STUDIES ON LEACHING AND DISSIPATION OF COMMONLY USED ORGANOPHOSPHORUS PESTICIDES IN CARDAMOM ECOSYSTEMS OF IDUKKI DISTRICT, KERALA

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of requirements for the Degree of
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in
ENVIRONMENTAL SCIENCE

by

BINDUMOL G.P.

Division of Environmental Science
Department of Botany
University of Calicut
Kerala- 673635
India
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DECLARATION

This thesis entitled **"Studies on leaching and dissipation of commonly used organophosphorus pesticides in cardamom ecosystems of Idukki District, Kerala"** submitted by me in partial fulfilment of requirements for the award of the degree of Doctor of Philosophy in Environmental Science of University of Calicut embodies the results of an original research work carried out by me under the guidance and supervision of Dr C.C. Harilal, Associate Professor, Division of Environmental Science, Department of Botany, University of Calicut. No part of the work has formed the basis for the award of any other degree or diploma of any University.

Calicut University **BINDUMOL G. P.**
18 May 2018

Dedicated to

INDIAN CARDAMOM RESEARCH INSTITUTE

(SPICES BOARD OF INDIA)

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ABBREVIATION

Abbreviation	**Expansion**
µg/g	Microgram per gram
µg/L	Microgram per litre
µg/mL	Microgram per milliliter
^{0}C	Degree centigrade
a.i.ha^{-1}	Active ingredient per hectare
ANOVA	Analysis of variance
BDL	Below detection limit
CFU/100g	Colony forming unit per 100gram
cm	Centimeter
EC	Emulsifiable concentrate
FYM	Farmyard manure
GC- MS	Gas chromatography- mass spectrometry
ha	Hectare
Kg/ha	Kilogram per hectare
Kg/yr	Kilogram per year
M	Molar
m^3	Cubic meter
meq/100g	Milliequivalents per 100gram
ng/g	Nanogram per gram
rpm	Rotations per minute
SPSS	Statistical Package for Social Sciences
g/cc	Grams per cubic centimeter
dS/cm	Decisiemens per centimeter

CONTENTS

Title	Page No
GENERAL INTRODUCTION	1-10
Chapter 1	11-91
EVALUATION OF THE EXTENT OF CHLORPYRIPHOS AND QUINALPHOS IN SOIL AND AQUATIC ENVIRONMENTS ASSOCIATED WITH CARDAMOM PLANTATIONS OF KERALA	
Introduction	12
Review of literature	14
Materials and Methods	27
Results and Discussion	53
Summary and Conclusion	89
Chapter 2	92-138
LEACHING, DISSIPATION AND SORPTION KINETICS OF CHLORPYRIPHOS AND QUINALPHOS IN CARDAMOM PLANTATIONS OF KERALA	
Introduction	93
Review of literature	97
Materials and Methods	112
Results and Discussion	121
Summary and Conclusion	137
General Summary and Conclusion	139-143
References	144-166

BINDUMOL G.P. “STUDIES ON LEACHING AND DISSIPATION OF COMMONLY USED ORGANOPHOSPHORUS PESTICIDES IN CARDAMOM ECOSYSTEMS OF IDUKKI DISTRICT, KERALA”. THESIS. DEPARTMENT OF BOTANY, UNIVERSITY OF CALICUT, 2018.

GENERAL INTRODUCTION

Pesticide is defined as any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal diseases, unwanted species of plants or animals causing harm during, or otherwise interfering with, the production, processing, storage, transport or marketing of food, agricultural commodities, wood, wood products or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids, or other pests in or their bodies (WHO, 1990). Codex Alimentarius Commission and Council of Europe have also adopted similar definition for pesticides.

The history of crop protection practices in agriculture evolved through ‘trial and error’ experiences, which included agricultural practices such as sanitization, tillage, crop rotation, pruning, use of insect free seeds and seedlings. In early stages of insect and disease control, materials of natural origin like plant materials, animal manures, dry ashes, soot, urine, sea water, soap, turpentine, etc. were used. During eighteenth and nineteenth centuries, due to intensification of agriculture, pest attack also increased and this led to the development of more effective pest control measures. Early concept on the effectiveness of a chemical or mixture was related to its offensiveness with regard to its odour or taste (Smith et al. 1976).

First synthetic groups of insecticides were inorganic in nature. The development of ‘Paris Green’, a crude form of copper arsenite for the control of Colorado potato beetle in 1865 was the first record of synthetic chemicals in pest control (Green et al. 1987). Further, Bordeaux mixture and potassium dinitro-o-cresylate were evolved. Various other arsenites and arsenates were tested against insect damage to crops. Sodium fluoride, a highly toxic insecticide has been evolved against cockroaches, earwig's ants and other crawling species. Borax and boric acid are still in use against cockroaches.

However, the development of synthetic organic pesticides during and following World War II revolutionized the area of pest control (Matthews, 2008). The first synthetic organic chemical for insect control was DDT (1,1-bis (4-chlorophenyl)-2,2,2-trichloroethane). Even though it was discovered in 1874, its insecticidal property was unknown for about 65 years. During initial period of its discovery, DDT was used in health care sector. It was also used in various countries against the control of insect-borne diseases such as typhus and malaria.

Since then, there was a boom in the diversity and magnitude of pesticides. Presently there is a multitude of pesticides used for various purposes. They are classified into different groups based on the type of pest they control, mode of action and their chemical properties (Kumari and Kathpal, 2010). Some of such classifications are given below.

1) Type of pest

With regard to the type of pest they encounter, pesticides are classified as:

Algicides: used for the control of algae in water bodies.

Antifouling agents: kill or repel organisms attached to surfaces which are immersed in water.

Antimicrobials and biocides: kill bacteria and viruses.

Disinfectants and sanitizers: inactivate disease causing microorganisms and inanimate objects.

Fungicides: control different types of fungi.

Fumigants: used to produce gas or vapour, which destroys pests.

Herbicides: control weeds and other unwanted plants.

Microbial pesticides: inhibit the microorganisms and insect pests.

Molluscides: kill snails and slugs.

Nematicides: control root nematodes.

Pheromones: disrupt the hormonal activities in insects.

Rodenticides: kill mice and other rodents.

Defoliants: help to drop leaves and foliages from plant to facilitate harvest.

Desiccants: promote drying of living tissues in plants.

Growth regulators: alter the growth and reproduction in animals and plants.

2) Structural relationship

Synthetic organic pesticides are classified into various groups according to the structural similarity of the active ingredient. They include organochlorines, organophosphates, carbamates, pyrethroids, neonicotinoides, phenyl pyrazoles and benzoyl ureas.

Organochlorines

Dields-Alder condensation reaction of hexachloropentadiene with various adducts produces a range of broad spectrum organochlorine insecticides in high yield. DDT is an example. DDT and its analogues act as nerve poison (Smith et al. 1976). Others like lindane (gamma HCH), aldrin, endrin and dieldrin are also powerful in this category. Endosulphan is a mild organochlorine insecticide, which is being used in orchards and plantations. Due to high persistence and mammalian toxicity, most of the organochlorine pesticides have been banned globally.

Organophosphates

Organophosphates are the most versatile group of chemicals, which are being used as insecticides, fungicides, herbicides, nematicides, chemosterilants, etc. Usually, organophosphate pesticides are synthesized by neutralizing phosphorus acid chloride with alcohol, amines or mercaptans (Green et al. 1987). All these category of pesticides inhibit the ester splitting enzyme like cholinesterase in living organisms. In the absence of cholinesterase enzymes, acetyl choline accumulates and interferes in the coordination of nerve-muscle relation in animals.

Carbamates

Carbamates are closely related to organophosphate insecticides in their biological mode of action. These groups of pesticides are very much toxic and are allowed to register as granules and not as sprays to reduce potential exposure (Matthews, 2008). There are three classes of carbamates having commercial importance. They are:

- N-methylcarbamates of phenols and hydroxyl heterocyclic compounds such as carbaryl and carbofuran.
- N- methylcarbamates of oximes like methomyl.
- N, N-di methylcarbamates of hydroxyl heterocyclic compounds like pirimicarb.

Synthetic pyrethroids

In ancient times, pyrethroids were applied for pest control as crude extracts of *Chrysanthemum roseum* and *Chrysanthemum. carneum*. As pyrethrins are soluble in various organic solvents; natural pyrethrins are extracted and concentrated for pest control. Active esters of pyrethrum flowers are Pyrethrin I & II, Cinerin I & II and Jasmoline I & II. The wide spread popularity of pyrethrins is owing to its low mammalian toxicity. Among different pyrethroids, Pyrethrin I is lethal to insects. Allethrin is the first synthetic pyrethroid in which 2-butenyl group of Cinerin I is substituted by allyl group. As it is less toxic and has thermal stability, it is used in mosquito coil. Its insecticidal potency could also be enhanced by substituting alpha-cyano group with 3-phenoxybenzyl ester.

Neonicotinoids

Neonicotinoids are the newest class of pesticides having outstanding potency and systemic action in pest control. Imidacloprid is the first member of this family. Further, Acetamiprid and Thiacloprid are also developed for pesticide applications.

Phenyl pyrazoles

Recently, Phenyl pyrazoles are introduced for pest control when insects developed resistance against pyrethroids, organophospahates and carbamates. They are reported to exert direct excitatory effects on the nervous system of pests. Fipronil is an example.

Benzoyl ureas

They are chemical derivatives of N-benzoyl-N’-phenylurea. They act as growth regulators by inhibiting the synthesis of chitin in the body of the insect. Most commonly used pesticides are Diflubenzuron, Chlorfluazuron, Flufenoxuron, Hexaflumuron and Triflumuron.

3) Mode of action of pesticides

Mode of action of a pesticide refers to the way in which it causes physiological disruption at its target site. Pesticides having similar chemical structures have common target sites and mode of action. They are being classified into Acetylcholinesterase inhibitors, GABA-gated chloride channel antagonists, Sodium channel modulators, Nicotinic acetylcholine receptor agonists and Juvenile hormone mimics.

Organochlorine pesticides

Organochlorines are broad-spectrum contact pesticides. They are extremely rapid in action and have high “knock-down” properties. They also cause damages on the leaves of crop plants and skin irritation in human beings. Certain organochlorine pesticides which were in use in healthcare sector were withdrawn due to their irritant effect (Green et al. 1987).

Experimental evidences suggest that mode of action of DDT and pyrethriods is similar. They react with voltage–gated sodium channels. Pyrethoids prolong the period of open state of sodium channels (Stenersen, 2004). Even now the precise biochemical lesion responsible for the toxic action of organochlorine pesticides is uncertain. The symptoms related to the poisoning of organochlorine pesticides are hypersensitivity and hyperactivity with involuntary muscular contraction in insects (Stenersen, 2004; White-Stevens, 2010).

Organophosphorus pesticides

Organophosphorus pesticides are systemic in nature. They have been used as systemic insecticides for plants, animals and also for soil and seed treatments. When these chemicals are applied, plants absorb them and translocate to various parts of the plant in quantity lethal to insects feeding thereon. Systemic compounds can be applied as direct sprays to the foliage, by drenching the soil or by direct application or injection of concentrates to the stem or as seed treatment before planting. Moreover, systemic pesticides could be able to minimize the uneven spray coverage by distribution of active ingredient in plant foliage. Soil and seed treatment by systemic pesticides protects young plants from the infestation by mites, aphids, thrips and leaf hoppers.

The mode of action of organophosphorus pesticides is as cholinesterase inhibitors. The toxicity of each compound depends on its reactivity, which is determined by the electrophilic character of phosphorus atom, strength of P-X bond and steric effect of other functional groups.

Worldwide, growing demand for food and changes in dietary habits escalated the need to improve crop yield and quality through the control of insect pests. The rate of consumption of agrochemicals has thus become a measure of agricultural progress (Banaszkiewicz, 2010). Apart from agriculture, pesticides and insecticides are extensively in use to control pest /insect population in public health system. Pesticides play a major role in the control of epidemics through effective control of vectors alone or in combination with other technologies (Perry, 1997). Thus pesticides/insecticides continue to provide farmers and public health workers to manage their systems from pest attack, quickly and effectively (Sparks, 2013).

Crop loss due to agricultural pests and plant diseases are quite high in developed and developing countries. Chemical control of pests and diseases has been practiced for minimizing the loss. Global consumption of pesticides has thus gone to two million tonnes per year, of which 45% is consumed in Europe and 25% in USA (De et al. 2014).

Agriculture is the backbone of Indian economy. India accounts for 15% of world population. In order to meet the demand of growing population, agricultural production and protection technologies have to be improved substantially. The production of pesticides started in India in the year 1952, with the production of HCH and DDT. Domestic pesticide industry has developed since then and contributed significantly towards pest management in agriculture and public health. Indian agricultural sector has accelerated in recent times from 1.2% to 4.1% (http://ecomonictimes. indiatimes.com). Currently, India is able to meet 95% of its domestic demand of pesticides. Also it is the fourth largest global producer of pesticides, with an estimated market size of around $4.9 billion, during the financial year 2016-2017, after United States, Japan and China (www.careratings.com). Though the use of various pesticides in India has been reduced from 47020 MT to 37979 MT during 2001-07 (Kumari and Kathpal, 2010), the per-hectare consumption is amounting to 0.5 kg/ha (Kumai and Kathpal, 2010; De et al. 2014). It is also reported that India is the first developing country to initiate large scale use of pesticides for the control of insect pests in public health and agriculture (Dhaliwal and Singh, 2000).

In India, major portion of pesticides are consumed for cotton and paddy cultivation, followed by wheat, fruits and horticultural crops. Pesticide use is essential in the country to ensure food security to its increasing population. Pesticides are also significant as they protect high productivity per unit area. It is obvious that, judicious use of pesticides will definitely enhance the world wide capacity to produce more food to feed the expanding population. Thus pesticides are benefitting mankind through improving agricultural productivity, controlling disease outbreaks and checking pest attack in heterogeneous living conditions (Aktar et al. 2009).

Kerala, ‘The Land of Spices’, secured a premier position in global spice market with its variety of spices in terms of quality and quantity. The trade of spices plays a significant role in the economy of this state owing to its domestic and global market, which brings lot of revenue to the state. The climate of Kerala is highly favorable for the cultivation of a wide variety of spices including cardamom, pepper, ginger, turmeric, nutmeg, vanilla, clove, etc.

Cardamom (*Elettaria cardamomum* Maton) often referred to as the 'The Queen of Spices' is a gift of the Western Ghats to the world of flavour. The cardamom growing region of South India lies within 8^0 and 30^0 N latitudes and 75^0 and 78^0 30' E longitudes. In India, cardamom is cultivated in an area of 70080 ha, out of which Kerala occupies 60%, followed by Karnataka (30%) and Tamil Nadu (10%). Cardamom is a major flavouring agent used in food products, beverages and medicines. It is used in Indian systems of medicine like *Ayurveda*, *Sidda* and *Unani*. Cardamom production in India during 2015-16 was 19,625 MT (www.indianspices.com) which earned Rs.25 Crore to export basket. Presently Guatemala is the largest producer and exporter of cardamom with about 25,000 MT of production annually. Since cardamom cultivation is almost confined to forest ecosystems, cardamom plants are prone to a large variety of insect pests such as cardamom thrips (*Sciothrips cardamomi*), shoot and capsule borers (*Conogethes punctiferalis*), root grub (*Basilepta fulvicorne*), root knot nematodes (*Meloidogyne incognita and Meloidogyne. javanica*) and hairy caterpillars (*Eupterote cardamomi, Eupterote. canarica and Eupterote. fabia*) (Spices Board, 2001).

The use of agrochemicals in cardamom protection and production has increased over the years due to the cultivation of high yielding varieties and crop management for better pest control and yield (Murugan et al. 2011). Moreover continuous cultivation of cardamom in this area is likely to degrade the soil/water quality in terms of physical, chemical and biological properties and increase the accumulation of heavy metals and pesticide residues, which will ultimately degrade the entire agro-ecosystem.

The present study envisages the spatio-temporal assessment of commonly used organophosphorus pesticides like Chlorpyriphos and Quinalphos in associated cardamom ecosystems of Kerala. The major objectives are outlined as:

- To evaluate the extent of Chlorpyriphos and Quinalphos in soil and aquatic environments associated with cardamom ecosystems of Kerala.
- To study the leaching and dissipation pattern of Chlorpyriphos and Quinalphos in cardamom growing soils under controlled conditions.
- To evaluate the sorption characteristics of Chlorpyriphos and Quinalphos in cardamom growing soils of Kerala.

The first objective attained is depicted in Chapter 1 and the second and third objectives are depicted in Chapter 2.

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CHAPTER 1

EVALUATION OF THE EXTENT OF CHLORPYRIPHOS AND QUINALPHOS IN SOIL AND AQUATIC ENVIRONMENTS ASSOCIATED WITH CARDAMOM PLANTATIONS OF KERALA

INTRODUCTION

Cardamom plantations of Idukki district are unique in the state of Kerala. There are alarming reports on the unsystematic and unhealthy practices of pesticide application in these plantations (Usha, 2007). The indiscriminate use of Endosulphan in Kasargod district of Kerala has awakened the authorities for a statewide ban on this pesticide (Misra, 2011). But still the unscientific practice of pesticide application continues in cardamom plantations. Even though the present pesticide use in our country is 0.5 kg/ha, cardamom plantations receive an extent of about 2.7 kg of pesticides per hectare. Major health disorders such as cancer, asthma and dermatitis are very common among people living close to cardamom plantations (Misra, 2011). There were lots of reports in local dailies regarding the indiscriminate use of agrochemicals, including toxic pesticides in large scale cardamom plantations of Nedumkandam, Udumbanchola, Santhanpara, Pooppara, Pethotty and Parathode areas. Thus intensive cultivation coupled with unscientific use of various persistent plant protection chemicals would intensify environmental pollution and contamination through leaching and run off of residues to various domains of these plantations.

Integrated pest management envisages the use of all available pest control techniques to reduce pest populations. Integrated pest management programmes take a comprehensive and multidisciplinary approach in tune with the type of plantations. Pest control strategies have been expanded from the use of pesticides to other means such as growing genetically engineered crops designed to produce their own insecticides or exhibit resistance to wide spectrum of pests and weeds. A bio-rational pest control relies heavily on cultural and biological tactics which are supplemented with timely and careful applications of highly selective chemical insecticides (Jamal, 2017).

For bringing sustainability in the use of pesticides in agro-ecosystems, there has to be serious studies on the types of pesticides, their chemical configuration, mode of application, dosage, effectiveness and environmental persistence. The present study is an attempt in this direction with the objective of evaluating the extent of widely used pesticides like Chlorpyriphos and Quinalphos in soil and aquatic environments associated with cardamom ecosystems of Kerala.

REVIEW OF LITERATURE

Modern crop protection and production activities cause challenges to the total health of associated environments, especially soil and water. The residues associated with them are potential hazards to non-target organisms, including human beings. Several attempts are going on world-wide to assess the environmental mobility and fate of these synthetic chemicals. The present study attempts to monitor the dispersal of organophosphorus pesticides like Chlorpyriphos and Quinalphos in soil and aquatic systems associated with the cardamom ecosystems of Kerala. Attempts were also carried out to assess the influence of physico-chemical characteristics of soil and water and their interrelationship with respect to the persistence and fate of these residues in the cardamom growing soils of Idukki district, Kerala. Following review of literature pertains to studies which were carried out in a global/national perspective with regard to the persistence of pesticides in various agro-ecosystems.

Shallow ground water contamination due to organochlorine pesticides (OCPs) was studied in Taihu Lake Region, China (Wu et al. 2014). All organochlorine pesticides were detected in shallow ground water samples with high detection frequency, except p,p’-DDD and p,p’-DDT. Compositional analysis suggested that there were fresh input sources of Heptachlors, Aldrins and Endrins, in addition to the historical residues.

Guo et al. (2014) evaluated the effect of aquatic hydrophytes on the distribution of organochlorine pesticides in wetland sediments in Baiyangdian, China. The study revealed that the surface sediment concentration was higher than those near roots of aquatic hydrophytes. DDT predominated in sediments. Compared to other aquatic plants, *Phragmites* showed more effective organochlorine pesticide removal from the sediments in the wetland.

The influence of agricultural activities such as intensive cultivation of potatoes and cereals on the quality of groundwater and drinking water supplies of households has been studied. Pesticides and their metabolites *viz*, Metribuzin, Bentazone, MCPA, 2,4-D, Propachlor, 2,6-dichlorobenzamid, Metalaxyl and Macozeb were found in a majority of the sampled wells. The results also showed that alluvial plains can diffuse pollutants from spraying area and can cause contamination in shallow groundwater wells in Nordic areas (Kvaener et al. 2014).

Organochlorine pesticides and polychlorinated biphenyls (PCBs) in surface soils along a transect from a petrochemical industrial city (Lanzhou) and adjacent agricultural areas were studied by Gai et al. (2014). Organochlorine pesticides were dominated by HCHs in highland Prairie. The studies also indicated that land type, organic carbon contents and pH had affected the persistent organic pollutant preservation in soil.

In integrated pest management (IPM), module of pesticide residues on Basmati rice was conducted in North India during 2005-2008. The pesticide residues were found below the detection limit in soil, rice grains and irrigation water samples in Kaithal region and Dehra Dun region (Arora et al. 2014).

Isolation and identification of bacterium capable of degrading organophosphate pesticide was conducted in pesticide contaminated soil samples by selective enrichment on Quinalphos. The bacterial strain *Ochrobactrum* sp. strain HZM was identified and it's morphological and biochemical characteristics were elucidated. The organism was capable of utilizing various organophosphate pesticides such as Quinalphos, Profenofos, Parathion-methyl and Chlorpyrifos as growth substrate. This bacterial strain could be used for the bioremediation of contaminated soil and water, containing organophosphate pesticides (Talwar et al. 2014).

Mohapatra and Ajithakumar (2014) evaluated the residue persistence of fungicides (Trifloxystrobin and Tebuconazole) applied for the control of Sigatoka leaf spot disease of banana. The commercial formulation Nativo 75 WG was applied on fruit and soil at various doses. Trifloxystrobin and its metabolite were not detected in fruit pulp. Trifloxystrobin and Tebuconazole were degraded with half-life of about 11 days.

Occurrence of currently used persistent organochlorine pesticides (Chlordanes, HCB, Endosulfan and their isomers) with regard to an altitudinal gradient was analysed in Mianzhu-Aba prefecture transect in eastern region of Tibetan plateau. The study indicated that mean concentrations of Hexachlorobenzene, Heptachlor, Heptachlor epoxide, Chlordane, Nonachlor and Endosulfan in soil changed during winter and summer. Soil concentration of organochlorine pesticides was slightly higher in Mianzhu-Aba, than mountainous regions (Liu et al. 2015).

An extensive monitoring of pesticide residues in river basin of Llobregat River (Catalonia, Spain) revealed residues of pesticides in 50% of the water samples analysed, followed by sediments and biota. Residues of Benzimidazoles such as Carbendazim in 22% of the analyte, organophosphate pesticide like Malathion in 54% of the samples and urea compounds like Diuron in 54% of the samples were detected. Chlorpyriphos was detected in 93% of the sediments (Masia et al. 2015).

Contamination levels and sources of organochlorine pesticides in surface soils from Urumqi, China were assessed from five functional zones. The measured concentration and occurrence rate of the pollutants DDTs, HCHs and Methoxychlor dominated in all the zones (Min et al. 2015).

Abdollahzadeh et al. (2015) conducted survey on the perception of farmers on the pros and cons of pesticides in rice cultivation in Iran. The results showed that high income, high grain yield and intense use of pesticides were associated with intensive management of cultivation, where high share of family labour force was required in farming with biological control agents.

VoPham et al. (2015) presented an improved Geographic Information System (GIS) and remote sensing method, the Landsat method, to estimate agricultural exposure through matching pesticide application to crops in California. The results demonstrated that the Landsat method can improve GIS based pesticide exposure by matching more pesticide applications to crops via temporally concurrent Landsat images to the standard method and updated land use survey crop data.

