98-106.

Ryeol, C. B., Woo, L. S., Yottan, S. and Bin, I. Y. 2001. Residual effect of imidacloprid 0.005% on *Nilaparvatha lugens*. *Korean J Appl. Ent.* 40:83-88.

*Sabbagh, G. J., Lenz, M. F., Fisher, J. M. and Arthur, E. L. 2002. Significance of binding on imidacloprid degradation in soils, and effects of soil characteristics on imidacloprid adsorption capacity. Report No. 200327. Bayer CropScience, Stilwell, Kansas. 80p.

Safiatou, B, D., Cobb, J. M., Mullins, D. E. 2007. Pesticide residues in soil and water from four cotton growing areas of Mali, West Africa. *J. Agricultural, Food, and Environmental Sciences.* **1**(1):1934-7235.

Sanyal, N., Pal. R. and Chowdhury. 2006. Dissipation of imidacloprid in tea soil at termiticidal application rate. *Intl. J. Soil Sci.* **1**(1):81-84.

Sarkar, M. A., Biswas, P. K. Roy, S., Kole, R. K. and Chowdhury, A. 1999. Effect of pH and type of formulation on the persistence of imidacloprid in water. *Bull. Environ. Contam. Toxicol.* **63**:604-609.

Scarlett, M. J.and Stott, A. D. 1997. Accelerated solvent Extraction :An evaluation for screening of soils for selected U.S. EPA Semivolatile organic priority pollutants. John A Fisher, Environmental Protection Authority of Victoria, Melbourne, Australia. *Environ. Sci. Technol.*31(4):1120-1127.

Schad, T. 2001. Calculation of temperature referenced first order DT50 of imidacloprid based on field dissipation studies conducted in Europe. Internal Report Bayer AG, Leverkusen. 850 p.

Scholz, K. and Spiteller, M. 1992. Influence of groundcover on the degradation of 14C-imidacloprid in soil. Brighton Crop Protection Conference. *Pests and Diseases*. pp 883-888.

Sharma, N. and Savita. 2007. Isoproturon persistence in field soil and its impact on microbial population under north western Himalayan conditions. *Pestic Res. J.* **19** (1):116-118.

Sharma, R. K., Sharma, K. and Sekhar, K. 2003. Evaluation of plant protectants on damage and yield of rainfed maize by termites. *Pestic Res. J.* **15** (1):36-39.

Shetty, P. K. 2000. Sustainable Agricultural practices and food ssecurity in Environment Management and Audit(eds) Sasi Bhushana Rao, P. and Mohan Rao, P. Newdelhi, Deep and Deep Publications. pp36-43.

Shetty, P. K., 2004. Socio-ecological implications of pesticide use in India. *Econ. Polit. Wkly*. **39**:5261-5267.

Shetty, P. K. 2008. Pesticide stewardship: Challenges and opportunities in developing countries;http://www.tpsalliance.org,accessed on 9 June.

Singh, J., Sabir, N., Singh, D. K., Singh, M. 2008. Plant available P and total P as affected by diazinon, imidacloprid and lindane treatments in groundnut field. *Pesticide Res. J.* **20**(1):146-150.

Singh, S. K. and Singh, G. 2002. Comparative evaluation of chemical and botanical insecticide against termites. *Entomon* **27**(2):153-160.

Singh, S. P. 2000. Survey of Indian Agriculture. 2000. The Hindu. pp159-163.

Singhal, S. 2000. 'There can be no single remedy for all pest problems'. Agriculture Today, August. pp 24-26.

Sivaveerapandian, D. 2000. Bioefficacy of imidacloprid against sucking pests on bhendi and determination of half-life. M. Sc (Ag) Thesis, Tamil Nadu Agricultural University, Coimbatore, India. 111p.

Spices Board, 2009. Cultivation practices for cardamom *Elettaria cardamomum* Maton. Spices Board, Cochin, Kerala, India. 40p.

Stanley, J. 2007. Chemical and behavioural approaches for pest management in cardamom. Ph. D. Thesis, Tamil Nadu Agricultural University, Coimbatore, India. 198p.

Su, N. Y., 2002. Novel Technologies for subterranean termite control. *Sociobiol.* **40**:95-102.

Suganthy, M. 2003. Bioefficacy and residues of Confidence (Imidacloprid 200% SL) on cotton, vegetables and mango. Ph. D. Thesis, Tamil Nadu Agricultural University, Coimbatore, India. 197p.