Bioaccumulation and persistence of organic pollutants (POPs) in the food chain air-grass, yak butter in the pasture region of Namco Tibetan plateau (TP) was studied by Wang et al. (2015). The concentration of pollutants in the TP was the lowest among the global scale. The relatively volatile compounds such as ∞-HCH and o,p'-DDT dominated in the atmosphere of Namco. During the growing season, continuous absorption of DDTs by grasses was observed. The concentration of OCPs and PCBs in air, grass and butter in Namco were generally lower than other parts of the world. HCB was the main pollutant in air and butter. DDTs and high molecular weight PCBs have noticed to have high biological concentration factor values.

Zeng-long et al. (2015) reviewed the management of pesticides in China, its laws and regulations, supervision, standard systems and quality and safety of agricultural products. Results showed that the progress in the management of pesticide residues has been steadily made in China. The study also emphasized aspects to update regulations, supervising efficiency, risk assessment and international cooperation and communication.

An extensive monitoring of organo-halogenated contaminants (OHCs) from surface soils and different land use types from Pakistan revealed that DDT contaminants dominated in industrial and agricultural soil, followed by HCH and PCB (Zehra et al. 2015).

The levels and pattern of organochlorine pesticides in rain water in Kibaha coast region of Tanzania revealed the presence of compounds like DDT, DDE, DDD, HCHs, Dieldrin, Heptachlor, Chlordane, Endrin and Hexachlorobenzene. Samples collected from the vicinity of contaminated site and other points even showed the distribution of contaminants (Mahugija et al. 2015).

Studies conducted by Allen et al. (2015) revealed that crop grown under protected cultivation have increased the frequency of pesticide residue detection in higher concentration than crops grown in open fields. The pesticides such as Cypermethrin, Cyprodinil, Fenhexamid, Boscalid and Iprodione were detected in the products of protected cultivation. The slow removal of pesticides in protected systems and different pesticide use regimes are attributed to the presence of such chemicals in various agricultural products.

The benefit of agricultural pesticides and its negative impact on the environment and food safety in California was reviewed by Zhang et al. (2015). Twenty years of pesticide residue monitoring data were analysed and results showed that more than 95% of the food samples were in compliance with US pesticide standards. A few detected residues had potential to cause health risk. The study established an effective food residue monitoring program to ensure food quality throughout the market place.

Water pollution caused by organophosphorus and carbamate pesticides and dibutylphthalate in different groundwater and surface water sources in

Mysore city was studied by Somashekhar et al. (2015). Results indicated that organophosphorus and carbamate pesticides were not detected in any of the water samples, whereas an intermediate of carbamate pesticide methylisocyanate was detected in five samples. Apart from methylisocyanate, a plasticizer called dibutylphthalate, which was used for flexibility of plastic, was also detected in water samples.

An extensive review and statistical analysis were performed on agricultural and background soil concentrations of DDT, HCB and HCH in 73 peer-reviewed journal publications from 1993 to 2012 by Camenzuli et al. (2016). The average concentration of pesticides in agricultural soils was significantly higher than in background soil for all chemicals during 2003 to 2012. The mean soil concentration was found to be decreased from first decade to the second, but it was not observed in the concentrations of p,p'–DDT and α-HCH.

The water and sediment quality and bioaccumulation of pollutants in fish, bivalves and birds were studied for a period of 22 years under Regional Monitoring Program (RMP) for water quality in San Francisco Bay for management decisions. The cornerstone of the RMP was to assess the status and trends through monitoring them in water, sediment, and bivalves. Emerging contaminants, PCBs, Selenium, and exposure effects were focused in the programme. Bioaccumulation of various pollutants including pesticides was also examined. RMP has become a model water quality monitoring programme, which has influenced water quality management decisions for ecosystems (Trowbridge et al. 2016).

Karasali et al. (2016) evaluated pesticide residues in soil and water samples of Kopaida region, Greece, before and after the implementation of low-input crop management protocols. During the monitoring programme, a total of sixty six soil samples were collected and analysed. Initially, the residues of herbicides such as Ethalfluralin, Trifluralin, Pendimethalin, S-metolachlor and Fluometuron were detected in most of the samples, but the concentration was reduced after the implementation of the low–input crop management programme.

A new and rapid method was developed for the determination of nine neonicotinoid insecticide residues and their two primary metabolites in soil and plant samples using HPLC - MS/MS (Abdel- Ghany et al. 2016). Limits of detection (LoD) and quantification (LoQ) of the compounds were in the range of 0.08- 6.06 ng/g and 0.26-20 ng/g, respectively.

Matache et al. (2016) monitored the residues of organohalogen pesticides such as DDT and its metabolite DDE and DDD and also HCH in biological samples of birds from lower Prut Floodplain Natural Park, Romania. The results revealed the presence of organochlorine pesticides (DDT and its metabolites and HCH congeners in eggshells and feathers of the birds, despite ban on the use of DDT in Romania for more than 20years.

Mekonen et al. (2016) evaluated the pesticide residues in drinking water, together with human exposure in Ethiopia by calculating estimated daily intake of residues with accepTable daily intake and acute reference dose. The residues of 2,4-D, Malathion, Diazinon, Pirimiphos methyl and Fenpropimorph were detected in drinking water sources from Jimma and Addis Ababa water sources, south western Ethiopia. The concentrations of residues of some pesticides were above the European drinking water guideline values, which indicated the illegal use of pesticides in that area. Chronic risk of human health was observed from exposure to Diazinon and Fenpropimorph in all the study areas. The study also showed essentiality of water quality monitoring programme to reduce the residue level in drinking water.

Nuapia et al. (2016) investigated the level of organochlorine insecticides in the raw food from open markets in Kinshasa, Democratic Republic of Congo (DRC) and Johannesberg, South Africa, to assess the potential health risks associated with the pesticide residues. The mean concentrations of organochlorine pesticides in raw foods collected from Johannesberg market were significantly higher than those from Kinshasa market.

Occurrence and assessment of pesticide residues in water, sediment and biota of Ebro River was studied during 2010 - 2011 (Ccanccapa et al. 2016). The results revealed that pesticides such as Chlorpyriphos, Diazinon and Carbendazim were frequently detected in water samples, wherein Imazalil and Diuron were in highest concentrations. In sediment samples, Chlorpyriphos, Diazinon and Diclofenthion were detected. Chlorpyriphos was the only pesticide detected in biota. Ecotoxicological studies revealed that organophosphorus and azol presented high risk for algae, whereas organophosphorus, Benzimidazoles, Carbamates, juvenile hormone and Azol mimic for daphnia and fish.

Land and water governance through an analysis of regulatory water quality programme in Wilconsin, USA, demonstrated the role of uncertainties in the measurement and prediction of pollution and to formulate the programme design. It comprehends that experimentation under uncertainty led to sustained dialogue and an iterative process of deciding how monitoring and modeling should be used to track and prove programme progress (Wardropper et al. 2017).

The exposure of pesticides to drinking water adversely affects health. A study was conducted to compare health outcomes between people who drink surface water and groundwater in a paddy cultivating area. The results indicated that, a 10% increase in rice pesticide use unfavorably altered the disability index (Activities of Daily Living) by 1% for rural residents who are of 65 years and above age. The results emphasize the unintentional policies such as support policies to boost farm production and rural income effect that diminish the health and escalated caring burden in affected households. The findings of this study also shed light on the tradeoff faced in agriculture and environmental policy design (Lai, 2017).

Pesticide toxicity was compared in small agricultural streams of Germany with and without waste water treatment plants in the upstream catchments. The results indicated that higher pesticide toxicity was found in sampling sites with waste water treatment plants. Further, toxicity was more due to residues of herbicides than insecticides and fungicides. Herbicide toxicity was noticed due to the residues of Diuron, Terbuthylazin, Isoproturon, Terbutryn and Metazachlor (Le et al. 2017).

Study has been conducted to assess the dietary risk of pesticides from vegeTable s and drinking water for children and adults in Loumbila Burkina Faso by Lehmann et al. (2017). The results showed that the maximum residue limits exceeded in 36% of the samples for seven pesticides like Acetamiprid, Carbofuran, Chlorpyriphos, lambda-Cyhalothrin, Imidachloprid and Profenophos. Risk was identified for Chlorpyriphos and lambda-Cyhalothrin in acute chronic exposure scenarios. The cumulative dietary exposure presented acute and chronic risk for children and adults. Processing factor was largely influenced by washing of vegeTable s with water and that considerably reduced the risk of hazardous exposure.

A multi catchment study of urban storm water pesticides across Australia and its dichotomous identity as well as spatio–temporal pattern of stormwater pesticide composition was conducted during 2011-2014. Out of 27 pesticides monitored, 19 pesticides were detected in Australian storm water. Diuron, MCPA, 2,4-D, Simazine and Trichlor were detected in more than 50% of the samples (Rippy et al. 2017).

The residues of organochlorine pesticides, including Chlorpyriphos, were determined in dried cocoa from Ondo and Ile-Ife, southern Nigeria. The higher levels of organochlorine pesticides were detected in the cocoa beans from Ondo than from Ile-Ife. The results of the study recommended environmental toxicological studies in that area (Oyekunle et al. 2017).

Strassemeyer et al. (2017) evaluated the upscale risk based on environmental parameters, pesticide properties, multi exposure toxicity assessment and fieldspecific information on pesticide usage on landscape level to soil, surface water, pollinators and groundwater. The model prediction tool SYNOPS-WEB reliably modeled aquatic exposure of pesticides, that were detected during monitoring and additionally revealed risks from pesticides that could not be detected in surface water due to concentrations close to limit of quantification. The model was also suiTable for future adaptation and integration of novel approaches to risk assessment for wider ranges of reference organisms and larger sets of mitigation measures.

A study was conducted by Donga and Eklo (2018) to document pesticide use and handling practices that influence pesticide exposure among sugarcane farmers in Malawi. The results indicated that herbicides and insecticides were widely used. Several pesticides such as Ametryn, Acetochlor, Monosodium methylarsonate and Profenofos which were not approved in the European Union because of their toxicity to terrestrial and aquatic life were also used.

A study was conducted to monitor a total of seven pesticide residues under organochlorine, organophosphorus and carbamate pesticides in three different sources of pond water, paddy field water and tube-well water from NagarpurUpazila and paddy field water in the company of Dhaleshwari and Gazikhali river water from SaturiaUpazila, Bangladesh by Hasanuzzaman et al. (2018). The results showed that, among the organophosphorus pesticides, Diazinon was detected in eight water samples at a concentration ranging from 4.11 to 257.91 µg/L whereas, Malathion was detected only in one water sample at a concentration of 84.64 µg/L. Chlorpyrifos pesticide was also detected only in one water sample and the concentration was 37.3 µg/L.

Several studies have been undertaken in Indian context to assess the extent of pesticide residues in associated environments. They are given below.

Pesticide residues of isomers of HCH and DDT were detected in water samples collected from the river Cavery and its distributor river Coleroon in Tamil Nadu, South India. HCH was present during pre-monsoon and monsoon seasons. The value of DDT was well below the EEC's maximum accepTable concentration for surface water (Rajendran and Subramanian, 1996).

The levels of organochlorine pesticides and heavy metal residues were analyzed from fish samples of different locations of Calicut region, Kerala, to study the status of these chemical contaminants in fish and shellfish meant for human consumption. BHC and Heptachlor epoxide were the major marine fish pollutants, whereas BHC was present in fresh water and brackish water fish. Chromium and mercury were also detected in marine fish samples (Sankar et al. 2006).

Evaluation of concentration levels and distribution pattern of organochlorine pesticide residues in the soil and surface water samples from the northern Indo-Gangetic alluvial plains was carried out by Singh et al. (2007). Theα and β isomers of HCH were detected frequently than others. The results showed contamination of soil and surface water of the region with these chemicals.

A comprehensive report on oraganochlorine pesticide residues (OCs) such as Hexachlorocyclohexane isomers (HCHs), Dichlordiphenyltrichloroethane and its six metabolites (DDTs) and Hexachlorobenzene (HCB) in core sediments from Indian Sunderban wetland showed a heterogenic distribution for HCH. HCB has not shown any sharp special variation. The peak concentrations of HCH isomers and DDT metabolites in sediments have potential to cause ecotoxicological impact (Sankar et al. 2008).

A study has been conducted during 2010-2011 to assess the contamination level of organochlorine pesticides in open wells of Kasaragod District. The results revealed that, maximum contamination was observed for Endosulphan, followed by Hexachlorobenzene (BHC). During post-monsoon season of 2010, contamination levels of ∞- Endosulphan were higher at Panathur (58 µg/L) followed by Periya (37 µg/L). The residue level of ∞-Endosulphan was the highest in open wells of Panathady (56 µg/L) in the pre-monsoon of 2011. Sum of all organochlorine pesticides was maximum in Mulleria and Cheemeni and the lowest in Panathady and Rajapuram (Akhil and Sujatha, 2012).

Studies on method validation for estimation of residues of Chlorpyriphos and lambda Cyhalothrin in cardamom were carried out in Cardamom Research Station, Pampadumpara, Idukki District of Kerala by Kerala Agricultural University during August 2009 (George and Kumar, 2013). The main recovery of Chlorpyriphos was 97.3% and lambda Cyhalothrin was 98.9%. The processing factor for Chlorpyriphos was 3.53 and that of lambda Cyhalothrin was 4.58. The study indicated that the residues were magnified during curing.

Monitoring studies on the residues of certain pesticides such as Dicofol, Ethion, Quinalphos, Hexaconazole, Fenpropathrin, Fenvalerate and Propargite used for the control of pests and diseases in tea plantations of South India were conducted. Out of 468 samples examined, only one sample contained Hexaconazole residue, exceeding maximum residue limit (MRL). The residues of Ethion, Quinalphos, Hexaconazole, Dicofol, Fenpropathrin and Propargite were detected below MRL, except one (Kottiappan et al. 2013).

Pesticide residues in two species of frogs were evaluated from organic and conventional paddy farms in Kerala (Kittusamy et al. 2014). Seven frogs from conventional farms showed deformity, while it was not observed in organic farm. The concentration of organochlorine and synthetic pyrethroid was significantly greater in deformed frogs. Among organophosphates, Phorate and Quinalphos were detected in traces.

Persistence of Endosulphan in water, soil and sediment samples were evaluated in three Panchayats of Kasaragod district, Kerala in four different phases to assess the contamination caused by the application of Endosulphan in cashew plantations. The residue of Endosulphan was detected in only two samples out of 22 water samples analysed during second phase but all others were below detection limit. The residue of Endosulphan was detected in soil samples from Mullayar and Panathadi Panchayats. The results indicated that the concentration of Endosulphan was decreasing and found to be persistent for 1.5 to 2years (Harikumar et al. 2014).

Though much of studies are carried out on pesticide residues with respect to heterogeneous habitats in India and abroad, less of reports are available on the environmental persistence of pesticides with respect to cardamom ecosystems, especially of Kerala. Considering this lacuna, the present study has been carried out to assess the extent of organophosphorous pesticides like Chlorpyriphos and Quinalphos in the soil and aquatic environments of cardamom ecosystems of Kerala.

MATERIALS AND METHODS

Cardamom Hill Reserve (CHR) of Idukki District of Kerala has been divided in to three zones based on agro-climatic conditions, soil productivity and yield. Zone A includes Peerumedu taluk, excluding Kokkayar and Peruvanthanam, Chakkupallam, Ayyappankovil and Vandenmedu villages of Udumbanchola, where cardamom productivity is 450 kg/ha and comes to about 34% of CHR. Zone B comprises of Chathurangappara, Rajakkad, Santhanpara, Pampadumpara, Parathode and Udumbanchola villages of Udumbanchola Taluk, which covers 43% of CHR and productivity is only 300 kg/ha. Rest of the cardamom growing area comes under zone C (MSSRF, 2008). Soil and water samples were collected from zones A, B and C periodically. From each zone, three sampling locations were identified and their details are given below.

Zone A: Amayar, Puttady, Vadenmedu.

Zone B: Udumbanchola, Myladumpara, Santhanpara.

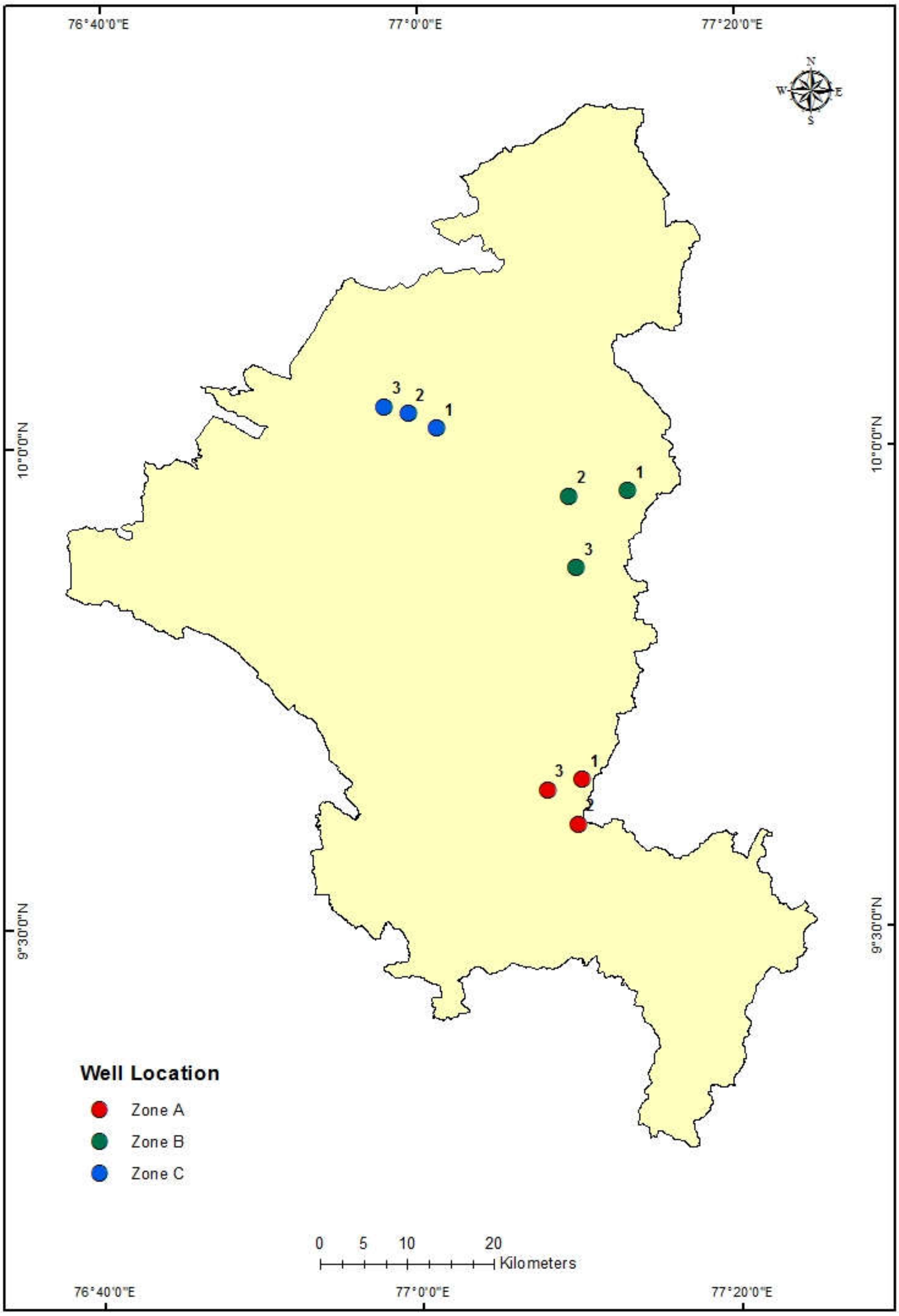
Zone C: Vattayar, Kurisupara, Peechad.

The sampling locations are depicted in Plate 1. Soil samples were collected from root zone area of cardamom plants, according to the cardamom package of practices (1997) of Spices Board, Kochi. Each soil sample has been collected from a plot of around 5 acre, leaving 30 cm from the plant base. The sites selected for sampling were cleaned from weeds, dry leaves and other mulch materials. A ‘V’ shaped hole to a depth of 15 cm was taken with a spade. Soil sample was scraped from both the sides of the ‘V’ shaped pit in a thin layer of 2 cm along the cutting of the full length as per Jackson (1973).

From each 5 acre plot, 10 sub samples were collected diagonally and were gathered in a polythene sheet. It was then mixed well, removed all plant materials and spread the soil in a square shape in thin layer and sectioned to four quarters by drawing diagonal lines and discarded the two quarters, which are falling opposite. The soil sample thus collected was dried under shade and sieved using 2 mm sieve. The material on the sieve was again ground and sieved till all the aggregate particles were fine enough to pass through and only stones and organic matter remained in the sieve. The whole sample was kept in plastic container. Three soil samples were collected from each zone on a bimonthly interval for a period of one year from August 2014 to June 2015.

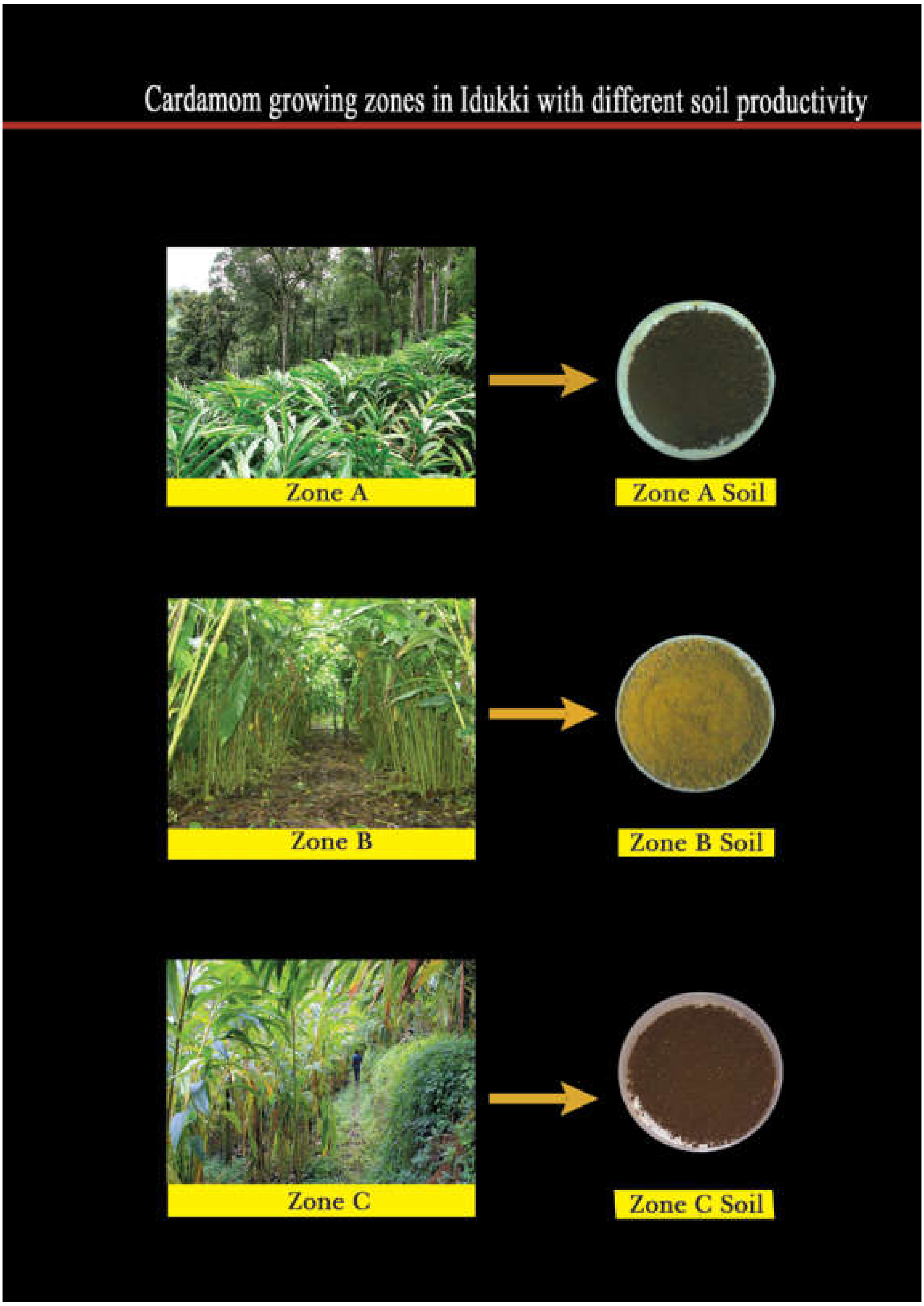
The nature of soil collected is given in Plate 2. Prior to analysis, the soil in the container was emptied to a clean polythene paper and spread evenly with a spatula. It was then heaped to a cone again by raising four ends of the sheet. The soil sample was again mixed well and spread evenly on the sheet. The process was continued for 3 to 4 times. The sample, which was thoroughly mixed and spread evenly on sheet, was divided into four equal quarters and a small quantity of soil was taken from various points in each quarter to get a representative sample for analysis.

PLATE 1



Zone A: Amayar, Puttady, Vadenmedu.
Zone B: Udumbanchola, Myladumpara, Santhanpara.
Zone C: Vattayar, Kurisupara, Peechad.

PLATE 2


Cardamom growing zones in Idukki with different soil productivity

Perennial water sources like open wells and streams in the same cardamom plantations were selected for water sampling. One litre each of the water samples was collected in plastic bottles (physico–chemical analysis) and amber coloured glass bottles (pesticide residue analysis). The samples collected for pesticide residue analysis were kept in ice chamber at 4 ^{0}C and transported to the laboratory. Water samples were analysed as per standard analytical protocols (APHA, 1999). Six water samples were collected from each zone. Altogether 18 water samples were collected in every sampling period. Water samples were also collected from August 2014 to June 2015.

Estimation of physical and chemical properties of soil

Soil physical properties are mechanical behavior of the soil which influence root penetration, drainage, aeration, retention of moisture and absorption of plant nutrients. Important soil physical properties are moisture content, texture, structure, porosity, colour, etc. In the present study physical properties like soil moisture content, pH, electrical conductivity, soil components like sand, silt and clay, bulk density, particle density, maximum water holding capacity, volume of expansion and cation exchange capacity were assessed and the methods followed are given below.

Determination of soil moisture content

Principle

A known weight of soil was dried at 105 ^{0}C until constant weight was obtained and the loss in weight was expressed as percentage.

Procedure

5 g of soil sample was taken in a previously weighed weighing bottle and dried in a hot air oven at 105 ^{0}C for 5 h. The bottle and contents were cooled and weighed. The process was continued until consecutive weights

were attained. From the loss of weight of sample, percentage of moisture content was determined.

Calculation

Weight of soil =5 g

Weight of bottle alone =b g

Weight of bottle + soil=a g

Weight of bottle + soil after drying= c g

$$\% \text{ moisture content}=\frac{\text{weight of moisture in the soil x 100}}{\text{weight of soil taken}}$$

Determination of soil pH

All water soluble materials contain free hydrogen and hydroxyl ions. When hydrogen ions exceed hydroxyl ions, the solution will be acidic. Similarly when OH^- ions are in excess, the solution turns alkaline. If hydrogen and hydroxyl ions are in equal share, the solution remains neutral. The pH is defined as the negative logarithm to the base 10 of H^+ ion concentration.

Principle

A glass electrode in contact with H^+ ions of the solution under test acquires an electric potential, which depends on the concentration of H^+ ions. It is measured potentiometrically against a reference electrode, which is usually a calomel electrode. The potential difference between calomel electrode and glass electrode is represented in pH units.

Reagents

pH buffers 4.0, 7.0 and 9.2

Procedure

20 g of soil sample was taken in a 50 mL beaker and 25 mL of distilled water was added and stirred 5 times over 30 min period and allowed to settle down to reach soil–water equilibrium. pH meter was switched on, temperature was set at room temperature and calibrated using standard pH buffers of 4.0, 7.0 and 9.2 by keeping the electrode in buffer.

Soil pH was determined by keeping the calibrated electrode in soil–water suspension until the stabilized reading was obtained.

Determination of Electrical Conductivity

Electrical Conductivity of a solution increases with soluble salt content of the solution. The measurement of conductivity is based on Ohm's Law. Since conductance is the reciprocal of resistance, it is expressed in mhos. If the relative concentration of an electrolyte is low, measurement of specific conductance is reported in millimhos or dS/cm.

Procedure

10 g soils sample was accurately weighed and taken in a beaker and 25 mL distilled water was added. The soil water suspension was stirred intermittently and kept overnight. The conductivity cell was calibrated using 0.01 M KCl solutions having specific conductance 1.412 dS/cm at 25 ^{0}C. After calibration, electrode was dipped in supernatant solution and recorded the conductivity in dS/cm.

Texture analysis (Mechanical Analysis - International Pipette Method)

Soil texture refers to the relative percentage of soil components such as sand, silt and clay. In field condition, the relative percentages of all the soil components are of indefinite composition. Soil texture is an important property related to the rate of water intake, water holding capacity, nutrient supply, etc.

Texture by mechanical analysis is based on the Stoke's Law, which states that the resistance offered by a liquid to the fall of a particle is proportional to the radius of the sphere. In this method, the soil is first dispersed using an agent and clay and silt are separated by sedimentation and coarse and fine sand by sieving.

Procedure

20 g of air dried soil sample was transferred to a 500 mL beaker. 60 mL of 6% H_2O_2 solution was added to remove the organic matter. It was then stirred well and kept on a water bath for 30 min. until the frothing ceased. After cooling, 200 mL of 0.2 N HCl was added and kept overnight. This was then filtered through Whatman No.50 filter paper until the extracts were free of chloride, which were tested using silver nitrate.

All the contents were transferred to another 500 mL beaker and diluted to 400 mL with distilled water. 8.0 mL of 1 N NaOH was added and stirred well using mechanical stirrer for10 min. The soil–water suspension was transferred to a 1000 mL measuring cylinder and the volume was made up to 1000 mL using distilled water. The cylinder was closed and shaken thoroughly with repeated inversions.

Clay + Silt

Immediately after shaking, the stopper was removed and placed the cylinder under a Robinson's pipette. After fine sand sedimentation time (3 min 25 sec at 31 ^{0}C), the pipette was lowered to 10 cm depth and pipetted out 20 mL sample to a previously weighed dish (W1) and dried the contents in a water bath, cooled, weighed (W2) and the silt and clay contents were calculated.

Clay alone

The suspension was again shaken and kept it undisturbed for silt sedimentation. 20 mL sample was collected after 6 h 45 sec at 31 ^{0}C and transferred to a pre weighed dish (W3) and dried over water bath, cooled and weighed (W4).

Coarse sand

The supernatant liquid was decanted and transferred the remaining contents into a tall beaker using a jet of water and the volume made to 1000 mL. The supernatant was decanted and the residue was transferred to a previously weighed crucible (W5), and the contents were dried and weighed (W6). From those values, percentage of sand content was calculated.

Calculation:

Wt. of soil taken = 20.0g
Wt. of coarse sand = b g
Wt. of silt + clay = c g
Wt. of clay alone = d g
M is the moisture content of the soil.

% coarse sand $= \frac{\text{b x100x100}}{a \text{ x } (100-\text{M})}$

% of silt + clay $= \frac{\text{c x 1000 x 100 x 100}}{a \text{ x 20 x } (100-\text{M})}$ ------A

% of clay alone $= \frac{\text{d x 1000x100x100}}{\text{a x 20 x } (100-\text{M})}$ ----- B

% of Silt = A-B

Determination of Bulk Density, Particle Density, Maximum Water Holding Capacity (MWHC), Percent pore space and Volume of Expansion (Keen’s cup method)

Bulk Density

Bulk Density is defined as the ratio of the weight of a unit volume of oven dry soil to the weight of the same volume of water. The Bulk Density of the soil indicates the degree of compactness and aeration status of soil. It is expressed in g/cc. Generally Bulk Density varies from 1.0 to 1.8 g/cc. Bulk Density usually increases with depth, owing to low organic carbon content and compactness of soil.

Particle Density

Particle density is the mass per unit volume of soil particles, usually expressed in grams per cubic centimeter (g/cc). It is the weight of individual soil particles per unit volume. The average value of particle density of soil is 2.66 g/cc.

Maximum Water Holding Capacity

Maximum Water Holding Capacity (MWHC) is the amount of water in a soil when its pores, both micro and macro or capillary are completely filled with water.

Pore Space

Pore Space is the space not occupied by soil particles or it is the area occupied by air and water. Pore space affects the gas exchange and water movement in the soil. Since it represents the space between the soil aggregates, both texture and structure affect pore space.

Volume of expansion

Volume of expansion of soil is defined as the increase in volume in cc per 100 cc of soil, when the soil is at its MWHC. It is influenced by the type and amount of clay present in the soil.

Keen and Raczkowski (1921) modified the Hilgard's experiment and introduced a single method for the estimation of Bulk Density, Particle Density, Water Holding Capacity, Pore Space and Volume of Expansion.The Keen's cup comprises of a circular brass cup of 5 cm diameter, 1.5 cm height with perforated base and a screw type ring, just fit in the cup as tightly as possible.

Materials required

Keen's Cup, spatula, moisture can, balance, oven, filter paper, camel hair brush and watch glass.

Procedure

The inner diameter and height of the Keen's cup was measured. A round filter paper was cut and fit in the cup. Weight of the cup along with filter paper and watch glass was determined. The cup was put on a sheet of paper; soil sample was packed, by putting small quantities at a time with gentle tapping on the work bench. The process was continued until the cup was completely filled. The surplus soil was removed by a sharp blade and soil from outer surface was removed using camel hair brush. It was then weighed accurately along with the watch glass. The cup and ring were then slightly screwed and placed it with a petri dish containing water to the depth of ¼ and allowed to absorb water till it was saturated. Then the cup was taken out, wiped the outer surface with a dry cloth and immediately weighed.

The ring was removed and scraped out the wet expanded soil by means of a clean spatula, and transferred to previously weighed porcelain dish and weighed. The cup with remaining wet soil was also weighed. Then the soil in cup and the porcelain dish were dried in an oven at 105 ^{0}C and weighed.

Calculation

Volume of Keen's cup (V) =25 mL

Weight of cup+ filter paper (FP) +watch glass (WG) =A g

Weight of cup +FP+WG +dry soil = B g

Weight of cup +FP+WG + saturated soil =C g

Weight of cup +FP+WG +wet residual soil =D g

Weight of cup +FP+WG + residual soil after drying =E g

Weight of porcelain Dish =F g

Dish+ wet expanded soil =G g

Dish + expanded soil after drying =H g

1. Bulk Density (g/cc) $= \frac{\text{Wt.of dry soil}}{\text{Bulk volume of the soil}}$

2. Particle density of soil (g/cc) $= \frac{\text{Wt.of oven dry soil}}{\text{Volume of the soil solids}}$

3. Max. Water Holding Capacity (%)

$$= \frac{(\text{Wt.of saturated soil} - \text{Wt.of oven dry soil})\text{x}100}{\text{Wt.of oven dry soil}}$$

4. % Pore space $= \frac{\text{Total Wt.of water in soil x 100}}{\text{V}}$

5. Volume of Expansion $= \frac{\text{Volume of expanded soil x 100}}{\text{V}}$

Soil chemical properties

Interaction of various chemical constituents takes place between soil particles and soil solution, which ultimately reflects in its chemical property. In the present study, soil chemical parameters, which have great impact on the fate of soil contaminants, were studied in detail. Soil properties such as cation exchange capacity, organic matter and total phosphorus content were analyzed along with an assessment of the residues of pesticides like Chlorpyriphos and Quinalphos.

Estimation of Cation Exchange Capacity (CEC) of soil

CEC of the soil is a measure of the quantity of readily exchangeable cations, neutralizing the negative charges in the soil. In a known quantity of soil sample, the cations are displaced by ammonium ions by leaching the soil with neutral normal ammonium acetate solution. The excess of ammonium acetate is removed with alcohol. Absorbed ammonium ions are then determined by steam distillation.

Reagents

1. Ammonium Acetate 1N - 77.09 g of Ammonium Acetate was dissolved in 1000 mL distilled water and pH was adjusted with NaOH / HCl.
2. Alcohol 95%
3. Boric acid- 4%
4. Mixed indicator
5. $KMnO_4$ 3.2%
6. NaOH solution -40%
7. Standard HCl -0.02 N

Procedure

10.0 g soil sample was taken in a 250 mL conical flask and 50 mL ammonium acetate was added. The contents were shaken for an hour and kept overnight. The contents were filtered through Whatman No.1 filter paper. The soil particles were completely transferred to the filter paper and washed with 25 mL ammonium acetate and allowed to leach completely. The soil left in the filter paper was washed with 60% alcohol to eliminate excess ammonium acetate. To the soil in filter paper, a pinch of ammonium chloride was added and washed with 95% alcohol until the washings were free of chloride.

Then the soil and filter paper was transferred to the distillation flask and 200 mL distilled water and 10 mL of 3.2% potassium permanganate was added. The flask was set to the distillation unit and 20 mL 40% NaOH was also added to liberate excess ammonia. The distillate was collected in 25 mL 4% boric acid mixed with 1-2 drops of mixed indicator. Distillation was continued until the volume of distillate reached 50 mL and it was back titrated against 0.02 N HCl.

Calculation

$$\text{CEC in milliequivalent / 100g of soil} = \frac{\text{Titre value x Normality of HCl x 100}}{\text{Wt.of soil}}$$

Determination of Organic Carbon in soil

The Soil Organic Matter (SOM) is defined as the organic fraction of soil, including plant, animal, microbial residues at all stages of decomposition. Soil Organic Carbon (SOC) fraction consists of microbial cells, plant and animal residues at various stages of decomposition, humus and highly carbonized compounds such as charcoal, graphite, coal etc.

Soil organic matter is a source and sink of nutrients and a site of ion exchange. It facilitates physical and chemical properties of soil and hence prevents aggregation of mineral particles, particularly clays, and in turn modifies soil physical structure and influences water regimes. It is the energy source of soil biota and thus influences many biologically mediated processes of soil. Hence organic matter in soil is a renewable resource. Usually soil organic carbon is determined by dry combustion method or wet digestion method. Soil organic matter is obtained by multiplying the SOC with a constant value 1.724, with the assumption that, 58% of carbon is present in soil organic matter.

Wet Digestion Method (Walkley and Black's method, 1934)

Principle

The SOM can be oxidized in wet condition by strong oxidizing agents such as $K_2Cr_2O_7$ in acidic medium. A known weight of the soil was treated with an excess volume of standard $K_2Cr_2O_7$ solution in the presence of conc. H_2SO_4. The soil digested by the heat of dilution of H_2SO_4 and organic carbon was oxidized to CO_2. The excess of $K_2Cr_2O_7$ unused in oxidation was titrated back against a standard solution of Ferrous ammonium sulphate (0.5 N) in the presence of 1,10 orthophenanthrolin reagent (ferroin indicator).

Procedure

1.0 g of 0.2 mm sieved soil was taken in a 500 mL conical flask. 10 mL of 1N $K_2Cr_2O_7$ solution was added and mixed well. Then 20 mL conc. H_2SO_4 was added through the sides of the flask. The flask with contents was kept for 30 min. Then the reaction mixture was diluted with 100mL distilled water and 1-2 drops of 1,10 orthophenanthrolin reagent was added and titrated against standard Ferrous ammonium sulphate until the colour changes to green.

Calculation

Weight of sample = S g

Volume of FAS for blank = X mL

Volume of FAS to oxidize SOC = Y mL

Normality of FAS = N

% Organic Carbon in the soil = $\frac{(X-Y) \times N \times 0.003 \times 100}{S}$

Estimation of Total Phosphorus ($HClO_4$ method)

Reagents

1. Conc. HNO_3 and $HClO_4$ (60 %)
2. 50 mg/L phosphorus solution
3. Vanadomolybdate reagent

Solution A– Solution 'A' was prepared by dissolving 25 g of ammonium molybdate in 400 mL water.

Solution B- Solution 'B' was prepared by dissolving 1.25 g ammonium metavanadate in 300mL boiling water and cooled. To that solution, 250 mL of conc. HNO_3 was added and again cooled. Finally Solution 'A' was mixed with solution 'B' and made up to 1000 mL.

Procedure

Powdered soil sample was passed through 0.5 mm sieve. 2.0 g of the same was taken in a digestion tube and 20 mL conc. HNO_3 was added and kept overnight. To this, 30 mL of 60% $HClO_4$ was added and digested at 130 ^{0}C until white fumes were obtained and solution become clear. After complete digestion, the tube was cooled and contents were quantitatively transferred to a 100 mL volumetric flask.A calibration curve for Phosphorus was plotted using 1.5, 2.5, 5, 7 & 10 mg/L standard P solutions. 10 mL extract was taken in 50 mL volumetric flask; 10 mL vanadomolybdate reagent was added and made up to 50 mL. The colour intensity was measured at 470 nm using UV-VIS spectrophotometer (Systronics, 2202). Concentration of the aliquot was recorded from spectrophotometer.

Calculation

$$\text{Total phosphorus mg/L} = \frac{\text{Conc.from graph x 100}}{\text{volume of extract}}$$

Estimation of Pesticide Residues in Soil (Kumari et al. 2008)

15.0 g of representative air dried and well ground soil sample was taken in a beaker. 0.25 mL of ammonia was added and mixed well using vortex mixer and kept for half an hour to evaporate off ammonia. Then 0.3 g of prewashed and activated florisil and 10 g of anhydrous sodium sulphate were added and mixed thoroughly.The soil mixture was packed in a glass column (60 cm x 22 mm fitted with Teflon cock) in between the two layers of 2-3 cm of anhydrous sodium sulphate.125 mL of acetone: hexane mixture (1:9 v/v) was eluted, adjusting flow rate at 4 mL/min. The extract was concentrated to 2 mL using rotary vacuum evaporator at low temperature and the solvent was changed to iso-octane to avoid evaporation. This extract was injected in GC-FPD capillary system (Shimadzu, GC-2014) for Chlorpyriphos and Quinalphos residues.

Calculation

Residue in (µg/g) =

$$\frac{\text{(Area of sample x volume of sample in mL x concentration of std µg/mL)}}{\text{(Area of Std.x wt.of samplein g)}}$$

Estimation of physical and chemical properties of water

In environmental monitoring, water quality parameters have significant effect on determining drinking water suitability as well as health of aquatic life. In the present study water quality parameters such as pH, electrical conductivity, total dissolved solids, total alkalinity, carbonate, bicarbonate, total hardness, calcium, magnesium, sodium, potassium, chloride, nitrate nitrogen and sulphate were analysed using analytical methods in APHA,1999. The residues of Chlorpyriphos and Quinalphos were analysed in samples collected from heterogeneous aquatic environments of cardamom plantations by Gas Chromatograph.

pH (Potentiometric method)

pH of water samples were assessed using a pH meter (Systronics, model 361). A glass electrode in contact with H^+ ions of the solution acquires an electric potential depending on the concentration of H^+ ions. It is measured potentiometrically against a reference electrode, which is usually a calomel electrode. The potential difference between calomel electrode and glass electrode is represented in pH units.

Reagents

1. pH buffer 4.0,7.0 and 9.2.

Procedure

25 mL of water sample was taken in a 50 mL beaker. pH meter was switched on, temperature was set at room temperature and calibrated using standard pH buffer of 4.0,7.0 and 9.2 by keeping the electrode in buffer.pH was determined by keeping calibrated electrode in water sample until the stabilized reading was obtained. Rinsed the electrode and kept in distilled water.

Electrical Conductivity

Conductivity of the samples was measured using a calibrated conductivity meter (Systronics, model 361).

Reagents

Standard Potassium chloride solution 0.01 M having conductivity 1412 µmho/cm at 25 ^{0}C.

Procedure

Conductivity cell was rinsed with at least three portions of 0.01 M KCl and recorded conductivity at 25 ^{0}C and calibrated. Similarly conductivity of the sample was recorded at 25 ^{0}C.

Total Dissolved Solids

Total dissolved solids is the sum of all dissolved constituents in a water sample and expressed as mg/L. Total dissolved solids were calculated from electrical conductivity by multiplying it with a factor of 0.60.

Total Alkalinity

Alkalinity is the sum of carbonates and bicarbonates present in water sample. It is estimated using titrimetric method.

Reagents

1. Standard sodium carbonate solution: 3-5 g of sodium carbonate was dried at 105^{0}C for 4hrs and cooled in a desiccator. 2.50 g of Sodium carbonate was weighed accurately and made up to 1L.
2. Standard H_2SO_4 solution: 2.8 mL of concentrated $H_2SO_4$was diluted to 1 L and standardized against 0.05 N sodium carbonate using methyl orange indicator.

3. Phenolphthalein indicator solution: 5 g of Phenolphthalein was dissolved in 95% alcohol and diluted to 500 mL.

4. Mixed indicator: 100 mg of bromocresol green sodium salt and 200 mg methyl red were dissolved in 100 mL alcohol.

Procedure

50 mL sample was taken in a conical flask and added with 2 - 3 drops of Phenolphthalein indicator. This (upon development of pink colour) was titrated against standard sulphuric acid to estimate carbonate content. Then added two drops of bromocresol green indicator and again titrated against standard sulphuric acid until change in colour was observed from blue to yellow.

Calculation

Titre volume of CO_3^{2-} = A

Titre volume ofHCO_3^- = B

X value of CO_3^{2-} $= \frac{\text{A x Normality of H2 SO4 x 50000}}{\text{Volume of sample}}$

CO_3^{2-}content = X x 0.6

Y value of HCO_3^- $= \frac{\text{B x Nor.H2 SO4 x 50000}}{\text{Volume of sample}}$

HCO_3^- content = Y x 1.22

Total Alkalinity = X + Y

Total Hardness

Total Hardness is estimated using EDTA titrimetric method.

Reagents

1. Standard EDTA titrant (0.01 M): 3.723 g of di-sodium salt of EDTA dehydrate was dissolved in distilled water and diluted to 1L and stored in polythene bottle.
2. Indicator- Eriochrome Black T sodium salt: 0.5 g of dye was dissolved in 100 mL triethanolamine.
3. Buffer solution: 16.9 g of NH_4Cl was dissolved in 143 mL of conc. NH_4OH. 1.25 g magnesium salt of EDTA was weighed and diluted to 250 mL with distilled water and stored in air tight container.
4. Standard calcium solution (1000 mg/L): 1.0 g of anhydrous $CaCO_3$ was accurately weighed and transferred to a 500mL flask. It was then dissolved in 5 N HCl and 200 mL distilled water was added and boiled for few minutes to expel CO2. The solution was cooled and volume was made up to 1 L.
5. Working Standard: 10 mL of 1000 mg/L stock standard solution was diluted to 100 mL in a volumetric flask.

Procedure

20 mL sample was taken in a conical flask and two drops of indicator and 2 mL buffer solution were added and titrated against standard EDTA, until colour changed from pink to blue. Normality of EDTA was determined by titrating 20 mL of working standard calcium solution with EDTA using Eriochrome Black T indicator.

Calcium and magnesium

Calcium and magnesium were estimated using titrimetric method.

Reagents

1. 1 N NaOH: It was prepared by dissolving 40 g NaOH in 1L water.
2. Murexide indicator: Mixed 200 mg ammonium purpurate with 100 g NaCl and ground well using a mortar and pestle to 100-500 mesh size.