Tomlin, C. D. S. 2000. The Pesticide Manual. Twelth Edition. British Crop Protection Council. Surrey, U. K. British Crop Protection Council. 1300p.

Usha, S. 2007. Pesticide use in the high ranges and its implications. in:Gleanimgs in cardamom(Eds)., Josephrajkumar, A., Backiyarani, S. and Sivakumar, G. KAU publication. 82p.

Vikas Singh., Thakur, B. S., Chandraker, M. K. 2005. Bio-efficacy of insecticides against insect pests of chilli. *Environ. Ecol.* **23** (Special 3): 600-604.

Vinoth Kumar, B., Kumaran, N., Boomathi, N. and Kuttalam. S. 2006. Harvest time-residues of imidacloprid in cardamom. *Madras Agric. J.* **96** (1-6):217-220.

Vishwakarma K., Samnani P., Panday S. Y. 2008. Development and validation of analytical method for determination of imidacloprid residues in/on soil and water by HPLC. *J. Environ. Ecol.* 26:32-36.

Wagner, T. L., 2003. U.S Forest service termiticide tests. *Sociobiol.* **41**:131-141.

Walker, A., 2000. A simple centrifugaton technique for the extraction of soil solution to permit direct measurement of aqueous phase concentrations of pesticide/ soil interactions-some Current Research Methods. Institute National De La Recherce Agronomique, Paris, pp.173-178.

*Ware, G. W., Whitacre, D. M. 2004. The Pesticide Book, Meister Pro Information Resources, Willoughby, Ohio. 496p.

Westwood, F., Bean, K., Dewar, A., Bromilow, R., Chamberlain, K. 1998. Movement and persistence of [14C] imidacloprid in sugar-beet plants following application to pelleted sugar-beet seed. *Pesticide Sci.* **52**(2) :97-103

http..//www. cibrc. nic.in/major uses/insecticides

Xin, F. H. and Xi, Q. 1995. An evaluation of the effect of imidacloprid on rice plant hopper and its natural enemies. *Pl. prot.* **21**: 42-44.

Zhu, G,Wu, H., Guo, J., Kimaro, F. M. E. 2004. Microbial degradation of fipronil in clay loam soil. *Water Air Soil Polut.* **153** (1):35-44.

*Original not seen

Abstract

DYNAMICS OF PESTICIDE RESIDUES IN CARDAMOM GROWING SOILS OF IDUKKI DISTRICT

SIJI N. NATH

(2009-11-114)

ABSTRACT

of the thesis submitted in partial fulfillment of the
requirement for the degree of

MASTER OF SCIENCE IN AGRICULTURE
(Soil Science and Agricultural Chemistry)

Faculty of Agriculture

Kerala Agricultural University

DEPARTMENT OF SOIL SCIENCE AND AGRICULTURAL CHEMISTRY
COLLEGE OF AGRICULTURE
VELLAYANI, THIRUVANANTHAPURAM- 695 522
KERALA, INDIA
2011

ABSTRACT

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. The decision regarding the type of chemicals to be used, dosage, frequency of application are fixed by the farmers themselves or as per the directions of company representatives and they are not following the recommendation of KAU or Spices Board. The improper usage of these chemicals resulted in pollution of the cardamom ecosystem especially the soil and water with toxic xenobiotics. Hence in order to assess the residue level and to study the extend of pollution due to pesticides, soil and water samples were collected from the cardamom growing plantations of Idukki district.

In multi residue method validation, soil samples were spiked at five different levels (0.01 $\mu g\ g^{-1}$, 0.05 $\mu g\ g^{-1}$, 0.1 $\mu g\ g^{-1}$, 0.5 $\mu g\ g^{-1}$, 1 $\mu g\ g^{-1}$) and extraction was carried out using various solvent/ solvent system and the method which gave 70-110 per cent recovery with RSD <20 per cent was selected. The same procedure was adopted for further estimation of residues from soil samples.

The pesticide hot spots, were selected mainly in three locations, Kattappana, Pampadumpara and Nedumkandam Panchayath in Idukki district and five farmers were identified randomly from each location. Soil and water samples were collected before and after spraying of insecticides for a period of six months starting from December to May at two different depth at 0-15 cm and 15-30 cm depth from the selected plantations.