Procedure

50 mL sample was taken in a conical flask and 2 mL NaOH buffer and a pinch of murexide indicator were added. The solution was titrated against Standard EDTA until colour changed from pink to violet.

Calculation

1. Total Hardness $= \frac{\text{Normality of EDTA x Eq.wt.of CaCO3 x 1000 x Volume of EDTA}}{\text{Volume of sample}}$

2. Calcium hardness $= \frac{\text{Normality of EDTA x 100 x 1000 x volume of EDTA}}{\text{Volume of sample}}$

3. Calcium content = Calcium hardness x $\frac{40}{100}$

4. Magnesium content = (Total hardness – Calcium hardness) x 0.243

Sodium and Potassium

Sodium and Potassium content of water samples were estimated using a Flame Photometer (Systronics, model 128).

Reagents

1. Standard NaCl solution (1000 mg/L Na): 2.5416 g of NaCl was dissolved in 1 L distilled water in a volumetric flask.
2. Working standard solution (100 mg/L Na): Working standard solution having concentration 100 mg/L was prepared by diluting10 mL stock solution to 100 mL in a volumetric flask.

3. Working standard solutions having concentration of 5, 10, 20 and 40 mg/L were prepared by diluting 5, 10, 20and 40 mL stock solution in separate 100 mL volumetric flask.
4. Standard KCl solution (1000 mg/L K): 1.9070 g of Potassium chloride was dissolved in1 L distilled water. Serial dilutions were prepared as in the case of NaCl and calibrated the flame photometer.

Procedure

25 mL sample was taken in a beaker and its sodium and potassium contents were analysed using calibrated flame photometer.

Chloride

Chloride content was estimated using Argenometric method.

Reagents

1. Silver nitrate: 2.395 g of silver nitrate was prepared and stored in amber coloured bottles.
2. K_2CrO_4 indicator solution– 50 g potassium chromate was dissolved in distilled water and filtered.

Procedure

50 mL sample was taken in a conical flask. 2-3 drops of K_2CrO_4 indicator was added and titrated against silver chloride indicator until the colour changed from yellow to pinkish yellow.

Calculation

$$\text{Chloride content mg/L} = \frac{\text{Titre volume x normality of AgNO3 x 35.4x 1000}}{\text{Volume of sample}}$$

Nitrate Nitrogen

Nitrate content of water samples were estimated using UV spectrophotometer method.

Reagents

1. Standard nitrate solution: Roughly 2 g KNO_3 was dried in hot air oven at 105 ^{0}C for one hour. Then 721.8 mg of KNO_3 was weighed accurately and dissolved in 1 L distilled water in a volumetric flask. The solution was equivalent to 100 mg/L NO_3-N.

2. Working standard solution: 0.5, 1, 2, & 4 mg /L solutions were prepared from stock standard solution by diluting 0.5, 1, 2, & 4 mL to 100 mL in separate volumetric flask.

3. Hydrochloric Acid 1 N – 83 mL of conc. HCl was diluted with 880 mL distilled water.

Procedure

25 mL of each working standard solutions were taken in separate test tubes. 0.5mL 1N HCl was added and its absorbance at 275 nm was recorded (Systronics, 2202). Calibration curve was plotted. Similarly 25mL water sample was taken in boiling test tube, 0.5 mL 1N HCl was added and absorbance at 220 nm and 275 nm were recorded.

Calculation

Concentration of Nitrate-N = $(\lambda_{220}- 2x\ \lambda_{275})$ x slope of curve.

Sulphate

Sulphate content of water samples were estimated using turbidimetric method.

Reagents

1. Stock Standard sulphate solution (1000 mg/L): 1.479g of anhydrous sodium sulphate was dissolved in 1 L water.
2. Working standard of 5, 10, 20 and 40 mg/L solutions were prepared in volumetric flask.
3. Conditioning reagent: 50 mL glycerol was mixed with a solution containing 30mL conc. HCl and 300 mL distilled water. Then 100 mL 95% ethanol and 75 g of NaCl were added and mixed well.
4. Barium chloride crystals.

Procedure

50 mL standard solutions of 5, 10, 20 and 40 mg/L solutions were taken in a beaker. 2.5 mL conditioning reagent and 1 g $BaCl_2$ crystals were added and stirred for 10 min. Absorbance was recorded after 10 min. at 420 nm (Systronics, 2202). Similarly sulphate content in water sample was analysed and recorded.

Pesticide Residues (Kumari et al. 2008)

Liquid–liquid extraction method was used for the extraction of pesticide residues from water samples at ng/L level. 500 mL of water sample was taken in a 1 L separatory funnel and 10 g of NaCl was added and dissolved completely. 50 mL of 15% dichloromethane (85 mL hexane + 15 mL dichloromethane) was added. The funnel was shaken vigorously for 1-2 min., releasing the pressure intermittently. The funnel was kept undisturbed and allowed the layers to separate. The lower aqueous layer was taken in another 1 L separatory funnel. The process of partioning was repeated twice using fresh portions of 50 mL of 15% dichloromethane in hexane. The organic phase was combined and passed through 2-3 cm layer of anhydrous sodium sulphate over a pad of glass wool at the bottom. The organic layer was concentrated to 2 mL using rotary vacuum evaporator and evaporated to dryness. Then the contents were dissolved in hexane and repeated thrice. Finally the solvent was changed to iso -octane and made up to 2 mL and analysed for Chlorpyriphos and Quinalphos in GC- FPD (Shimadzu, GC-2014) capillary system.

Residue in (µg/mL) =

$$\frac{\text{(Area of sample x Total volume of sample in mL x concentration of std } \mu\text{g/mL}}{\text{(Area of Std.x Weight of sample in g).}}$$

Statistical Analysis

SPSS (16.0) statistical software was used to select the best interaction of soil physico-chemical parameters with the residues of Chlorpyriphos and Quinalphos and to explain seasonal and zonal variation at P (0.05).

RESULTS AND DISCUSSION

In Kerala, cardamom grows well in forest loam soils of cardamom hill reserves of Idukki district. In recent times, introduction of improved varieties and the use of agrochemicals for crop protection have resulted in high yield and thereby production. However, continuous cultivation and the extensive use of fertilizers and pesticides in recent times are bringing pressures to these agro-ecosystems in terms of its environmental quality. The present study has been attempted to assess the physical, chemical and biological characteristics of associated environments like soil and water and to evaluate the extent of pesticide residues (Chlorpyriphos and Quinalphos) contained within them. Collection and analysis of soil and water samples were carried out on a bimonthly basis from three major cardamom growing zones of Idukki District (zone A, B and C) during August 2014 to June 2015. Similarly, assessment of the extent of pesticides associated with the soil and water samples from these agro-ecosystems were also carried out. Attempts were also carried out to assess the factors, which are likely to be responsible for the persistence of pesticides in these agro-ecosystems. The detailed evaluation of the results is given below.

The results of pH values, moisture content and electrical conductivity of soil samples are presented in Table 1. pH value of soils collected from the study area are in the acidic range. The average soil pH of zone A during pre-monsoon, monsoon and post-monsoon seasons were 4.85±0.16, 5.37±0.23 and 4.80±0.0, respectively. In zone B and C, the order of pH was 4.94±0.37, 5.15±0.12 and 5.22±0.09 and 5.01±0.18, 5.62±0.12 and 5.46± 0.41. Among the three zones, soil samples from zone C recorded the highest pH. As far as seasons concerned, soil samples collected during monsoon recorded the highest values, followed by post-monsoon and pre-monsoon.

Optimum pH of soil for cardamom cultivation is reported to be 5.5 to 6.5 (Spices Board, 2001). There is a practice of applying fermented slurry during dry seasons in cardamom plantations to enhance cardamom productivity. This agricultural practice would have contributed in lowering the pH of soil. Generally slurry application will be discontinued from the onset of monsoon, as this slurry application induces acidity and causes severe damage to crop by disease attack like Azhukal and root and clump rot.

In cardamom plantations, first dose of fertilizer application immediately follows the first shower of monsoon. Generally in acidic soils, two weeks before fertilizer application, 500 g of dolomite or lime is applied for better nutrient release and absorption. The average pH of the soil samples collected from zone A, B and C during monsoon was 5.37, 5.15 and 5.62 respectively. Even though pH was increased in zone A during monsoon, it has gradually reduced to very acidic condition in a short period of time. Due to low pH, liming is one of the managerial requirements along with application of fertilizers and manures (Premachandran, 2007). More application of agrochemicals in cultivated areas would also reduce soil pH. All the changes in pH indicate the continuous use of pH reducing materials such as fermented slurry and chemical fertilizers in cardamom ecosystems, especially in zone A.

The moisture content of soil samples varied considerably over the period of study. The moisture content in zone A ranged from 11.97±7.03 to 22.29±0.26. Similarly it has been ranged from 10.82±0.25 to 22.92±5.49 and 16.00±1.42 to 25.76±6.29 in zone B and C respectively. Zone B has recorded low moisture content than zone A and C. During pre-monsoon and post-monsoon seasons, soils of zone C have more moisture content than zone A.

Cardamom plants are very sensitive to moisture and air temperature. In order to regulate soil moisture and temperature, irrigation is done from January to May every year, at an interval of 10 to 15 days, until the onset of monsoon. The amount of water supplied is kept equivalent to 35-45 mm rain (IISR, 2015). Since panicle emerges from November to March and flowering season commences from February onwards, irrigation is essential for flower setting and yield quality. Hence most of the cardamom plantations are under irrigation. Due to continuous irrigation, the soil moisture remains constant throughout the year. This kind of irrigation practice might have reflected in moderate moisture content of soils under study.

Electrical conductivity of soil samples from zone A ranged from 0.095±0.021 to 0.360±0.014, while it was in the order from 0.043±0.18 to 0.387±0.038 and 0.105±0.035 to 0.262±0.059. The electrical conductivity of zone A samples was higher, followed by zone B and C. Seasonal variation in electrical conductivity was observed in all the three zones. In zone A, electrical conductivity reduced from pre-monsoon to post-monsoon whereas, in zone B, even though there was a slight decline in electrical conductivity during monsoon, it improved at the end of post-monsoon. Similar trend was observed in soil samples of zone C.

Electrical Conductivity (EC) is the measure of a soil relating to its texture, CEC, drainage condition, organic matter and sub soil characteristics (Clarson, 2002). Electrical Conductivity of soil is influenced by a combination of physico-chemical properties, including soluble salts, clay content, mineralogy, soil water content, bulk density and organic matter (Corwin and Lesch, 2005).

Analytical results of organic matter and cation exchange capacity of soil samples are presented in Table 2.Organic matter content in zone A has ranged from 3.13± 0.33 to 5.30±1.99, whereas it ranged from 3.28±0.52 to 5.91±0.63 and 3.59±5.20±0.91, respectively in zone B and C. The average organic matter content was more in soil samples collected from zone C. A linear seasonal variation was not observed in organic matter content among the zones.

Organic carbon and organic matter are the true indicators of soil health. Decomposition of organic matter is an integral part of any balanced ecosystem. Microbial decomposition of forest litter incorporates a major portion of organic matter. The availability of plant nutrients and uptake influences the ecosystem productivity and rate of decomposition. Slow rate of decomposition of organic matter is reported in high acidic soils and also at higher elevation (Firsova, 1967).

Table 1.Seasonal variation in pH, Moisture Content and Electrical Conductivity of soil samples from cardamom plantations.

ZONES	pH			Moisture Content (%)			Electrical Conductivity(dS/cm)		
	Pre-monsoon	Monsoon	Post-monsoo	Pre-monsoor	Monsoon	Post-monsoo	Pre-monsoor	Monsoon	Post-monsoo
		mean±stdev			mean±stdev			mean±stdev	
A									
1	5.21±0.55	5.25±0.08	4.94±0.23	16.91±4.09	17.61±1.27	14.68±0.96	0.270±0.071	0.360±0.014	0.354±0.062
2	4.92±0.40	5.88±0.46	5.04±0.48	21.07±6.41	22.29v0.26	11.97±7.03	0.253±0.008	0.170±0.085	0.214±0.105
3	4.43±0.46	4.99±0.16	4.43±0.24	19.15±0.91	22.25±2.19	18.80±2.55	0.305±0.034	0.185±0.092	0.095±0.021
mean	4.85±0.16	5.37±0.23	4.80±0.00	19.04±3.20	20.72±1.07	15.15±3.51	0.276±0.009	0.238±0.064	0.221±0.049
B									
1	5.40±0.71	4.85±0.06	4.94±0.05	16.17±2.88	17.45±3.61	12.61±0.56	0.387±0.038	0.310±0.028	0.325±0.064
2	4.67±0.18	5.30±0.14	5.15±0.24	22.92±5.49	17.94±2.07	20.43±0.61	0.157±0.008	0.145±0.092	0.225±0.035
3	4.76±.0.21	5.30±0.28	5.59±0.02	17.27±0.94	18.47±2.21	10.82±0.25	0.107±0.005	0.043±0.018	0.065±0.007

Table 2. Seasonal variation in organic matter content and cation exchange capacity of soil samples from cardamom plantations.

ZONES	Organic Matter Content (%)			Cation Exchange Capacity (meq/100g soil)			
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	
		mean±stdev			mean±stdev		
A							
1	5.30±1.99	4.62±0.83	4.41±0.83	19.73±0.88	13.80±4.18	18.45±0.63	
2	3.13±0.33	3.92±0.57	4.44±0.57	17.83±1.94	16.85±6.86	18.64v0.48	
3	3.46±0.87	3.97±0.09	4.22±0.09	15.96±0.21	19.40±5.22	17.44±2.64	
mean	3.96±0.26	4.17±0.50	4.36±0.50	17.84±0.42	16.68±5.42	18.18±0.93	
B							
1	4.38±0.68	5.59±0.63	5.91±0.63	15.79±1.97	19.13±7.16	19.49±1.05	
2	4.29±1.19	3.28±0.52	3.95±0.52	17.24±0.62	16.73±2.73	15.10±2.12	
3	3.65±0.20	4.13±1.23	4.58±1.23	16.98±4.27	20.65±8.70	16.60±4.68	
mean	4.27±0.11	4.33±0.80	4.81±0.33	16.67±1.69	18.84±6.19	17.06±1.92	
C							
1	5.62±0.39	3.59±1.28	3.98±1.28	19.37±0.62	17.52±1.36	17.92±0.45	
2	4.88±0.07	4.61±0.87	4.66±0.87	18.31±0.84	15.07±1.66	19.67±1.43	
3	4.84±1.49	4.99±0.91	5.20±0.91	17.94±0.66	25.45±1.74	16.56±0.47	
mean	5.11±0.65	4.40±1.02	4.61±0.71	18.54±0.70	19.35±0.43	18.05v0.17	

Cardamom plants grow in forest loam where organic manure application in any form is comparatively higher. The optimum soil organic carbon content for cardamom cultivation is 1.5 to 2.0% i.e., 2.6 to 3.5% SOM (Spices Board, 2001). In the present study, organic matter content of the soil samples ranged from 3.96% to 5.11%. Before the onset of monsoon, there is a practice of applying 1 kg neem cake and 10 kg farm yard manure per cardamom plant. The repeated application of farm yard manure is likely to enhance soil humus, which might have reflected in high organic matter content in these agro-ecosystems.

Cation exchange capacity of samples from zone A ranged from 13.80±4.18 to 19.73±0.88 meq /100 g soil. In zone B and C it varied from 15.10±2.12 to 20.65±8.70 and 15.07±1.66 to 25.42±1.74 respectively. Zone B and C samples recorded more cation-exchange capacity than zone A. It was observed that, cation- exchange capacity of zone B and C enhanced and zone A declined during monsoon.

In soil, organic matter has charge properties and that make it a site for ion exchange. Cation-exchange capacity of surface soils is reported to increase with organic matter content (Mandal et al. 1990; Gangopadhyay et al. 1990). There are reports on cation-exchange capacity, varying with pH and clay content of soils (Helling et al. 1964). The open pores in kaolinite type of clay minerals can exchange calcium and magnesium ions with other ions (Lal and Shukla, 2004). In the present study the average cation-exchange capacity of all zones were relatively high with a little superiority in zone C as in the case of organic matter content. Hence in cardamom growing soils, organic matter content might have influenced more to corresponding cation-exchange capacity.

Results of soil mechanical properties like Bulk density, Particle density, Water holding capacity, Pore space and volume of expansion attempted in the present study are presented in Table s 3 and 4.Bulk density of zone A samples ranged from 0.925±0.08 to 1.072±0.01. In zones B and C, it ranged from 1.028±0.04 to 1.482±0.44 and 1.007±0.16 to 1.181±0.01 respectively.It was noted that, the average bulk density of zone B samples was higher, followed by zone C and zone A. During pre-monsoon, average bulk density was reduced in all the three zones. Seasonal variation observed in all the locations was similar.

Particle density of the soil samples ranged from 1.87±1.12 to 2.68±0.39 in zone A, whereas it varied from 1.63±0.64 to 2.96±0.56 and 1.51±0.55 to 3.10±0.33 respectively in zones B and C. Zonal differences were noticed in particle density of the soil samples. The average particle density decreased from zone A to zone C, which was in the order of 2.41, 2.31 and 2.27. Irrespective of zonal differences, a linear seasonal variation was recorded in particle density. Maximum particle density was observed during monsoon and then reduced in post-monsoon.

Water holding capacity ranged from 53.41±2.84 to 74.17±4.21, 49.67±4.01 to 71.79±0.36 and 52.09±3.63 to 67.58±1.62 respectively in zone A, B and C. Zone A recorded highest water holding capacity. The average water holding capacity of zone B and C were similar. As in the case of particle density, water holding capacity of cardamom growing soils decreased from zone A to C.

In the present study, the pore space of soil samples collected from zone A was between 57.59±0.93 and 68.27±0.72, whereas it was in the order of 53.7±8.21 to 67.92±2.6 and 52.35±11.4 to 66.69±0.94 in zone B and C. Among the zones, soils of zone B had more pore space than zone A and C. Seasonal variation was noted in pore space with highest during monsoon season.

The average values of volume of expansion of soils ranged from 1.84±0.9 to 6.83±1.65 in zone A, while it varied from 2.98±1.78 to 7.55±1.83 in zone B and 4.77±0.4 to 8.46±1.08 in zone C. Zone C soils recorded higher volume of expansion followed by zone B and A. With respect to seasons, a regular change was not noticed in volume of expansion of soil.

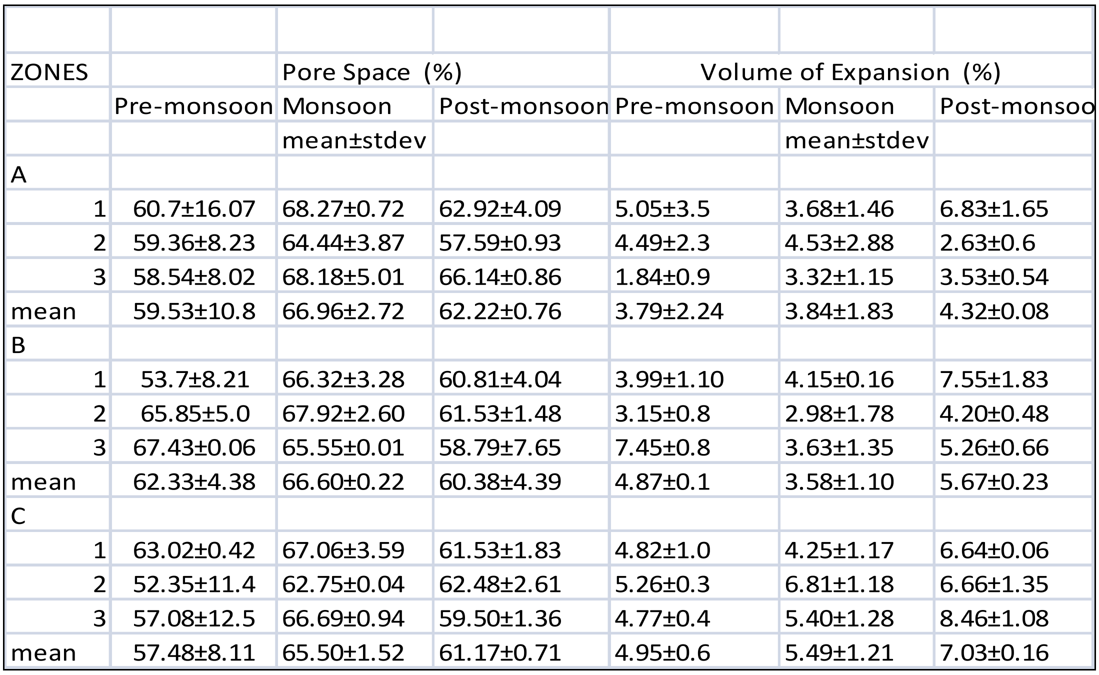
In general, soil physical attributes such as bulk density and volume of expansion was in the order of zone C> zone B> zone A, whereas particle density and water holding capacity were in the order of zone A> zone B> zone C. During monsoon, soil physical properties such as particle density, water holding capacity and pore space were highest. Bulk density was more in pre-monsoon and volume of expansion was high during post-monsoon.

Table 3. Seasonal variation in bulk density, particle density and water holding capacity of soil samples from cardamom plantations.

ZONES	Bulk Density (g/cc)			Particle Density (g/cc)			Water Holding Capacity (%)			
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoor	Pre-monsoon	Monsoon	Post-monsoon	
		mean±stdev			mean±stdev			mean±stdev		
A										
1	0.935±0.16	0.954±0.18	0.944±0.08	2.36±0.49	2.68±0.39	2.27±0.37	73.80±19.52	72.36±14.66	71.62±1.87	
2	1.004±0.09	0.959±0.03	1.072±0.01	2.36±0.18	2.44±0.02	2.40±0.08	64.44±6.17	70.03±8.31	53.41±2.84	
3	1.042±0.05	0.925±0.08	0.989±0.08	1.87±1.12	2.67±0.53	2.62±0.00	57.78±6.11	74.17±4.21	65.64±1.03	
mean	0.994±0.10	0.946±0.08	1.001±0.02	2.20±0.60	2.60±0.31	2.43±0.10	65.34±10.60	72.18±3.52	63.56±0.67	
B										
1	1.135±0.06	1.10±0.08	1.136±0.10	1.63±0.64	2.96±0.56	2.47±0.04	49.67±4.01	58.31±3.02	71.79±0.36	
2	1.062±0.14	1.007±0.08	1.041±0/08	1.78±0.87	2.89±0.03	2.45±0.17	60.93±5.76	67.45±5.31	59.46±1.60	
3	1.482±0.44	1.028±0.04	1.071±0.10	2.41±0.88	1.86±1.13	2.36±0.17	58.94±0.38	63.80±0.31	57.06±10.77	
mean	1.226±0.21	1.044±0.07	1.082±0.05	1.94±0.80	2.57±0.20	2.43±0.10	56.51±3.38	63.18±2.88	62.77±2.94	
C										
1	1.091±0.04	1.124±0.02	1.181±0.01	1.86±1.05	3.10±0.33	2.68±0.19	62.41±10.74	60.29±4.07	53.44±0.06	
2	1.069±0.10	1.022±0.04	1.162±0.02	1.52±0.54	2.38±0.08	2.61±0.19	55.65±8.14	63.82±0.41	52.09±3.63	
3	1.007±0.16	1.026±0.09	1.060±0.08	1.51±0.55	2.54±0.11	2.21±0.15	64.47±14.89	67.58±1.62	60.56±3.60	
mean	1.056±0.10	1.057±0.05	1.134±0.08	1.63±0.71	2.67±0.17	2.50±0.07	60.84±11.26	63.90±0.68	55.36±0.01	

Bulk density is reported to be inversely related to organic matter (Korschens and Greilich, 1981). Organic matter normally enhances water holding capacity, decreases soil compaction, breaking strength and bulk density (Cherreau, 1975; Ushakumari, 1987). Close association between organic matter and aggregation was reported by Singhal et al. (1976). Similar relationship was also noted in the present study.

Table 4. Seasonal variation in pore space and volume of expansion of soil samples from cardamom plantations.



ZONES		Pore Space (%)		Volume of Expansion (%)		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoo
		mean±stdev			mean±stdev	
A						
1	60.7±16.07	68.27±0.72	62.92±4.09	5.05±3.5	3.68±1.46	6.83±1.65
2	59.36±8.23	64.44±3.87	57.59±0.93	4.49±2.3	4.53±2.88	2.63±0.6
3	58.54±8.02	68.18±5.01	66.14±0.86	1.84±0.9	3.32±1.15	3.53±0.54
mean	59.53±10.8	66.96±2.72	62.22±0.76	3.79±2.24	3.84±1.83	4.32±0.08
B						
1	53.7±8.21	66.32±3.28	60.81±4.04	3.99±1.10	4.15±0.16	7.55±1.83
2	65.85±5.0	67.92±2.60	61.53±1.48	3.15±0.8	2.98±1.78	4.20±0.48
3	67.43±0.06	65.55±0.01	58.79±7.65	7.45±0.8	3.63±1.35	5.26±0.66
mean	62.33±4.38	66.60±0.22	60.38±4.39	4.87±0.1	3.58±1.10	5.67±0.23
C						
1	63.02±0.42	67.06±3.59	61.53±1.83	4.82±1.0	4.25±1.17	6.64±0.06
2	52.35±11.4	62.75±0.04	62.48±2.61	5.26±0.3	6.81±1.18	6.66±1.35
3	57.08±12.5	66.69±0.94	59.50±1.36	4.77±0.4	5.40±1.28	8.46±1.08
mean	57.48±8.11	65.50±1.52	61.17±0.71	4.95±0.6	5.49±1.21	7.03±0.16

Usually particle density of mineral soils varies from 2.6 to 2.8 with an average of 2.65 g/cc. If soil organic matter is high, particle density even reduces below 2.5 (Blanco-Canqui et al. 2006). Mulching the plant base with organic materials and tillage would have contributed in the decline of particle density during pre-monsoon.

Air and water have dynamic relationship in occupying pore space of soil. Water present in saturated soil drain rapidly and can quickly bring back to saturation during heavy rainfall. The presence of high organic matter in soil during monsoon would also contribute to the increase in water holding capacity. Significant positive relationship was observed between water holding capacity and organic carbon, clay, and porosity, and negative relationship was found with pH, bulk density, sand and silt content (Deb et al. 2014).

Hydraulic movement under gravitational force in soil profile, performed through macro pores is well established. The capacity of expansion depends on soil mineralogy, soil organic matter and soil physical properties. High organic matter in zone C might have contributed to soil volume of expansion in that location. Even though bulk density and volume of expansion are related, it was not pronounced much in these soil samples.

Analytical results concerning soil texture is presented in Table 5.

Sand, silt and clay are the three standard fractions attributing soil texture. Sand content of zone A samples ranged from 30.32±13.7 to 46.36±2.88, while it varied from 34.13±19.4 to 48.73±23.4 and 29.88±7.1 to 50.99±25.0 in zone B and C, respectively. Zone A soils were low in sand content followed by zone C and B. Irrespective of zonal differences, sand content was high during post-monsoon samples.

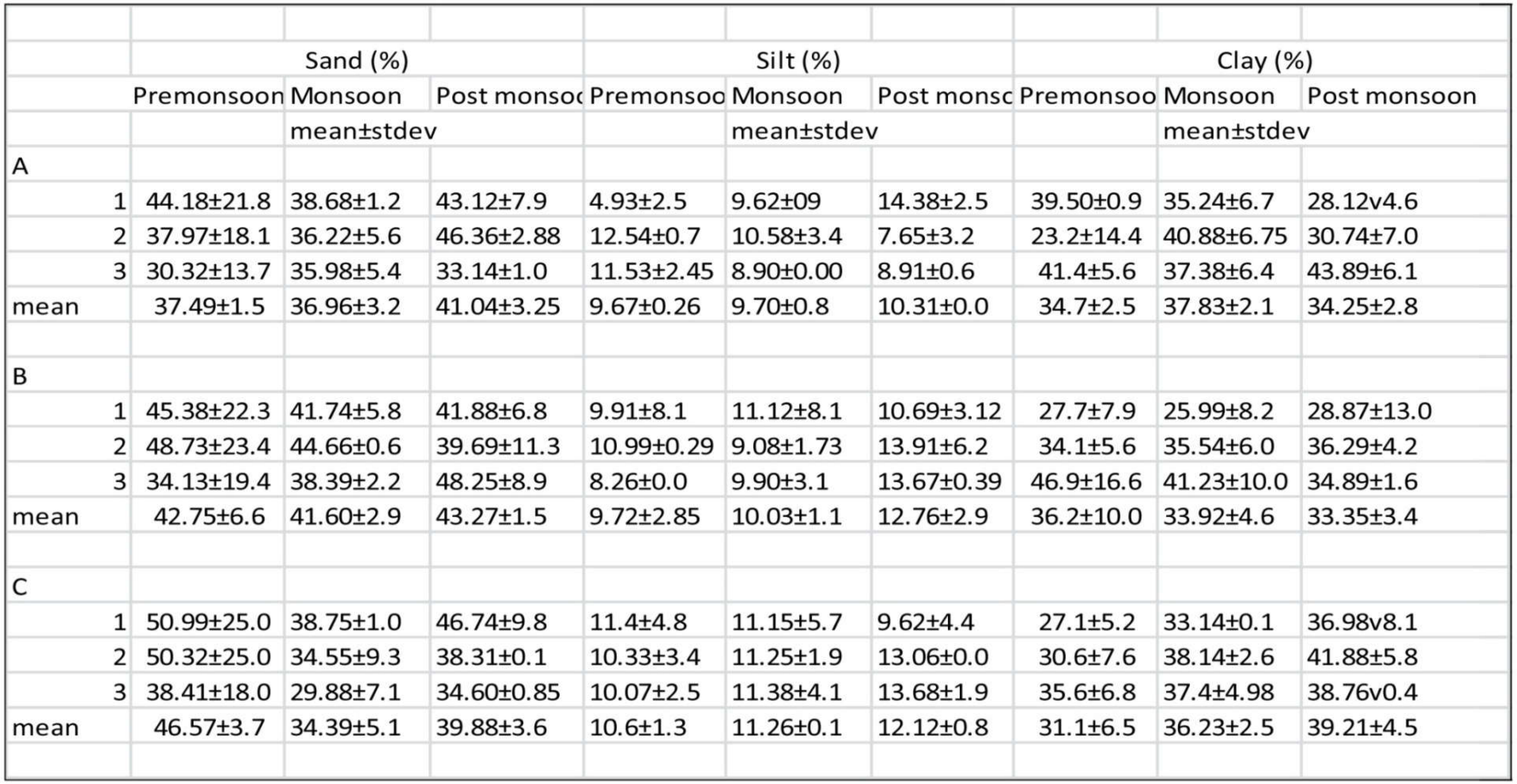
The average silt content in zone A samples were in the range of 4.93±2.5 to 14.38±2.5. In zone B and C, it varied from 8.26±0.0 to 13.91±6.2 and 9.62±4.4 to 13.68±1.9, respectively. Silt content was more in zone C than other two zones.

Soil samples from all the three zones were high in clay fraction. The average clay content in all the three zones was the same. Seasonal and zonal variation was not noticed in clay content.

Upon consolidation of the result, it has been noticed that there was marked variation in texture properties of all the three cardamom cultivating zones. In all the samples of the present study, sand and clay contributed the major portion.

The soils identified in Idukki District are Manakkad, Thommankuthu, Chinnar, Venmani, Pampadumpara and Anamudi series. Upland and highland areas of Idukki district comprise of Thommankuthu, Chinnar, Venmani and Pampadumpara series, which lies between 600 to 1200 MSL (Premachandran, 2007). All plantation crops such as rubber, pepper, tea, cardamom and other spices are cultivated along this region. Cardamom grows well in Pampadumpara (600-1200 MSL) series of soils and some parts of Venmani series (600-900 MSL).

Table 5. Seasonal variation in the textural properties of soil samples from cardamom plantations.



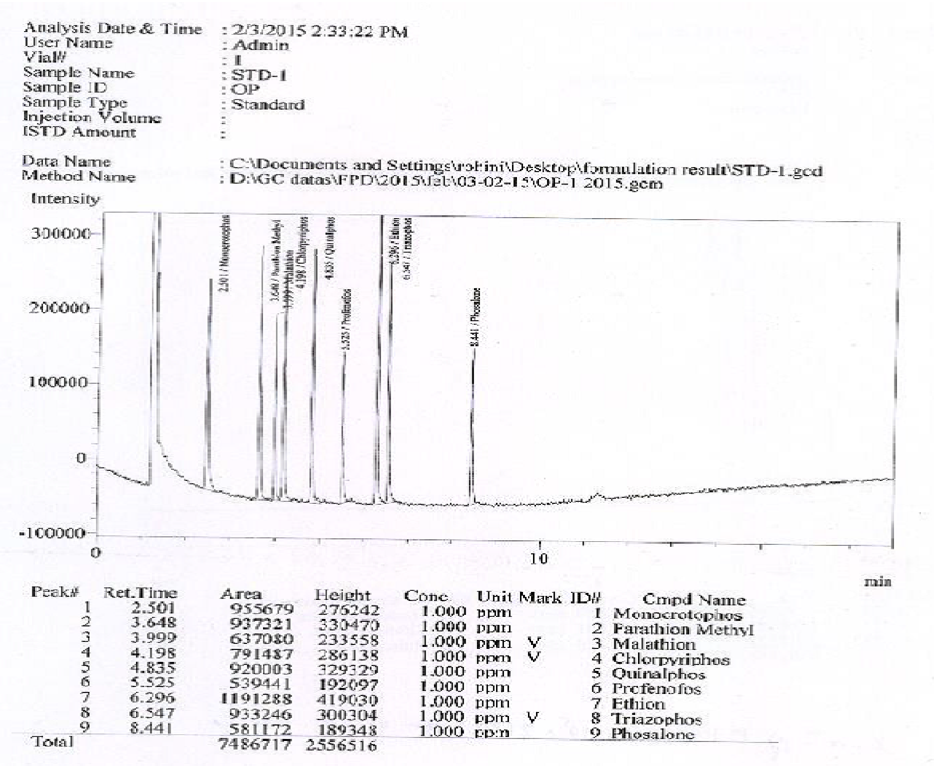
	Sand (%)			Silt (%)			Clay (%)		
	Premonsoon	Monsoon	Post monsoc	Premonsoo	Monsoon	Post monsc	Premonsoo	Monsoon	Post monsoon
		mean±stdev			mean±stdev			mean±stdev	
A									
1	44.18±21.8	38.68±1.2	43.12±7.9	4.93±2.5	9.62±09	14.38±2.5	39.50±0.9	35.24±6.7	28.12v4.6
2	37.97±18.1	36.22±5.6	46.36±2.88	12.54±0.7	10.58±3.4	7.65±3.2	23.2±14.4	40.88±6.75	30.74±7.0
3	30.32±13.7	35.98±5.4	33.14±1.0	11.53±2.45	8.90±0.00	8.91±0.6	41.4±5.6	37.38±6.4	43.89±6.1
mean	37.49±1.5	36.96±3.2	41.04±3.25	9.67±0.26	9.70±0.8	10.31±0.0	34.7±2.5	37.83±2.1	34.25±2.8
B									
1	45.38±22.3	41.74±5.8	41.88±6.8	9.91±8.1	11.12±8.1	10.69±3.12	27.7±7.9	25.99±8.2	28.87±13.0
2	48.73±23.4	44.66±0.6	39.69±11.3	10.99±0.29	9.08±1.73	13.91±6.2	34.1±5.6	35.54±6.0	36.29±4.2
3	34.13±19.4	38.39±2.2	48.25±8.9	8.26±0.0	9.90±3.1	13.67±0.39	46.9±16.6	41.23±10.0	34.89±1.6
mean	42.75±6.6	41.60±2.9	43.27±1.5	9.72±2.85	10.03±1.1	12.76±2.9	36.2±10.0	33.92±4.6	33.35±3.4
C									
1	50.99±25.0	38.75±1.0	46.74±9.8	11.4±4.8	11.15±5.7	9.62±4.4	27.1±5.2	33.14±0.1	36.98v8.1
2	50.32±25.0	34.55±9.3	38.31±0.1	10.33±3.4	11.25±1.9	13.06±0.0	30.6±7.6	38.14±2.6	41.88±5.8
3	38.41±18.0	29.88±7.1	34.60±0.85	10.07±2.5	11.38±4.1	13.68±1.9	35.6±6.8	37.4±4.98	38.76v0.4
mean	46.57±3.7	34.39±5.1	39.88±3.6	10.6±1.3	11.26±0.1	12.12±0.8	31.1±6.5	36.23±2.5	39.21±4.5

Main characteristics of Pampadumpara series are acidic, clayey with low nutrient holding capacity. Sand, silt and clay content of A horizon of Pampadumpara series are in 39%, 19.7% and 42.3%, respectively. In the present study soil texture of zone A and B were similar to Pampadumpara series and zone C could be categorized in Venmani series. Thus zonal bifurcations in cardamom hills were also related to soil physical properties. These changes in elevation and soil physical properties were also reflected in the growth and yield of cardamom.

In addition to an investigation on the physico-chemical properties of soil, an attempt has been carried out to assess the extent of pesticide residues of Chlorpyriphos and Quinalphos associated with the cardamom plantations under study. Attempts were also carried out to estimate the magnitude of total phosphorus associated with the soils of these agro-ecosystems. The results are represented in Table 6.

The residue of Chlorpyriphos was detected in all soil samples of the cardamom ecosystem in various quantities (Figure 1 and 2). There was also seasonal variation in the magnitude of the residue of Chlorpyriphos in soil. Chlorpyriphos residue was more in pre-monsoon season in zone A and B. The highest quantity of Chlorpyriphos residue detected in post-monsoon soil samples collected from zone C was 254.3 µg/g. Average Chlorpyriphos residue estimated in all locations were low during monsoon. It was also noted that, out of nine plantations, only one plantation had very low content of Chlorpyriphos residue, irrespective of seasonal variation. In all the other cardamom plantations, Chlorpyriphos might have applied either through soil drenching or as foliar spray in any of the seasons for pest control. Chlorpyriphos has been used generally for the control of shoot borers and root grubs. Drenching of 3-4 L of Chlorpyriphos (0.04% a.i) is recommended during May – June and September – October (Kerala Agricultural University, 2007) for the control of root grub, which coincides with the analytical results of the present study.

Figure.1.: Chromatogram of organophosphorus mix standard

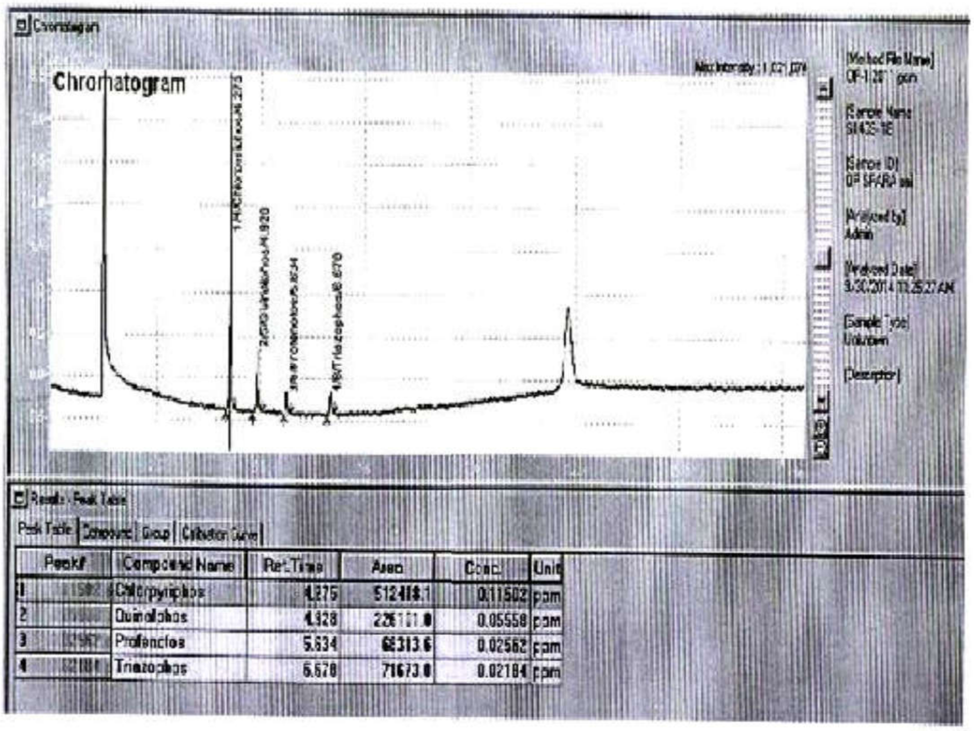


```
Analysis Date & Time  : 2/3/2015 2:33:22 PM
User Name             : Admin
Vial#                 : 1
Sample Name           : STD-1
Sample ID             : OP
Sample Type           : Standard
Injection Volume      :
ISTD Amount           :

Data Name             : C:\Documents and Settings\rohini\Desktop\formulation result\STD-1.gcd
Method Name           : D:\GC datas\FPD\2015\feb\03-02-15\OP-1 2015.gcm
```

```
Peak#  Ret.Time    Area     Height    Conc.  Unit Mark ID#   Cmpd Name
   1     2.501    955679    276242    1.000  ppm          1  Monocrotophos
   2     3.648    937321    330470    1.000  ppm          2  Parathion Methyl
   3     3.999    637080    233558    1.000  ppm    V     3  Malathion
   4     4.198    791487    286138    1.000  ppm    V     4  Chlorpyriphos
   5     4.835    920003    329329    1.000  ppm          5  Quinalphos
   6     5.525    539441    192097    1.000  ppm          6  Profenofos
   7     6.296   1191288    419030    1.000  ppm          7  Ethion
   8     6.547    933246    300304    1.000  ppm    V     8  Triazophos
   9     8.441    581172    189348    1.000  ppm          9  Phosalone
Total            7486717   2556516
```

Figure 2. Chromatogram of pesticides detected from soil sample1



[Method File Name]

[Sample Name]

[Sample ID]

[Analyzed by]
Admin

[Analyzed Date]

[Sample Type]
Unknown

[Description]

Peak#	Compound Name	Ret.Time	Area	Conc.	Unit
1	Chlorpyriphos	4.275	512418.1	0.11502	ppm
2	Quinalphos	4.928	226101.0	0.05558	ppm
3	Profencfos	5.634	68313.6	0.02562	ppm
4	Triazophos	6.678	71673.0	0.02184	ppm

The residue of Quinalphos was also detected in all soil samples throughout the year. Quinalphos content was more in monsoon season in zone A and B. In zone C, the residue was more during post monsoon. Moreover, in one location of zone C, the residue was extremely high. Quinalphos is normally sprayed in cardamom plantations to control pests like shoot borer, shoot fly, cardamom thrips and other minor pests. The recommended dosage of Quinalphos for the management of cardamom pests is 0.025% (a.i.ha^{-1}) and should be sprayed during December to May (Kerala Agricultural University, 2007).

While examining the concentration of pesticide residues in soil, it has been noticed that both the pesticides persisted in soil throughout the year. Among the two pesticides studied, residue of Quinalphos was comparatively less than Chlorpyriphos. The concentration of chemical used for soil drenching (Chlorpyriphos) is found to persist in the soil for long period, than sprays. The persistence of this pesticide in soil for a long period of time will affect the soil biota and will also contaminate the associated domains like water and air, eventually leading to severe health effects.

Total Phosphorus content

Total phosphorus includes all inorganic and organic phosphorus compounds, including residues of pesticides, which are brought about by exhaustive digestion process. In the present study, along with other physico-chemical parameters, the extent of total phosphorus associated with the soil of three cardamom growing soils were attempted. Attempts were also carried out to correlate the extent of phosphorus with organo-phosphorus pesticides like Quinalphos and Chlorpyriphos.

The average concentration of total phosphorus in zone A ranged from 306.3 to 348 mg/kg. The average total phosphorus content recorded was very high in zone A, B and C. Seasonal variation was also observed in the case of total phosphorus content. Pre-monsoon samples showed high total phosphorus content than other two seasons. Normally in cardamom plantations, fertilizer application initiate with the onset of monsoon. Due to acidic nature of cardamom growing soils, all available phosphorus in the form of calcium phosphate will be converted to plant unavailable form of iron and aluminum phosphate (Kanwar and Grewal, 1990).

Table 6. Seasonal variation in the residues of Chlorpyriphos and Quinalphos in the soil samples from cardamom plantations.

ZONES	Chlorpyriphos (µg/g)			Quinalphos (µg/g)			TotalPhosphorus (mg/g)		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
A									
1	379.3	5.9	16.8	10.1	11.5	5.5	433.42±207.1	349.4±164.6	413.7±18.1
2	39.4	11.4	31.5	14.8	94.5	1	295.02±77.76	253.8±83.3	325.3±64.9
3	47.3	162.8	322.4	42.4	25.4	39.9	315.52±62.8	315.6±41.0	284±3.12
Mean	155.3	60	123.5	22.4	43.8	15.4	347.98±115.9	306.3±40.8	340.9±26.7
B									
1	22.6	101.5	25.2	14.2	38.3	2	286.7±24.68	260±14.14	281.6±64.5
2	5.8	45.1	167.6	9.9	25.7	5.5	266.41±184.6	175.3±40.3	258.3±74.8
3	261.7	10.7	10	24.85	46.6	3	178.39v17.28	198.2±21.2	160±12.8
Mean	96.7	52.4	67.6	16.3	36.8	3.5	243.83±59.06	211.2±11.1	233.3±50.8
C									
1	53	62.3	169.3	14.6	24.6	19.5	168.34±94.67	164.5±24.5	110.5±42.7
2	117.50	12.4	357.1	8.8	14	0.5	21.59±17.66	233.7±4.8	239±22.2
3	168.50	15.6	236.4	9.2	7.5	179.8	424.75±5.74	255.8±106.8	263.8±28.8
Mean	113.00	30.2	254.3	10.8	15.3	66.6	268.56±39.36	218±25.8	204.4±12.0

If the estimated total phosphorus has been extracted from the fixed soil phosphorus alone, total phosphorus estimate should have been more during monsoon and post monsoon seasons. Hence it can be assumed that, soil bound residues of pesticides might have also contributed to the high value of total phosphorus in the soils from cardamom ecosystems.

Pesticides and their degradation products are directly related to the ecology of agro-ecosystems in many ways. Separate analysis was carried out for both pesticides and seasons. Tests of Pearson's correlation were carried out by testing null hypothesis according to the significance level at 0.05.

Seasonal and zonal correlation between various soil parameters and pesticide residues were presents in Table s 7 and 8.

Interaction between residues of individual pesticides and most related soil properties were analysed. Residues of Chlorpyriphos and Quinalphos were correlated with soil organic matter content, total phosphorus content, cation exchange capacity, bulk density, silt and clay content. Correlation of pesticide residues with soil organic matter, total phosphorus, CEC, bulk density and silt were not significant. Irrespective of seasonal variation, residues of Chlorpyriphos and Quinalphos in soil was positively correlated to clay content throughout the year (Table 7). Similarly residues of Chlorpyriphos and Quinalphos were also positively and significantly correlated to clay content with respect to zones. Soil organic matter had little effect on the persistence of pesticides in soil, but clay mineral content is a leading factor in sorption of pesticide in soil as reported by Spark and Swift (2002). Similarly a negative linear correlation was reported between the log of the solubility and association coefficient for pesticides like Napropamide, Lindane, Prometryn and DDT (Lee and Farmer, 1988). Hence, bound residues of pesticides in soil play a significant role in the immobilization of soil applied chemicals in the environment.