In the monitoring study, samples collected at 0-15 cm depth were found to contain higher level of pesticide residues. The samples were frequently detected with residues of organophosphorus insecticides like phorate, chlorpyriphos, quinalphos, profenophos, methyl parathion and relatively lower number of samples were found to contain residues of endosulphan and synthetic pyrethroids. The samples collected from the lower depth 15-30 cm were contaminated with residues at a lower level.

The physico chemical properties of the soil were analysed and it was found that the soils were rich in organic matter content (3.63-3.74%), acidic to near neutral pH (5.72-6.04) and have higher fertility status. The higher organic matter content of the soil favours higher rate of adsorption of the insecticide.

Water samples were collected from the selected locations and analysed for the presence of pesticide residues and it was found that none of the samples were contaminated with pesticide residues.

A field dissipation study was carried out with the neonicotinoid group of insecticide, imidacloprid applied at three different levels (0.05 ml l^{-1}, 0.10 ml l^{-1}, 0.20 ml l^{-1}) in cropped and non-cropped condition. The half life of the chemical calculated under both the situation. The highest half life (4.25 days) was obtained when imidacloprid applied in non- cropped situation at double the recommended dose (0.20 ml l^{-1}) and the lowest half life (2.55 days) was obtained in cropped situation when the insecticide was applied at the lowest dose (0.05 ml l^{-1}). The half life value obtained in cropped condition was lower compared to the non cropped situation. The faster degradation of the chemical under the cropped situation may be due to the higher activity of soil microorganisms and rhizosphere effect in addition to other soil factors like pH and organic carbon content.

Appendices

APPENDIX I

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

Sl No.	Particulars	
1.	Location	
	Block	
	Taluk	
	Panchayat	
2.	Name & Address of farmer	
3.	Age	
4.	Education	
5.	Size of holding(ha)	
6.	Land status	
a.	Own land	
b.	Leased land	
7.	Irrigation status	
a.	Irrigated	
b.	Rainfed	
8.	Average yield (kg/ha)	
9.	Annual income	
10.	Soil type	
11.	Topography	
12.	Cropping pattern	
13.	Pesticide availability	
14.	Cost for plant protection measures	
a.	Cost of chemicals	
b.	Cost of labour	
c.	Total cost	
15.	Type of sprayer used	
16.	Whether applying pesticides continuously for the last ten years. If withdrawn, when? and why?	
17.	Whether organic farming is possible ?	

18.	Method of application	
a.	Foliar	
b.	Soil application	
19	Is there any practice of manual mixing of pesticides and spaying?	
20.	Is there any prophylactic application of PP chemicals?	
21.	Application of plant protection chemicals as per the recommendations of KAU or not.	
22.	Whether following the directions in the pesticide label during handling and application of pesticides	
23.	Most frequently used	
a.	Insecticide	
b.	Fungicide	
c.	Herbicide	
24.	Habit of taking food, water, smoke or chew tobacco while spraying of pesticides:	
25.	Time of application of pesticides	
a.	Early Morning	
b.	Morning	
c.	Afternoon	
d.	Evening	
26.	Degree of awareness regarding the adverse health effects of pesticides	
a.	Well aware	
b.	Aware of some adverse health effects	
c.	Totally ignorant	
27.	Pesticide application by	
a.	Himself	
b.	Labour	
28.	Type of clothing while spraying	
29.	Safety precautions taken while spraying	
a.	Use of gloves	
b.	Wearing mask	
c.	Wearing boots	
d.	Nothing adopted	
30.	Reasons for non-adoption of safety measures	

31.	Method of disposal of pesticide containers	
a.	Dumping in the field	
b.	Putting in drainage channels	
c.	Burning	
d.	Burrying deep in soil	
32.	Type of heath hazard due to pesticide application	
a.	Some irritation during the time of spraying	
b.	Continuous coughing, difficulty to breathe, skin diseases etc.	