Similar to soil, water samples collected on a bimonthly interval from the open wells and streams adjoining the study area were analyzed for drinking water quality parameters and pesticide residues using standard methods. Physico-chemical attributes of water such as pH, electrical conductivity, total dissolved solids, total alkalinity, carbonate, bicarbonate, total hardness, calcium, magnesium, sodium, potassium, chloride, nitrate nitrogen, and sulphate were analysed. Also, attempts to assess the extent of residues of Chlorpyriphos and Quinalphos in the water samples from these ecosystems were attempted, as most of them are under use by people for day-to-day activities. The results of the study are presented.

Table 7.Correlation between soil parameters and pesticide residues with respect to seasons.

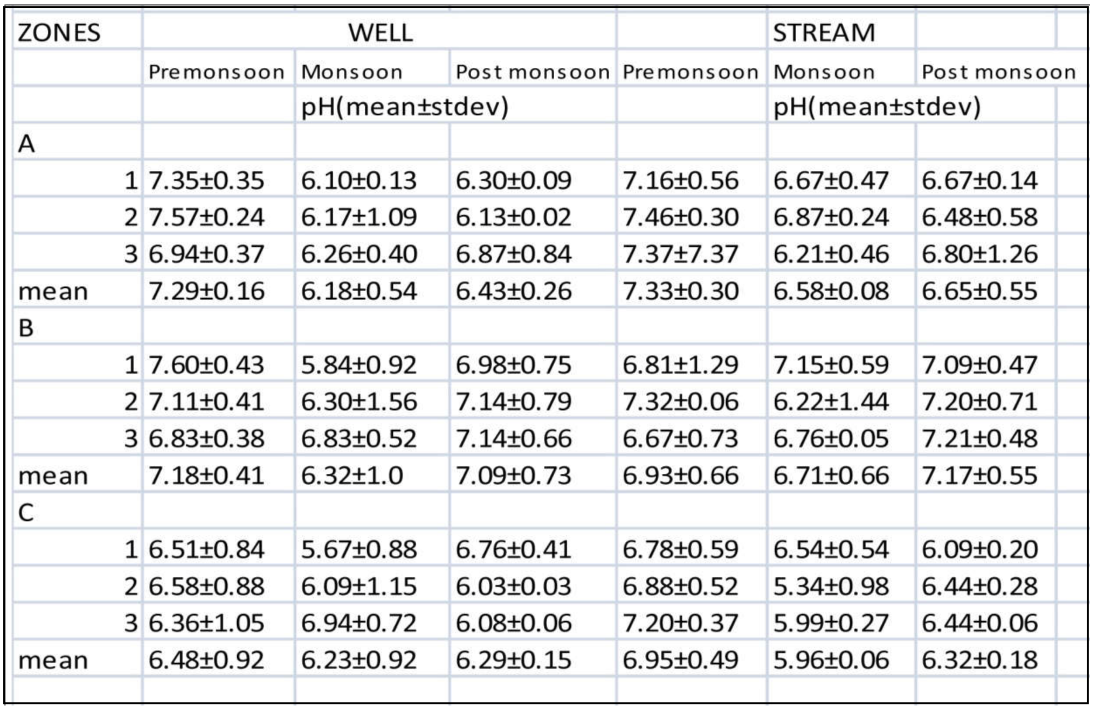
Parameter	Chlorpyriphos			Quinalphos		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
Organic matter	-0.134	0.233	-0.137	-0.311	-0.276	-0.022
Cation Exchange capacity	0.121	0.116	-0.163	-0.461	0.322	-0.238
Total Phosphorus	-0.084	-0.086	-0.175	0.142	0.1	-0.031
Bulk Density	0.384	0.45	0.079	0.264	-0.073	-0.16
Silt	-0.24	-0.136	-0.191	0.121	0.092	-0.173
Clay	0.476*	-0.536*	0.669**	0.395	0.189	0.276

Table 8. Correlation between soil parameters and pesticide residues with respect to zones

Parameter	Chlorpyriphos			Quinalphos		
	zone A	zone B	zone C	zone A	zone B	zone C
Organic matter	-0.185	0.049	0.001	-0.269	0.063	-0.037
Cation Exchange capacity	0.219	-0.316	-0.158	0.33	0.168	-0.367
Total Phosphorus	0.319	0.349	0.39	-0.311	0.234	0.586*
Bulk Density	0.203	-0.703	0.342	-0.023	0.116	-0.179
Silt	-0.035	0.073	-0.019	-0.197	-0.237	0.151
Clay	0.306	0.43	-0.597**	0.478*	0.067	0.158

Analytical results of the pH of water samples collected from open wells and streams are presented in Table 9. On analyzing the pH values of both water bodies, open well water samples were more acidic than stream samples. Seasonal variations noted in the pH of both water sources were similar. Pre-monsoon samples were having almost neutral pH, while it has reduced during monsoon and post-monsoon. Among the three zones, zone C has very low pH. Erosion from plant nutrients and other agrochemicals to surface water sources such as streams reflect in water quality. According to IS 10500:2012, accepTable limit of pH for drinking water sample is 6.5- 8.5. About 50% of well water samples and 20% of stream water samples were less in pH than desirable range.

Table 9. Analytical results of the pH of water samples from various water resources of cardamom plantations



ZONES		WELL			STREAM	
	Premonsoon	Monsoon	Post monsoon	Premonsoon	Monsoon	Post monsoon
		pH(mean±stdev)			pH(mean±stdev)	
A						
1	7.35±0.35	6.10±0.13	6.30±0.09	7.16±0.56	6.67±0.47	6.67±0.14
2	7.57±0.24	6.17±1.09	6.13±0.02	7.46±0.30	6.87±0.24	6.48±0.58
3	6.94±0.37	6.26±0.40	6.87±0.84	7.37±7.37	6.21±0.46	6.80±1.26
mean	7.29±0.16	6.18±0.54	6.43±0.26	7.33±0.30	6.58±0.08	6.65±0.55
B						
1	7.60±0.43	5.84±0.92	6.98±0.75	6.81±1.29	7.15±0.59	7.09±0.47
2	7.11±0.41	6.30±1.56	7.14±0.79	7.32±0.06	6.22±1.44	7.20±0.71
3	6.83±0.38	6.83±0.52	7.14±0.66	6.67±0.73	6.76±0.05	7.21±0.48
mean	7.18±0.41	6.32±1.0	7.09±0.73	6.93±0.66	6.71±0.66	7.17±0.55
C						
1	6.51±0.84	5.67±0.88	6.76±0.41	6.78±0.59	6.54±0.54	6.09±0.20
2	6.58±0.88	6.09±1.15	6.03±0.03	6.88±0.52	5.34±0.98	6.44±0.28
3	6.36±1.05	6.94±0.72	6.08±0.06	7.20±0.37	5.99±0.27	6.44±0.06
mean	6.48±0.92	6.23±0.92	6.29±0.15	6.95±0.49	5.96±0.06	6.32±0.18

Total dissolved solids of water samples from wells and streams are presented in Table 10. From the results, it is evident that the total dissolved solids in both the water sources were similar. Well water samples from zone A and B had more TDS than zone C, which has only half of the dissolved solids than the other two sources. During pre-monsoon, TDS of streams were lower than wells in all the locations.

In stream water samples, dissolved solids were more from zone B during pre-monsoon and it has reduced in monsoon. There was only slight decline in TDSin zone A samples. Even though average TDS of stream samples from zone C was lower than other sources, TDS of one location was as high as that of other zones. All water samples analysed was within the desirable limit (500 mg/L) of drinking water standard (IS 10500:2012).

TDS in water is a measure of minerals and organic molecules that contribute nutrients or contaminants such as toxic metals or organic pollutants. TDS in natural water depends on the geology and geography of the location, drainage pattern and precipitation rate (Weber-Scannell and Duffy, 2007). Cardamom growing soils are well drained and receive more than 3000 mm rainfall in a year, which reflects in the low TDS content of water samples.

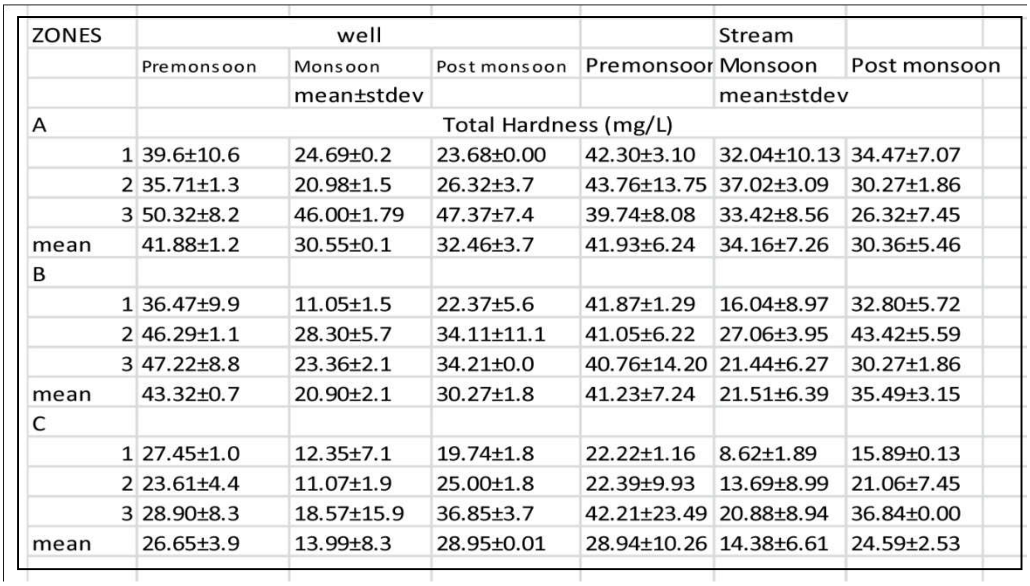
Table 10. Analytical results of Total dissolved solids of water samples from various water resources of cardamom plantations

ZONES	WELL			STREAM		
	Pre-monsoon	**Monsoon**	**Post-monsoon**	**Pre-monsoon**	**Monsoon**	**Post-monsoon**
		mean±stdev			mean±stdev	
A		TDS				
1	57.35±17.04	47.05±1.2	45.89±3.6	67.98±7.89	58.62±14.69	77.93±5.76
2	48.85±9.26	36.65±10.9	42.98±1.5	69.39±10.48	68.70±8.06	52.68±15.20
3	114.35±11.4	112.6±19.6	99.68±19.4	69.06±9.25	67.72±0.88	52.79±16.39
mean	73.52±4.97	65.43±3.3	62.85±8.2	68.61±3.95	65.01±1.92	61.13±12.45
B						
1	76.95±16.33	42.25±32.1	53.49±36.6	95.82±48.11	41.66±0.93	89.92±59.66
2	86.15±13.22	77.75±5.5	84.50±8.0	60.05±2.47	70.94±15.2	81.24±12.64
3	64.40±3.96	56.70±7.0	53.65±7.1	60.60±7.64	56.53±7.74	51.18±2.15
mean	75.83±8.53	58.90±14.9	63.88±12.5	72.16±14.32	56.38±7.34	74.08±23.38
C						
1	36.10±11.03	23.50±1.7	14.65±0.6	23.76±3.73	14.87±6.41	26.61±4.09
2	23.25±5.44	17.25±3.0	24.95±0.3	19.67±4.26	21.64±4.86	24.74±3.45
3	39.30±17.39	38.15±34.2	67.78±0.7	69.85±31.33	65.00±30.26	93.43±2.02
mean	32.88±11.29	26.30±9.85	35.79±0.1	37.76±10.62	33.84±9.57	48.26±1.84

Total Hardness content of water samples from wells and streams are presented in Table 11. Results revealed that during pre-monsoon season, total hardness of water samples ranged from 26.65 to 43.32 mg/L and 28.9 to 41.93 mg/L in open wells and streams, respectively. In both water sources, hardness of samples was not varied much. In monsoon period, hardness of well water samples were declined and were in the range of 13.99 to 30.55 mg/L. similar results were obtained for stream water samples. In post-monsoon season, the hardness of well water samples increased in zone A and C. The stream samples were recorded relatively low hardness during post-monsoon. Moreover, the pattern of hardness in stream samples was similar. All water samples were of soft water type (<75 mg/L).

Hardness of water is due to higher level of mineral content such as calcium and magnesium ions. Rainwater percolated through deposits of limestone and dolomite dissolves calcium and magnesium ions in ground water. The salts of calcium and magnesium are responsible for hardness in water. The extent of calcium and magnesium associated with the water samples were also attempted in the present study.

Table 11. Analytical results of total hardness of water samples from various water resources of cardamom plantations



ZONES	well			Stream		
	Premonsoon	Monsoon	Post monsoon	Premonsoor	Monsoon	Post monsoon
		mean±stdev			mean±stdev	
A	Total Hardness (mg/L)					
1	39.6±10.6	24.69±0.2	23.68±0.00	42.30±3.10	32.04±10.13	34.47±7.07
2	35.71±1.3	20.98±1.5	26.32±3.7	43.76±13.75	37.02±3.09	30.27±1.86
3	50.32±8.2	46.00±1.79	47.37±7.4	39.74±8.08	33.42±8.56	26.32±7.45
mean	41.88±1.2	30.55±0.1	32.46±3.7	41.93±6.24	34.16±7.26	30.36±5.46
B						
1	36.47±9.9	11.05±1.5	22.37±5.6	41.87±1.29	16.04±8.97	32.80±5.72
2	46.29±1.1	28.30±5.7	34.11±11.1	41.05±6.22	27.06±3.95	43.42±5.59
3	47.22±8.8	23.36±2.1	34.21±0.0	40.76±14.20	21.44±6.27	30.27±1.86
mean	43.32±0.7	20.90±2.1	30.27±1.8	41.23±7.24	21.51±6.39	35.49±3.15
C						
1	27.45±1.0	12.35±7.1	19.74±1.8	22.22±1.16	8.62±1.89	15.89±0.13
2	23.61±4.4	11.07±1.9	25.00±1.8	22.39±9.93	13.69±8.99	21.06±7.45
3	28.90±8.3	18.57±15.9	36.85±3.7	42.21±23.49	20.88±8.94	36.84±0.00
mean	26.65±3.9	13.99±8.3	28.95±0.01	28.94±10.26	14.38±6.61	24.59±2.53

Calcium and magnesium content of water samples are presented in Table 12. In the present study, **c**alcium and magnesium content in all water sources were comparatively low. Calcium and magnesium content of both water sources of zone A and B were the same. Calcium content in all locations was more than magnesium content. In zone C, calcium ions predominate over magnesium. Pre-monsoon samples were more in calcium ions in stream samples.

Mean analytical results of sodium and potassium in water samples are presented in Table 13. Potassium ions contribute as a major nutrient for cardamom production. General fertilizer recommendation for cardamom production is 250 kg of K_2O/ha as three split applications (Spices Board, 2001).

Table 12.Analytical results of Calcium and Magnesium content of water samples from various water resources of cardamom plantations

	Calcium content (mg/L)							**Magnesium content (mg/L)**				
ZONES	Well			Stream			Well				Stream	
	Pre-monsoon	Monsoon	Post-monsoo	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoo	Pre-monsoon	Monsoon	Post-monsoo
		mean±stdev			mean±stdev			mean±stdev			mean±stdev	
A												
1	7.49±7.7	5.53±0.5	4.21±1.1	6.23±5.41	5.89±2.70	7.80±0.28	5.06±2.1	2.65±0.3	3.15±0.7	6.49±2.53	4.16±0.76	3.67±1.51
2	5.51±4.3	4.13±0.3	4.20±0.5	5.78±3.08	7.51±0.64	6.30±0.00	4.78±1.7	1.09±1.5	3.80±1.2	7.12±5.20	4.41±1.12	3.50±0.41
3	10.80±0.4	9.97±2.7	8.0±3.5	6.78±0.71	5.10±0.66	5.28±0.32	5.67±1.7	5.12±1.2	6.60±0.4	5.54±1.53	5.02±2.48	3.24±2.03
mean	7.93±3.9	6.54±0.8	5.47±1.3	6.26±2.60	6.17±0.46	6.46±0.01	5.17±1.8	2.95±0.2	4.52±0.0	6.38±3.09	4.53±1.45	3.47±1.32
B												
1	9.35±4.7	5.87±5.4	3.99±0.8	8.94±3.56	3.64±0.08	5.27±0.30	4.28±2.0	0.9±0.4	3.01±0.8	4.75±2.50	1.66±2.27	4.82±1.10
2	8.68±2.5	5.32±1.4	9.05±2.0	6.98±0.79	5.52±1.75	5.49±0.01	5.99±1.2	3.59±0.5	2.80±3.9	5.74±1.99	3.17±0.04	7.18±1.30
3	8.20±0.5	6.24±2.0	6.34±1.2	7.76±1.13	9.70±4.46	6.30±0.00	6.26±2.1	1.57±2.2	4.43±0.6	5.19±2.76	1.76±2.48	3.52±0.45
mean	8.74±2.6	5.81±2.0	6.46±0.5	7.89±1.07	6.29±0.93	5.69±0.10	5.51±1.8	1.02±1.0	3.41±0.8	5.22±2.42	2.19±1.57	5.17±0.65
C												
1	4.95±1.1	3.29±1.8	1.85±0.3	3.77±0.12	2.74±1.63	4.07±1.60	3.76±0.5	4.01±1.4	3.63±0.2	3.11±0.35	0.73±1.03	2.36±0.20
2	3.59±0.43	4.31±2.16	4.59±0.0	4.00±1.01	7.90±4.02	5.05±1.77	3.44±0.6	0.67±0.9	3.27±0.4	3.01±1.80	0.85±1.20	2.07±0.75
3	4.58±0.69	5.33±2.5	9.89±2.1	8.65±4.71	7.80±1.12	7.14±3.61	4.09±1.3	1.45±2.0	2.96±2.1	5.00±2.85	1.40±1.98	4.59±2.14
mean	4.37±0.00	4.31±0.4	5.44±0.5	5.47±1.95	6.15±1.17	5.42±0.08	3.76±0.8	2.04±0.5	3.28±0.9	3.70±1.44	0.99±1.40	3.01±1.03

It was observed that in pre-monsoon and post-monsoon seasons, potassium content was exceptionally high in certain wells. The potassium content ranged from 0.21 to 4.46 mg/L in streams, while the range was 0.35 to 15.7 mg/L in wells. More amounts of potassium ions in stream samples might be attributed to the movement of applied chemicals to water bodies through percolation or run off, which was supported by the seasonal variation in potassium content.

The average sodium content in zone A well samples ranged from 4.81±0.7 to 11.56±0.9 mg/L, while it was 4.36±0.9 to 9.95±1.3 mg/L and 0.59±0.8 to 7.30±0.3 in zone B and C respectively. The average sodium content of water samples collected from both water bodies located in zone A was 7.0mg/L. In zone B, the average sodium content was 6.97 mg/L and 6.39 mg/L in well and stream, whereas it was 6.94 and 4.8 mg/L in zone C, respectively. Sodium content was more observed during pre-monsoon season (6.94 mg/L) and then reduced. In general, sodium content in both water bodies located in zone C were lower than zone A and B.

Table 13. Analytical results of Sodium and Potassium content of water samples from various water resources of cardamom plantations

	Well			Stream			Well			Stream		
ZONES	Sodium (mg/L)						Potassium (mg/L)					
	Pre-monsoon	Monsoon	Post-monsoo	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoo	Monsoon	Post-mons	Pre-mons	Monsoon	Post-monsoon
		mean±stdev			mean±stdev			mean±stdev			mean±stdev	
A												
1	5.99±0.3	5.49±1.4	5.77±0.6	5.75±1.74	6.75±0.36	7.81±1.14	0.91±0.5	2.53±0.2	0.48±0.0	3.34±0.61	3.04±0.94	2.95±0.13
2	4.81±0.7	5.08±3.0	5.02±0.4	6.47±2.30	6.30±0.57	6.09±0.48	0.91±0.6	1.60±0.1	0.79±0.0	3.09±1.62	4.13±0.61	2.26±0.17
3	11.56±0.9	10.50±1.7	8.77±1.2	8.95±0.40	8.70±0.29	6.16±3.32	0.91±0.7	7.22±2.1	5.27±0.27	1.56±0.39	2.73±1.17	1.48±1.12
mean	7.45±0.6	7.02±0.03	6.52±0.7	7.05±1.48	7.25±0.21	6.68±1.65	0.91±0.8	3.78±0.6	2.18±0.1	2.66±0.21	3.30±0.28	2.23±0.47
B												
1	8.58±0.8	6.84±5.3	4.76±5.4	14.05±10.08	5.51±0.72	5.30±0.24	3.30±0.4	1.77±0.1	15.70±22.1	2.58±0.95	1.68±0.69	3.17±0.04
2	9.95±1.3	8.21±0.6	8.67±0.4	6.06±0.17	6.67±1.56	3.83±1.00	1.50±0.17	2.36±0.8	0.96±0.0	1.42±0.23	2.49±1.02	2.04±0.20
3	5.49±0.1	5.88±0.3	4.36±0.9	6.35±0.35	5.57±0.11	4.15±1.43	3.08±0.0	2.40±0.0	0.82±0.5	1.10±0.23	2.04±0.73	0.62±0.13
mean	8.00±0.7	6.98±1.4	5.93±1.6	8.82±3.19	5.92±0.32	4.43±0.22	2.63±0.1	2.18±0.2	5.83±7.2	1.70±0.32	2.07±0.33	1.94±0.10
C												
1	2.08±0.0	2.05±0.5	0.13±0.1	1.98±0.78	1.30±0.21	0.34±0.19	1.84±0.7	1.82±0.6	0.44±0.0	1.14±0.98	1.38±0.18	3.65±0.64
2	1.15±1.1	0.59±0.8	1.53±0.04	1.04±0.18	1.08±0.95	0.37±0.14	1.51±1.1	1.25±0.6	0.35±0.0	0.54±0.52	1.31±0.62	0.21±0.15
3	4.70±4.4	4.01±5.3	7.30±0.3	8.43±3.25	11.46±5.15	17.20±0.99	1.77±0.8	2.13±1.8	1.92±0.0	4.46±2.36	1.10±0.11	1.17±0.14
mean	3.94±2.6	2.21±2.2	2.98±0.0	3.82±1.40	4.61±1.97	5.97±0.35	1.70±0.9	1.73±1.0	0.90±0.0	2.05±1.29	1.26±0.23	1.68±0.21

The extent of chloride and sulphate present in water samples are depicted in Table 14. It has been noticed that stream water samples were low in chloride content compared to well water samples. The chloride content has reduced during monsoon and then increased in both type of water sources. In zone A, the average chloride content of well and stream samples were 21.23 mg/L and 20.19 mg/L respectively, where as it was 19.62 mg/L and 14.98 mg/L in zone B and 12.98 mg/L and 14.98 mg/L in zone C. Chloride content was more observed during post-monsoon and least during monsoon in both water sources.

All the water samples analysed were very low in sulphate content. In all these samples, sulphates have contributed less to total anionic concentration. Sulphates of calcium and magnesium contribute to permanent hardness in water. Desirable limit of sulphate in drinking water is 250 mg/L, as per drinking water standard IS 10500:2012. Sulphate content of all samples was within the desirable limit.

Table 14.Analytical results of Chloride and Sulphate content of water samples from various water resources of cardamom plantations

ZONES	Chloride						Sulphate					
	Well			Stream			Well			Stream		
	Pre-monsoon	Monsoon	Post-monsoon	Premonsoon	Monsoon	Post monsoon	Premonsoo	Monsoon	Post monsc	Premonsc	Monsoon	Post mons
		mean±stdev			mean±stdev			mean			mean±stdev	
A												
1	21.51±10.5	12.19±0.9	22.01±3.2	19.09±1.23	15.35±5.45	24.35±0.00	1.38	5.00	0.12	2.38±0.39	5.2	0.40±1.8
2	21.75±10.2	9.46±5.5	19.13±0.8	22.67±7.61	15.48±1.52	22.61±4.09	0.8	1	0.15	2.45±1.6	3.61	0.42±1.9
3	21.51±9.9	28.76±0.3	34.78±3.2	18.88±4.89	18.37±5.18	24.93±4.09	1.8	0.71	0.73	1.41±0.6	0.42	0.77±2.0
mean	21.59±3.65	16.80±1.6	25.31±1.9	20.21±4.58	16.40±3.04	23.96±0.00	1.33	2.24	0.33	2.08±0.8	3.08	0.53±2.1
B												
1	21.79±3.3	11.85±3.7	23.19±1.6	25.04±8.53	10.19±0.11	15.08±9.34	5.81	0.00	0.02	1.53±1.0	1.71	0.61±2.2
2	19.44±3.5	14.60±2.11	24.35±6.5	18.16±2.55	12.51±0.78	24.35±1.65	0.77	0	2.09	2.55±1.2	9.28	2.0±2.3
3	27.35±17.6	12.02±1.8	22.03v0.0	5.63±0.37	12.63±1.37	23.77±0.83	2.63	4.33	0.31	2.90±1.6	4.61	0.17±2.39
mean	22.86±5.8	12.82±0.0	23.19±2.7	20.67±0.12	11.77±0.16	21.06±3.01	2.54	1.44	0.81	2.32±0.2	5.2	0.93±2.5
C												
1	13.87±2.5	6.48±1.9	13.33±2.4	11.04±2.50	5.79±0.93	19.71±4.91	1.54	0.97	0.05	1.60±0.4	1.69	0.05±2.8
2	11.79±3.56	5.10±0.6	16.23±0.0	9.68±5.83	5.55±0.59	17.97±0.82	0.23	1.92	1.1	1.28±0.5	1.35	0.1±2.9
3	15.96±2.35	9.70±5.7	24.35±0.0	19.79±9.63	16.90±8.06	28.41±4.09	1.13	1.04	3.38	5.11±4.9	4.32	6.06±2.79
mean	13.87±1.2	7.09±2.7	17.97±0.8	13.50±5.98	9.41±3.19	22.03±3.28	0.97	1.31	1.51	2.66±1.9	2.45	2.07±0.88

Results of alkalinity and bicarbonate content of water samples are presented in Table 15. Normally, the extent of carbonates and bicarbonates present in water contribute to total alkalinity. As the pH of all water samples were below 8.3, all types of carbonates are expected in the form of bicarbonates. Bicarbonate content and total alkalinity of well and stream samples were same in zone A and B. Bicarbonate content was more observed in stream water samples in zone C.

Total alkalinity of well water samples ranged from 11.21±0.9 to 29.25± 7.7, 12.71±1.6 to 30.02± 3.7 and 8.17±4.1 to 25.93±2.1, respectively in zone A, B and C. Total alkalinity of stream water varied from 16.67±0.9 to 31.25±5.3 in zone A, 16.59±3.8 to 30.70±4.2 in zone B and 4.63±4.9 to 45.00±7.0 in zone A. In general, zone A samples were high in chloride content in both water sources. In both water sources, post-monsoon samples were more alkaline than other seasons. The primary sources of natural alkalinity in groundwater are dissolved carbon dioxide from atmosphere and dissolution of carbonate minerals. Alkalinity present in water samples were reported to be contributed completely by bicarbonates (Kumar and Suseela, 2013; Kumar and Kumar, 2013). The present study also supports these finding. From the above finding, it could also be concluded that the low concentration of dissolved solids in water samples reflected in the concentration of major an ions such as chloride, sulphate, carbonate and bicarbonate content.

Table 15. Analytical results of total alkalinity and bicarbonate content of water samples from various water resources of cardamom plantations

	WELL			Stream			WELL			Stream		
ZONES		Total Alkalinity (mg/L)							Bicarbonate (mg/L)			
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoor	Pre-monsoor	Monsoon	Post-monsoo
		mean±stdev			mean±stdev			mean±stdev			mean±stdev	
A												
1	29.25±7.7	17.91±7.0	26.50±5.6	16.90± 2.9	18.91±2.6	31.25±5.3	35.69±9.4	19.56±1.7	28.98±2.1	21.61±3.55	23.04±3.3	38.13±6.4
2	25.04±1.8	26.34±7.3	21.25±5.3	26.64±18.3	16.67±0.9	21.25±5.3	30.55±2.1	28.29±9.0	29.00±2.1	32.50±22.3	20.33±1.1	10.93±14.7
3	11.21±0.9	19.14±6.02	16.56±2.3	21.45±0.93	23.97±2.1	23.75±8.8	13.68±1.1	16.94±4.33	18.30±0.0	26.16±1.1	18.01±18.4	28.98±10.7
mean	21.83±2.8	21.13±5.7	21.47±0.9	21.66±4.8	19.85±1.9	25.42±6.4	26.64±3.4	21.59±2.1	25.43±0.1	26.42±5.8	20.46±7.62	26.01±0.84
B												
1	18.85±1.3	14.28±5.2	20.00±3.5	30.70±4.2	16.85±2.3	23.75±5.3	22.99±1.6	16.38±10.0	21.93±0.8	37.44±5.1	20.58±2.8	28.95±6.4
2	12.72±1.6	14.85±5.1	23.45±1.3	19.28±4.9	16.59±3.8	17.50±7.0	15.52±1.9	16.95±9.2	25.93±2.1	23.52±6.0	20.21±4.6	21.38±8.5
3	30.02±3.7	15.43±5.1	24.43±4.3	21.42±0.5	19.13±1.3	18.75±5.3	36.62±4.5	17.53±8.4	27.45±8.6	13.63±18.3	23.35±1.6	22.88±6.4
mean	20.53±2.2	14.85±4.8	22.63±0.1	23.80±0.4	17.52±0.1	20.00±2.36	25.04±2.7	16.95±9.2	25.1±3.3	24.86±6.39	21.38±0.1	24.40±2.8
C												
1	11.67±3.1	8.17±4.1	11.10±1.5	11.20±0.9	5.86±1.7	12.50±0.0	14.23±3.7	8.97±0.3	12.20±0.0	13.67±1.17	7.17±2.1	15.28±0.04
2	10.21±0.4	8.75±4.8	15.68±8.0	10.65±3.1	4.63±4.9	16.25±5.3	12.47±0.5	9.55±1.2	16.78±6.4	12.99±3.84	5.65±6.0	19.85±6.4
3	13.21±2.3	10.70±6.0	25.93±2.1	23.43±1.8	26.85±22.1	45.00±7.0	16.12±2.8	11.12±8.8	23.45±1.3	28.58±2.2	28.05±20.4	54.9±8.6
mean	11.70±1.66	9.21±4.4	17.57±2.4	15.09±1.9	12.45±5.1	24.58±4.1	14.27±2.0	9.88±3.4	17.48±2.6	18.41±2.4	13.62±4.1	30.01±5.0

The results of Nitrate–Nitrogen content of water samples are presented in Table 16. The average Nitrate nitrogen in well water samples were ranging from Below Detection Limit (BDL) to 9.13 mg/L, while it ranged from 0.4 mg/L to 5.65 mg/L in stream water samples. The concentration of Nitrate nitrogen was more in well water samples. One location in zone A has recorded Nitrate nitrogen content, exceeding the desirable limit for drinking purposes (10 mg/L). In general, average Nitrate nitrogen content was less during monsoon.

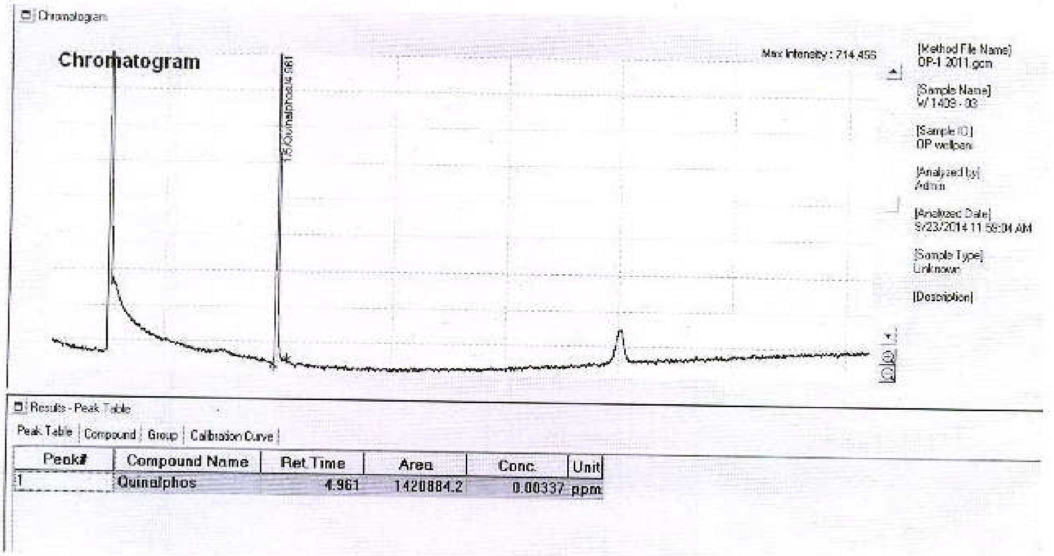
Nitrate is a minor constituent of rocks. Average concentration of nitrate in rain water is less than 0.2 mg/L and normally concentration in ground water remains below 5 mg/L. Other sources of nitrate are decayed organic matter, sewage and fertilizers. Recommended dose of nitrogen fertilizer in one hectare of cardamom plantations is 125 Kg/year. Soil, climate, agriculture and land use pattern etc. has great influence in the nitrate nitrogen content in groundwater sources (Di and Cameron, 2002). The occurrence of Nitrate –N in well water sources might be due to the percolation of nitrogenous fertilizers, being applied in cardamom plantations for productivity enhancement.

Table 16. Analytical results of nitrate nitrogen content of water samples from various water resources of cardamom plantations

ZONES	Well			Stream		
	Pre-monsoon	Monsoon	Post-monsoon	Pre-monsoon	Monsoon	Post-monsoon
		mean±stdev			mean±stdev	
A						
1	0.93±0.2	0.58±0.1	1.18±0.0	2.37±0.37	1.81±1.7	2.97±3.5
2	0.0±0.0	0.32±0.1	0.92±0.2	1.63±0.46	3.14±0.14	3.36±4.5
3	8.77±2.3	8.79±9.5	9.13±8.16	3.16±3.08	5.65±6.0	1.07±1.0
mean	3.23±0.7	3.23±3.2	3.74±2.5	2.38±1.30	3.53±2.5	2.46±3.04
B						
1	3.14±1.3	0.97±0.75	1.48±0.1	0.91±0.15	0.51±0.02	0.62±0.6
2	7.27±0.47	3.46±2.32	4.80±5.0	1.91±0.29	2.35±0.74	1.32±1.3
3	0.11±0.1	1.58±0.3	3.88±3.71	3.85±0.29	2.0±0.86	2.07±2.4
mean	3.50±0.3	2.00±0.62	3.38±2.9	2.22±0.05	1.62±0.54	1.34±1.4
C						
1	1.84±0.5	1.08±0.2	1.20±0.4	1.60±0.45	0.57±0.28	1.97±2.6
2	2.58±1.5	0.34±0.4	3.44±0.8	1.28±0.56	0.27±0.19	0.40±0.4
3	1.44±0.1	1.25±1.2	5.84±6.7	5.11±4.93	0.48±0.68	4.55±4.7
mean	1.95±0.3	0.89±0.3	3.49±1.8	2.66±1.9	0.44±0.07	2.31±0.5

Concentration of pesticide residues in water sources are listed in Table 17 and 18. The results revealed that the residues of Chlorpyriphos was not detected in open well water samples, whereas it was detected in water samplescollected from adjoining streams in zone A and zone C (Figure.3.). In zone A, residue of Chlorpyriphos was detected in one sample collected from stream adjacent to cardamom plantations during monsoon season. Similarly residue of Chlorpyriphos was detected in one stream water sample in zone C. As per IS 10500:2012 drinking water standards, maximum residue limit (MRL) in drinking water for Chlorpyriphos is 30 µg/L. Even if, residue of Chlorpyriphos was detected in water bodies, the concentration was below MRL stipulated by standards.

Figure.3.Chromatogram of water samples from zone C



[Method File Name]
OP-1 2011.gcm

[Sample Name]
W 1409 - 03

[Sample ID]
OP wellpani

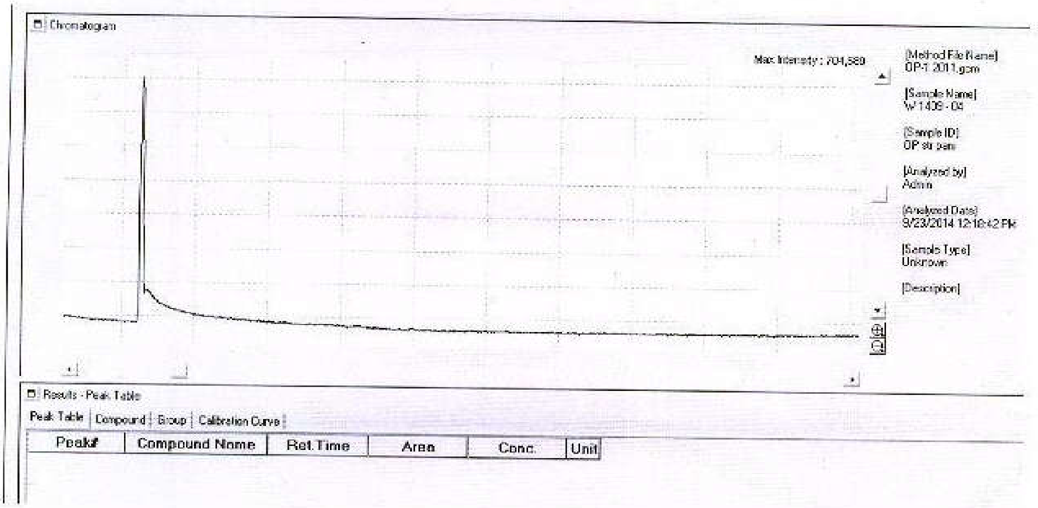
[Analyzed by]
Admin

[Analyzed Date]
9/23/2014 11:59:04 AM

[Sample Type]
Unknown

[Description]

Peak#	Compound Name	Ret.Time	Area	Conc.	Unit
1	Quinalphos	4.961	1420884.2	0.00337	ppm



[Method File Name]
OP-1 2011.gcm

[Sample Name]
W 1409 - 04

[Sample ID]
OP st pani

[Analyzed by]
Admin

[Analyzed Date]
9/23/2014 12:18:42 PM

[Sample Type]
Unknown

[Description]

Peak#	Compound Name	Ret.Time	Area	Conc.	Unit

Residue of Quinalphos was detected in well water sources in zone A and C. in zone A, residue of Quinalphos was detected in two open wells during post-monsoon. It was not detected in any of the open well samples in zone B. Similarly in zone C, one open well situated in cardamom plantation was contaminated with residues of Quinalphos during monsoon. Similar to open well, pesticide contamination was observed during post-monsoon in zone A. The residue of Quinalphos was detected in streams adjacent to cardamom plantation, where open wells were contaminated during post-monsoon. In zone C, residue of Quinalphos was also detected in another cardamom plantation. The residues of pesticides were not detected in zone B. In general Quinalphos was observed as a frequent water pollutant in cardamom plantations. In cardamom plantation, Quinalphos (0.025% a.i.ha^{-1}) is being sprayed for the management of wide variety of insect pests during pre-monsoon and post-monsoon seasons (Kerala Agricultural University, 2008 and Spices Board, 2001). Residues of applied chemicals might have reached water sources through leaching and run-off.

Table 17.Analytical results of the residue of Chlorpyriphos in water samples from various water resources of cardamom plantations.

			Chlorpyriphos (µg/mL)									
	Well						Stream					
Sampling	Pre monsoon		Monsoon		Post monsoon		Pre monsoon		Monsoon		Post monsoon	
Zone A												
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.200	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zone B												
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zone C												
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.300	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Table 18. Analytical results of the residue of Quinalphos in water samples from various water resources of cardamom plantations

			Quinalphos (μg/mL)									
	Well						Stream					
Sampling	Pre-monsoon		Monsoon		Post-monsoon		Pre-monsoon		Monsoon		Post-monsoon	
Zone A												
1	BDL	BDL	BDL	BDL	0.28	BDL	BDL	BDL	BDL	BDL	0.27	BDL
2	BDL	BDL	BDL	BDL	0.42	BDL	BDL	BDL	BDL	BDL	0.12	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zone B												
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Zone C												
1	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
2	BDL	BDL	BDL	3.98	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
3	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.33	BDL

SUMMARY AND CONCLUSION

An attempt has been carried out to assess the seasonal changes in the physico-chemical characteristics of soil and water samples from three cardamom growing zones falling in Idukki district, Kerala. Attempts were also made to assess the extent of pesticides like Chlorpyriphos and Quinalphos in the soil and other water resources associated with cardamom plantations on a seasonal basis.

From the results, it has been noticed that the cardamom growing soils are acidic. Zonal variation was observed in pH of soil in the study area. Zone A samples recorded low and zone C samples recorded high soil pH. Since cardamom plants are very sensitive to soil moisture and humidity, all plantations were irrigated and maintained with adequate soil moisture. Electrical conductivity of zone A samples were higher than that of zone B and C. Electrical conductivity of soil samples reduced during monsoon. Cardamom growing soils were having moderately high organic matter content. Organic matter content was more recorded in zone C samples. Cation exchange capacity of zone B and C have recorded more than zone A.

Soil physical and hydrological properties such as bulk density, particle density, water holding capacity, pore space and volume of expansion were analyzed. Bulk density of zone B samples was higher than zone C and zone A. Bulk density was less during pre-monsoon season. Zonal and seasonal variation was observed in particle density of cardamom growing soil. Zone A samples had more particle density and water holding capacity than other two zones. Zone B samples were having more pore space than zone A and C. Pore space was high during monsoon and least during pre-monsoon. Zone A soils were low in sand content followed by zone C and B. Silt content was more in zone C than other two zones. The average clay content in all the three zones was same. Seasonal and zonal variation was not noticed in clay content.

In general, soil physical attributes such as bulk density and volume of expansion were in the order of zone C> zone B> zone A, whereas particle density and water holding capacity were in the order of zone A> zone B> zone C. During monsoon soil physical characteristics such as particle density, water holding capacity and pore space were highest. Bulk density was more in pre-monsoon and volume of expansion was high during post-monsoon.

Apart from elevation and climate, soil physico-chemical properties have great influence on the growth and yield of cardamom. Cardamom productivity is more in zone A due to soil factors like high electrical conductivity, moderately high organic matter, total phosphorus content and cation exchange capacity as well as high water holding capacity and particle density and low bulk density , volume of expansion and sand content. All these factors have influenced positively in the root proliferation and nutrient uptake than other two zones. Further these factors also have facilitated sustainable cultivation and production of cardamom.

Similar to soil, water quality parameters were periodically analysed for samples collected from open wells and streams adjoining cardamom ecosystems. From the water quality data it was significant as both water sources are being used for various purposes, including drinking.

Both essential and general water quality parameters such as pH, total dissolved solids, total hardness, calcium, magnesium, sodium, potassium, alkalinity, carbonates, chloride and sulphate of open well and streams were within the drinking water standards stipulated by IS 10500:2012. Seasonal variation was observed in the quality of water bodies. Nitrate –nitrogen was present in well and stream water samples. However their concentration was higher in well water samples. Average Nitrate nitrogen content was less during monsoon.

The residues of Chlorpyriphos and Quinalphos were detected in all soil samples of the cardamom ecosystem in various quantities. There was seasonal variation in the residue of Chlorpyriphos and Quinalphos in soil. Chlorpyriphos was more in pre-monsoon season in zone A and B. The residue of Quinalphos was detected in all soil samples throughout the year. Residues of Quinalphos were detected in both water bodies during monsoon and post-monsoon. Quinalphos was mobile than Chlorpyriphos. Residue of Chlorpyriphos and Quinalphos were not significantly correlated to soil physical and chemical attributes such as bulk density, organic matter, cation exchange capacity, total phosphorus and silt content. Zonal and seasonal correlation was observed for Chlorpyriphos and Quinalphos residues with soil clay. Retention and dissipation of Chlorpyriphos and Quinalphos in soil was influenced by soil physical attributes.

BINDUMOL G.P. “STUDIES ON LEACHING AND DISSIPATION OF COMMONLY USED ORGANOPHOSPHORUS PESTICIDES IN CARDAMOM ECOSYSTEMS OF IDUKKI DISTRICT, KERALA”. THESIS. DEPARTMENT OF BOTANY, UNIVERSITY OF CALICUT, 2018.

CHAPTER II

LEACHING, DISSIPATION AND SORPTION KINETICS OF CHLORPYRIPHOS AND QUINALPHOS IN CARDAMOM PLANTATIONS OF KERALA

INTRODUCTION

Globally agricultural ecosystems are the most vulnerable ecosystems due to the over use of agrochemicals for enhancing crop growth and productivity. In modern agriculture, introduction of high yielding hybrid varieties has become an integral part. In addition to the application of agrochemicals for crop growth and productivity, hybrid varieties require additional plant protection measures as they are easily prone to pests and diseases. Moreover the diversity and complexity of pests attacking crop plants have also increased. This has led to a drastic situation of selection of plant protection chemicals based on their efficacy to control pests/diseases, rather than their dissipation kinetics or probability of environmental contamination. In addition to this, unscientific dosages and unsystematic practices of such chemicals at various stages of crop growth had eventually resulted in their environmental persistence in varying magnitude. Among various agrochemicals, pollution due to pesticides had everlasting ecological impacts (Lai, 2017). India ranks tenth position in Global market on account of consumption of pesticides (Devi et al. 2017). Of various agricultural systems, cotton cultivation consumes around 37%, followed by paddy (20%)(Jindal, 2017). The share for vegeTable s is 9%. In the state of Kerala, major share of pesticide usage is for paddy cultivation, followed by spices.

Kerala is popular for plantation crops, especially spices. Worldwide acceptance of spices from Kerala is linked to its appearance, cleanliness and intrinsic quality. Climate and weather parameters of Kerala are very much conducive for the cultivation of spices, such as cardamom, pepper, ginger, turmeric and tree spices. Small cardamom is the dried fruit of the perennial plant, *Elettaria cardamomum* Maton. It is a shade loving plant, which is cultivated at an altitude of 600 to 1200 m above MSL, with an annual rainfall of 1500 to 4000 mm and a temperature of 10 to 35 ^{0}C (Madhusoodanan et al. 1994). It is indigenous to the evergreen rain forests of Western Ghat of South India. Cardamom is a high valued spice crop, which is cultivated under shade with much care. As it is a native to Western Ghat, Cardamom Hill Reserve (CHR) is rich in its genetic resources. New high yielding varieties of cardamom are developed by planters as well as scientific community. These high yielding cultivars of cardamom naturally requires more plant production and protection measures than natural varieties. Traditional planters of these areas apply large quantity of fertilizers, other growth enhances and pesticides to protect their crop. Lot of unsystematic and unadvisable practices are followed in this plantation system, which include application of over concentrated spray solutions, application during off seasons as well as other prophylactic measures. Quinalphos is one of the most widely used systemic pesticides in cardamom plantations for controlling insect pests such as cardamom thrips and shoot/panicle/capsule borers (Beevi et al. 2014; George et al. 2013; Mohanan, 2006). Root grubs attack cardamom roots and reduces nutrient uptake and yield. Chlorpyriphos is another pesticide used in cardamom ecosystems, wherein they are commonly applied through drenching for the control of grub attack. These unscientific methods of pest control are leading to environmental hazards not only to the human beings, but also to the flora and fauna associated with CHRs of Kerala.