33. Details of organic manures used:

Sl No.	Type of manure used	Quantity Applied	No. of applications	Time of application

34. Details of chemical fertilizers used:

Sl No.	Type of fertilizer used	Quantity Applied	No. of applications	Time of application

35. Details of major insect pests / diseases / weeds:

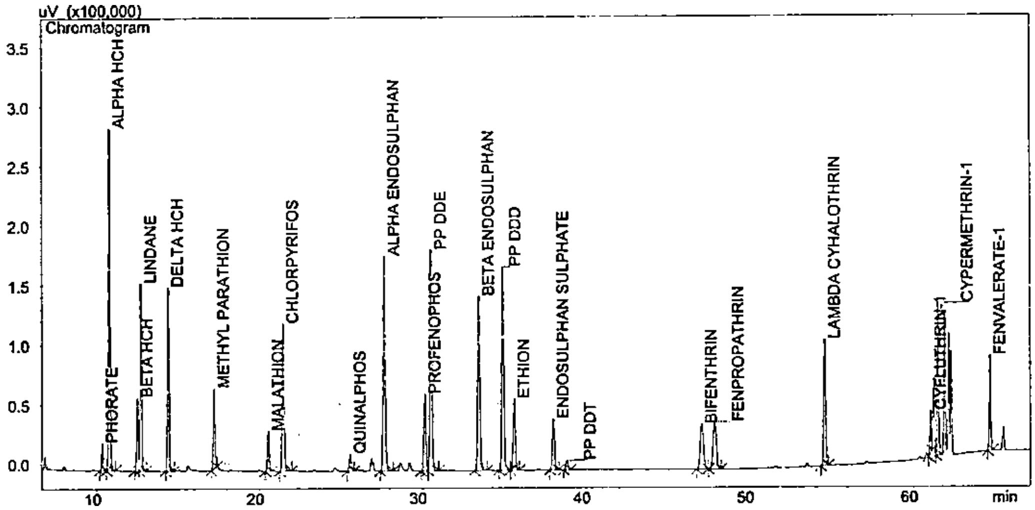
Sl No.	Name of pest/disease/weeds		Percentage of yield dose
	Nursery	Mainfield	

36. Information regarding plant protection chemicals used:

Sl No:	Particulars of insecticides used			Particulars of fungicides used		
	Name of chemical	Aware of active ingredient	Dosage/Quantity applied	Name of chemical	Aware of active ingredient	Dosage/Quantity applied

APPENDIX II

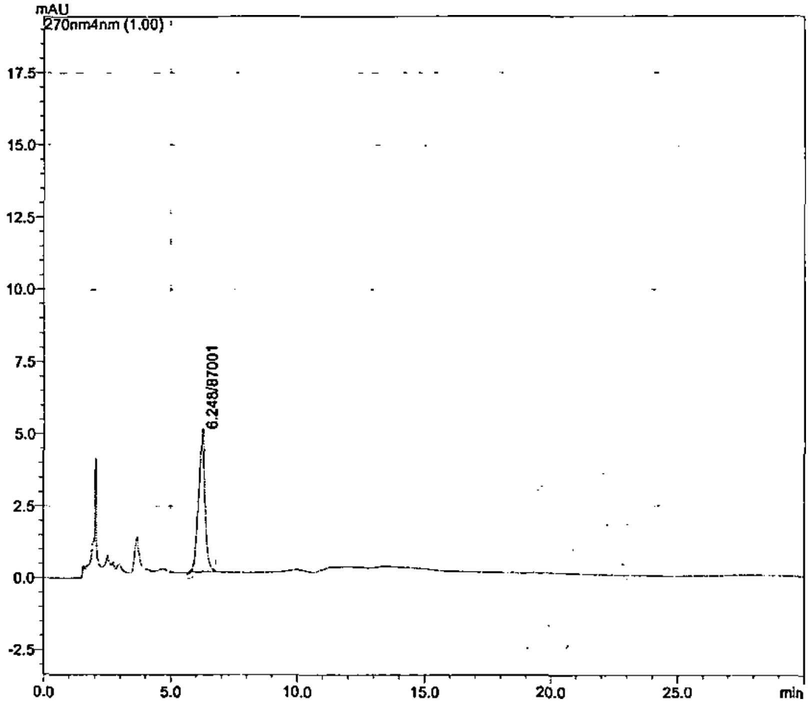
Chromatogram of standard insecticide mixture (0.5 ppm)



Sl no:	Name of the compound	Retention . Time	Conc. (ppm)	Area
1	PHORATE	10.335	0.46	148389
2	ALPHA HCH	10.774	0.48	1714751
3	BETA HCH	12.500	0.46	405543
4	LINDANE	12.714	0.45	971482
5	DELTA HCH	14.392	0.47	995404
6	METHYL PARATHION	17.22	0.45506	500483
7	MALATHION	20.548	0.45	263378
8	CHLORPYRIFOS	21.453	0.46	1035046
9	QUINALPHOS	25.578	0.46	125067
10	ALPHA ENDOSULPHAN	27.663	0.48	1616679
11	PROFENOPHOS	30.146	0.46	562803
12	PP DDE	30.516	0.48	1586888
13	BETA ENDOSULPHAN	33.435	0.47	1321768
14	PP DDD	34.90	0.47	1492637
15	ETHION	35.606	0.46	560120
16	ENDOSULPHAN SULPHATE	38.004	0.45	399342
17	PP DDT	38.834	0.48208	77515
18	BIFENTHRIN	47.065	0.47928	547026
19	FENPROPATHRIN	47.849	0.48	563491
20	LAMBDA CYHALOTHRIN	54.575	0.49	832178
21	CYFLUTHRIN-1	61.057	0.40	188627
22	CYPERMETHRIN-1	61.508	0.47	739993
23	FENVALERATE-1	64.676	0.49	483456

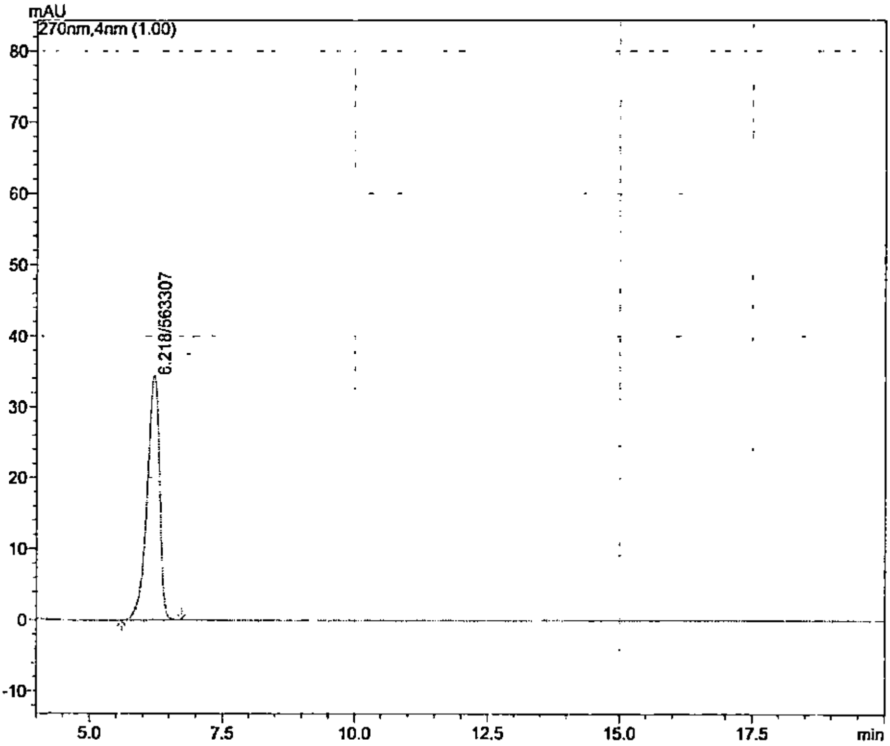
APPENDIX III

Chromatogram of 1ppm fortified sample of imidacloprid



APPENDIX IV

Chromatogram of 1ppm standard imidacloprid



APPENDIX V

Monthly Weather data during the experimental period

(December2010- May2011)

Location :ICRI, Myladumpara

Months	Max temp (°C)	Min temp (°C)	RH (%)	Rainfall (mm)
December 2010	24.6	16.5	98.2	33.4
January 2011	25.3	14.9	96.9	94.2
February 2011	26.9	15.3	87.6	107.4
March 2011	28.6	16.2	85.0	22.2
April 2011	29.0	17.5	94.8	268.8
May 2011	29.4	18.5	93.8	28.6

Location :CRS, Pampadumpara

Month	Max temp.	Min. temp	RH (%)	Wind Speed	Sunshine	Rain Fall (mm)	Evaporation (cm/hr)
Dec-10	23.2	16.4	95	5.6	4.3	45.4	1.9
Jan-11	24.6	15.5	92	6.9	6.7	68.6	3.2
Feb-11	26.3	16.1	89	6.0	7.7	100.4	3.6
Mar-11	28.0	17.1	87	4.4	8.2	41.3	4.3
Apr-11	27.7	18.6	93	3.0	6.0	178.8	3.3
May-11	27.6	19.4	93	4.4	7.5	24.0	3.4