Agrochemicals, apart from the target, will undergo adsorption, retention, dissipation or leaching in associated environments. Once these organic pollutants reaches the environment, their transport to associated environments is influenced by climate, soil characteristics, topography of the cultivating area, cultivation practices, method of irrigation and soil disturbances (El- Kilani and Belal, 2010). Hence residues of these pesticides are to be monitored periodically to evaluate their presence and persistence in associated environments. Solute transport of pesticides in such systems can be systematically studied by diverse methods like in situ / ex situ lysimeters, adsorption kinetics in various soil components or by isotopic studies using radioactive tracers.

Pesticide-soil interaction is a complicated process. Soils normally act as a matrix for the transport of pesticides or in the transformation or degradation of pesticides. Well known individual processes such as volatilization, leaching, adsorption and degradation determines the activation / inactivation of a chemical applied to the soil (Imache et al. 2009; Marin-Benito et al. 2018). The residue of agrochemicals diffuses to soil, further leads to the contaminant transport in soil profile and subsurface migration. The fate and transport of these contaminants depend on many environmental factors. Soil physical and chemical characteristics have very much influence in solute transport and its dissipation. Interaction and fate of these synthetic molecules in soil has to be studied in detail to establish their mobility and dissipation and thereby environmental sustenance.

Mobility of pesticides, in general, is determined by the vertical as well as horizontal motion of chemicals in soil. Such mobilizations, as stated earlier, are dependent on the intensity and frequency of rainfall, soil characteristics and pesticide properties. Soil components such as clay minerals, metallic oxides and organic colloids interact with such chemicals in various ways. Adsorption studies are useful to elucidate the behavior of each pesticide in soil and its further leachability. In batch or slurry method, a known quantity of soil/soil components and molecules under study are allowed to equilibrate under optimum temperature and partitioning of the solute between soil and water can be determined (Handa et al. 1999).

Among several techniques being employed to study the leaching and dissipation of pesticides in soil, soil column technique is the most efficient, accurate and widely used method for prediction and numerical modeling. In the present study, leaching of two synthetic chemicals being used in the cardamom plantations of Idukki District of Kerala (Chlorpyriphos and Quinalphos) have been attempted to evaluate the mobility and dissipation under controlled laboratory conditions. Similarly soil adsorption kinetics of these chemicals at different concentrations was also attempted. The overall objectives of this study are listed below:

1. To study the leaching and dissipation pattern of Chlorpyriphos and Quinalphos in cardamom growing soils of Kerala under controlled conditions.
2. To evaluate the sorption characteristics of Chlorpyriphos and Quinalphos in cardamom growing soils of Kerala under controlled conditions.

REVIEW OF LITERATURE

There are reports on studies being carried out on the leaching and dissipation pattern of various agrochemicals in heterogeneous systems across the globe. Some of the relevant studies are listed here.

Undisturbed lysimeter studies were conducted on five different soil types cropped with winter wheat in two seasons by Brown et al. (2000). The lysimeters were treated with Isoproturin, Linuron and bromide tracer during autumn, whereas Dimethoate and MCPA were applied in spring. Total flow from the lysimeters ranged from 335 to 477 mm over two seasons. The results revealed that leaching of bromide was faster in alluvial clay loam and unstructured sand. Mineral soils were noticed with less pesticide loss than sandy soil.

A molecular topology model was derived for determining groundwater pollution due to pesticides on the basis of adsorption and desorption constants. Such attempts are prone to site variability and measurement error, to the extent that compounds cannot be reliably classified on the chemistry of pollution extrapolated from them. A logistic regression model has been developed, which explained 97 percentage of the variation in the data with 86 percent of the variation being explained by the rule that a compound will be found in the groundwater. It has also discussed about understanding pollution at the molecular level and their application to agrochemical development and risk assessment (Worrall, 2001).

Influence of topsoil tilth and moisture on soil has been investigated using lysimeter experiments on heavy clay soils (Brown et al. 2001). The influence of top soil tilth on leaching of the herbicide Isoproturon and bromide tracer was evaluated during winter season. The results revealed that soil moisture status during and after pesticide application has immediate effect on leaching of Isoproturon, Chloroluron and Linuron. Topsoil tilth and total flow affect the maximum concentration and total loss of Isoproturon in drainflow.

Mikata et al. (2003) studied the mobility and degradation of Imazosulfuron labeled with carbon-14 in lysimeters with 1 m^2 surface and 110 cm depth, for three years. The concentration of Imazosulfuron and their degradation products in leachate water ranged from 0.01-0.06 µg/L. The main portion of ^{14}C was detected in the 30 cm soil layer in each lysimeter, and no ^{14}C was detected below the depth of 15 cm.

Efficacy of leaching models such as PELMO, PRZM, PESTLA and MACRO were evaluated in sandy loam and clay loam soils of Europe. The study showed that predictions for pesticide loss were sensitive to large number of input parameters. Volume of percolated water predicted by these models was influenced only by meteorological variables. The significant influence of soil properties such as field capacity, bulk density and other parameters defining the boundary between the flow domains were noted, at least in one scenario for all models (Dubus et al. 2003).

Studies on the efficacy of bio beds to treat contaminated water from pesticide spillages, leakages, decontamination of tractors and sprayers were carried out. A lined bio-bed system and an unlined bio-bed system have been assessed using a range of pesticides. Applied pesticides were retained within the 0-5 cm layer. Unlined bio-beds effectively removed pesticides and degraded within 9 months (Fogg and Boxall, 2004).

A study on the dissipation and movement of Chlorpyriphos in the sandy loam and loamy sand soils of semi –arid India and its residues in harvested groundnut seeds were monitored. Chlorpyriphos was moderately sTable in both soils, with half-life of 12.3 and 16.4 days in loamy sand and sandy loam soils, respectively. The principal breakdown compound of Chlorpyriphos in soil was 3,4,6-trichloro-2-pyridinal (TCP) (Menon et al. 2004).

The leaching, soil sorption and degradation of the herbicides Tebuthiuron and Diuronin in different soil types were studied using undisturbed soil column (Matallo et al. 2005). Tebuthiuron leached in greater quantity than Diuronin in both soils. Rapid rate of degradation of Diuron and Tebuthiuron were noted in both soil types.

Fate of Chlorothalonil, Chlorpyrifos and Profenofos in sandy clay loam soil under tropical conditions was studied in a vegeTable plot in the Cameron Highland, Malaysia. The residues of all pesticides were detected in runoff from lysimeter and soil samples. Dissipation rate of all the tested chemicals were higher in Cameron Highland soil (Ngan et al. 2005).

Javadi and Najjar (2007) developed a numerical model for simulation of flow of air, water and contaminant transport through unsaturated soil with special attention to chemical reaction. The mathematical model was capable of predicting the effect of chemical reaction with very high accuracy.

Arias-Estevez et al. (2008) reviewed the influence of physical and chemical characteristics of the soil system, such as moisture content, pH, organic matter and clay contents, sorption and degradation of pesticides and possible route to groundwater and surface waters in heterogeneous systems. Adequate understanding in soil science, clay mineralogy, physical chemistry, surface chemistry, environmental microbiology, plant physiology and other disciplines were found essential to integrate developmental tools and techniques. The review also pointed out the need of studies to improve formulations, which will reduce environmental contamination.

Rao et al. (2009) conducted an in-situ soil lysimeter investigation on contaminant transport and hydraulic conductivity of a waste disposal site in India. The results were compared using analytical and regression-models. The results demonstrated that this kind of lysimeter studies are helpful in determining the in-situ hydraulic conductivity of soil mass under saturated and partially saturated conditions.

Investigations on the leaching behaviour of five pesticides (Atrazine, S-metochlor, Imazaquin, Sulfometuron, Imidachloprid and Trifloxystrobin) in the groundwater bodies were carried out in five different sites in Hawaii. The results which were correlated with laboratory studies revealed that, most of the applied mass of pesticide was persisted in 80cm depth of topsoil, 16 weeks after application. Among the pesticides tested, Trifloxystrobin was noted to have very high potential to leach (Dusek et al. 2009).

Wang et al. (2009) investigated the heterogeneity of solute transport related to soil water flow using infiltration experiments and characterized heterogeneous water flow and solute transport in soils using the information theory. Field experiments of dye infiltration were performed to characterize information contents and complexity of water flow and solute transport in soils. The results indicated that more heterogeneous processes of soil water flow and transport result in higher information/complexity values. It also indicated that the transport processes were more heterogeneous than the water flow processes.

Pesticide transport from point of application through sub-surface drains were worked out. It has been noted that such a transport influenced significantly to the contamination of surface waters. Maximum concentration of pesticide in drain flow and seasonal loss of pesticide to drains were significantly related to the strength of pesticide sorption in the soil, half-life of the pesticide in soil, the interval between application and first drain flow and clay content of the soil. The review suggested possible management ways to protect environment with the balanced use of pesticidal products to support agriculture (Brown and Beinum, 2009).

The efficacies of farmyard manure (FYM) and conjoint application of FYM and microbial consortium (*Gordonis*sp.) were evaluated for reducing residues of Lindane in soil, plant and percolated water in lysimeters filled with gravel and river bed sand and cropped with rice and maize. The results indicated that, the residues of pesticides in drainage water were well above the USEPA limit. The conjoint application of FYM with microbial consortium was found to be more effective (Bhatia et al. 2012).

A field experiment on the transport of Carbofuran molecule, which is known for its high mobility in sandy soils with high hydraulic conductivity and low organic matter, has been carried out in Mnasra in Morocco. The model developed could accurately reproduce the measured values. Carbofuran had practically leached beyond the root zone and reached 100 cm depth under irrigated conditions (Hmimou et al. 2014).

Pesticide leaching model can be used to describe soil water dynamics and pesticide transport to soils. Experiment was conducted to evaluate the transport of Atrazine in an irrigated corn field in the plains of the Ardas River in north –eastern Greece. Laboratory and field data were compared with MACRO and PEARL model. The results showed that the coefficient of residual mass values for both models is positive, which indicated that both models had underestimated the measured data. MACRO model simulated the fate of Atrazine in soil than PEARL (Giannouli and Antonopoulos, 2014).

Investigation on leaching bahaviour of contaminated soil and organic pollutants were carried out with soil column experiments by Kalbe et al. (2014). The results indicated that the differences in the leaching behavior are mainly due to the differences in partitioning of organic carbon and water, which can be estimated from log K_{ow} values as well as size and shape of molecules.

Srinivasan and Sarmah (2014) evaluated the sorption potential and transport behavior of Sulfamethoxazole (SMO), Sulfachloropyridazine (SCP), Sulfamethazine (SM) and a bromide tracer (Br^-) in undisturbed soil column collected from dairy farming regions of North Island of New Zealand. All the Sulfaonamides have recorded high mobility and are potential surface and groundwater contaminants. Significant difference was noticed between estimated model and batch sorption experiments.

Marin-Benito et al. (2014) evaluated the efficacy of three pesticide transport models such as PEARL, MACRO and PRZM to describe mobility of S- metachlor and Mesotrione in an irrigated maize field at Toulouse area in France. The models were parameterized and compared with field, laboratory data and pedo-transfer functions. The studies revealed that PRZM model was not able to simulate water transport in soil profile, whereas PEARL and MACRO have properly simulated water dynamics. Among the two herbicides tested, Mesotrione loss by leaching was higher than the simulated values.

Pesticide leaching assessment programme to evaluate the leaching risk posted by pesticides and degradation products to avoid unaccepTable influence on groundwater was conducted by Danish scientists. Twelve-year's results were created on long term leaching of degradation products of pesticides applied on potato crops cultivated in sand and loam during various seasons. Comparison of pesticide detection frequency in water from installations in the variably saturated and saturated zones provided a good indication of the hydraulic contact between the zones and quality of water in variably saturated zone could serve as early warning in the trends in water quality in the saturated zone or surface waters (Rosenbom et al. 2015).

A study was conducted to determine the combined effect of the capillary barrier and soil layer slope on the transport of water, bromide and nanoparticles through an unsaturated soil in a lysimeter (1 x 1x 1.6 m^3). The results showed that with the effect of capillary barrier, water accumulated at the interface of the two materials. The sloped structure affects flow in distinction with the structure with zero slopes. The study also helped in better understanding of the effect of capillary barrier on nanoparticle transfer in an unsaturated heterogeneous soil (Predelus et al. 2015).

Pullan et al. (2016) developed an integrated model for pesticide transport for predicting diffuse-source pesticide concentrations in surface waters used for drinking water supply. The computational efficiency of the model established that, most of the soil parameters can be derived from soil property and can be used for rapid prediction of multiple surface water resources.

Pesticide transport and fate of five pesticides (Atrazine, S- metochlor, Imazaquin, Sulfometuron, Imidachloprid and Trifloxystrobin) in tropical soil at different temperature regimes was investigated by Dusek et al. (2015) through an undisturbed soil column of tropical Oxisol. A laboratory soil column experiment was also conducted for uncertainty analysis. The experimental data indicated the significant non-conservative behavior of bromide tracer in pesticide transport studies. All pesticides were found to be relatively mobile and less persistent, except Imidacloprid.

Sorption and leaching studies of Endosulphan and Chlorpyriphos in an uncultivated plot at central-western region of Brazil was conducted. The results revealed that field dissipation of Chlorpyriphos and Endosulphan was more rapid than reported in temperate climates. Further, the residues of Endosulphan and Chlorpyriphos were detected in percolated water. The leaching loss and run off of Endosulphan were 0.0013 and 1.04% of the applied amount (Dores et al. 2016).

Excess irrigation and unreasonable pesticide application causes potential threat to aquatic environments. A study conducted to explore the transport and fate of Triadimefon in subsurface environment of winter wheat field in China revealed that Triadimefon concentration in surface soil layer was directly affected by pesticide application and irrigation. The soil pesticide levels at different pesticide and irrigation modes showed considerable differences (Wu et al. 2017).

Mobility of Ethofumesate and Terbutrynin a soil of five low cost organic sorbents and two types of organo-clays modified with octadecyltrimethylammonium were studied under saturated flow conditions. The effect of organic sorbents incorporated as barriers in soil columns increased the retention and decreased the leaching of herbicides. Significant inverse correlation was found between the leached quantity and sorption coefficients of Ethofumesate with organic residues (Marin-Benito et al. 2018).

Similarly studies are being attempted worldwide on the sorption of various agro chemicals in soil components. Investigations by Gaillardon (1996) on the sorption of Diuron and Isoproturon in clay loam for nine weeks showed 70% adsorption of Diuron within a day. The concentration of Diuron and Isoproturon in soil solution has decreased to 50% and 38% respectively for two weeks, however, equilibration of sorption process required about one month period. The partition coefficient values of soil and soil solution were increased for 75-125% and 29-67% for Diuron and Isoproturon. High soil moisture enhanced the rate of sorption of both herbicides and hence moisture content in soil is noted to be an important factor in sorption process of pesticides.

Brusseau et al. (1991) reported that the process responsible for non-equilibrium sorption of hydrophobic organic chemicals (HOCs) by natural sorbents were comparable to rate data obtained from system, wherein rate limited sorption was caused by specific sorbate – sorbent interactions. The solute transport related to diffusive mass transfer conceptual models retarded intra particle diffusions and intra-organic matter diffusion. The analyses provide strong evidence that intra-organic matter diffusion was responsible for thenon-equilibrium sorption exhibited by soil column.

The adsorption and mobility of Diazinon in 25 soils having different physico-chemical properties were analysed (Arienzo et al. 1994). The results indicated that organic matter (OM) content above 2% in the soil was the most influential parameter on Diazinon adsorption by soil. The adsorption of pesticide in soil having OM below 2% was influenced by silt and clay content of the soil. The Diazinon was immobile in soil, with high OM content.

The fundamental role in the transport, reactivity and bioavailability of organic pollutants in soil column was related to the organic matter fraction of soil (Pignatello 1998). A new concept of soil organic matter, which functions as dual- mode (dissolution-hole-filling) sorbent has been emerged. The nano-porous structure of SOM was related to CO_2 adsorption at 273 K. The reduced bioavailability of contaminants was due to the sorption in the hole-filling domain with low desorption rates.

Among the various correlations on partition coefficient between the organic carbon/water partition coefficient, Koc, and other molecular properties, the most preferred approach was to correlate with octanol and organic carbon, *ie*, the quantity log (Koc/Kow) for estimating the partitioning of hydrophobic chemicals. This approach was found to be simplest and easy (Seth et al. 1999).

Studies on the potential contributions of clays and soil organic matter (SOM) to pesticide retention on soils were carried out by measuring the sorption of seven pesticides (4,6-dinitro-o-cresol, Carbaryl, Diuron, Atrazine, Dochlobenil, Parathion and Biphenyl) on K-saturated reference smectite clay (SWy-2) and SOM, on unit mass basis. The results revealed that K-SWy-2 clay was more effective sorbent than SOM for 4, 6–dinitro – o – cresol(DNOC), Dichlobenil and Carbaryl of the seven pesticides evaluated of which, DNOC sorbed to the greater extent (Sheng et al. 2001).

Spark and Swift (2002) examined the sorption behavior of pesticides such as Atrazine, 2,4-D, Paraquat and Isoproturon in solid and dissolved organic matter fractions, mineral composition and ionic strength of soil. The studies revealed that the sorption behavior of Atrazine, Paraquat and Isoproturon was controlled by solid state soil components. The study had also emphasized the significance of solid state organic fractions and clay minerals on the sorption of pesticides.

A review on theoretical aspects, measurements, uses, its limitation and reliability were evaluated in detail (Wauchope et al. 2002). Environmental fate and behavior of pesticides were described by the soil sorption coefficient Kd and the soil organic matter coefficient Koc of pesticides. These factors were directly related to the strength of sorption of pesticides to the soil and other geo-sorbent surfaces at the water /solid interface and in turn affect the environmental mobility and persistence of these chemicals.

Sorption kinetics, degradation and isotherm measurements were carried out in Bentazone for different times. Bentazone mineralization varied from 2.1% in sandy soil and 14% in clay soil after 160 days of incubation. The extracTable quantity of Bentazone become lower and a greater number of desorption series was needed to extract completely. A small amount of Bentazone was extracTable by water even after 160 days. The quantity of bound residues of Bentazone was enhanced to 65% in clay soil (Boivin et al. 2004).

Pesticide sorption kinetics in soil is controlled by their diffusion into soil aggregates and microscopic sorbent particles. Adsorption of pesticides like Azoxystrobin, Chlorotoluron and Cyanazine in dispersed soil was dependent on intra particle sorption and diffusion. Adsorption and desorption processes were reversible and explained by pore diffusion into aggregates with effective diffusion coefficients. Intra-particle diffusion has not contributed to sorption in the aggregate. Apparent hysteresis on desorption was explained by non-attainment of equilibrium during the sorption studies (van Beinum et al. 2005).

Brown et al. (2005) studied the sorption of pesticide in soil and the diffusion processes in soil aggregates and microscopic sorbent particles. The adsorption on dispersed soil was due to intra particle sorption and diffusion. He also reported that adsorption and desorption were reversible and intra particle diffusion has not contributed to sorption in the aggregates on time scale.

Rates of degradation of seven organophosphate nematicides and insecticides in different soils indicated that degradation of Fenamiphos and Chlorpyriphos were accelerated by cross-enhanced process. Fumigation has completely inhibited the degradation of pesticides in soils (Singh et al. 2005).

Burauel and BaBmann (2005) conducted experiments on spatio-temporal perspective of organic carbon dynamics to find out Natural Organic Matter (NOM) in soil and resultant CO_2 production and formation of organic carbon pools of different stabilities. The humification products were responsible for binding and remobilization of pesticides in soil.

Bound residues of pesticides are tightly bound to soil organic matter and become unavailable. Simple model of organic matter turn over suggested the release of individual compounds, which will be very slow and closely depend on soil organic matter breakdown. Even though single addition of individual compounds are suiTable for sustainable environmental solution, long term significance of bound residues formed from multiple addition of a number of compounds are to be evaluated extensively for risk assessment procedures employed for environmental protection (Barraclough et al. 2005).

Sorption studies using batch method was conducted for thirteen agricultural soil samples and five pesticides. The adsorption of pesticide on soil was in the order of Trifluralin>>2,4-D>Isoproturon>Atrazine>> Bentazone. Adsorption of Atrazine, Isoproturon and Trifluralin were Bentazonecorrelated to soil organic matter content and that of Bentazone was governed by soil pH. Adsorbed pesticide molecules were released into aqueous solution, which was in the order of >>Atrazine>Isoproturon>2, 4-D>>Trifluralin (Boivin et al. 2005).

Even though chemical composition of soil organic matter (SOM) significantly influenced sorption of pesticides and other pollutants, *in situ* determination of their molecular structure was difficult (Ahmad et al. 2006). Substantial variations were revealed by the study on molecular components of SOM in 24 soils from various agro-ecological regions using ^{13}C NMR. The sorption per unit mass of organic carbon (K*oc*) was significantly influenced by molecular nature of Carbaryl, Phosalone and organic matter in the soil. The sorption of Carbaryl and Phosalone were positively correlated with lignin and charcoal contents in soil, whereas aliphatic carbohydrate and protein contents negatively correlated with the K*oc*.

Degradation and sorption of six acidic and four basic pesticides were studied in nine temperate soils (Kah et al. 2007). The results indicated that there were marked differences in their ability to degrade the different pesticides. There was a positive influence on the degradation of pesticides with soil organic carbon. Positive relationship was obtained in sorption and rate of degradation of Metsulfuron-methyl, Pirimicarb and all other acidic insecticides studied.

Field aging immobilizes and reduces pollutants and their toxicity and enhances the accumulation and holds the risk of slow release. Ciglasch et al. (2008) studied the aging of six insecticides such as isomers of Endosulphan, Chlorpyriphos, Malathion, Dimethoate and Mevinphos in tropical fruit orchard under natural weather conditions. The degree of aging was related to hydrophobicity of insecticides and was most pronounced for Endosulphan. The aging of Chlorpyriphos remained constant and decreased. The different dynamics, aging mechanisms, Koc(app) and MAR were noticed for all insecticides.

A laboratory study on the persistence of α and β isomers of endosulphan in three different soils of Kerala at three concentration levels were carried out (George et al. 2009). The persistence of Endosulphan was maximum in laterite soil, followed by sandy loam and red loam. The half-life of α – isomer was lower than β-isomer in all the three soils.

Batch equilibrium and degradation studies of Imidacloprid, a Neonicotinoid insecticide revealed that Imidacloprid was weakly sorbed and persisted with a half-life of 1 to 2.6 years. It also had the potential to leach below the root zone after the soil-drench applications (Levia et al. 2015). The leaching potential of pollutants to groundwater over large areas was studied for complex vadose zone models. The revised model was consistent with the analytical and numerical models. This model can be widely used for intrinsic groundwater vulnerability assessment to contamination by pesticides.

There are also reports on the uptake, solubility, degradation, removal, etc. of a wide range of agrochemicals from various domains of the environment.

A study conducted to investigate the potential uptake of soil bound ^{14}C residues by oat plants revealed that soil-bound ^{14}C residues were adsorbed by oat plants grown in an organic soil treated with ^{14}C –ring labeled Prometryn. Among the different plant parts analysed, the root contained more ^{14}C residues than shoots. In plant tissue, majority of extracTable ^{14}C residues was in the form of conjugates. ^{14}C unextracTable residues were lower in roots. A major portion of bound ^{14}C residues in plant tissues was associated with lignin (Khan 1980).

Chlou et al. (1987), evaluated the water solubility enhancement of p,p’ - DDT, 2,4,5,2’,5’-PCB and 2,4,4’-PCB by dissolved organic matter in acidic water, natural humic extract and commercial humic acids. The partition coefficient (Kdoc) calculated on dissolved organic carbon basis indicated that enhancement effect on solubility varied with the molecular composition of the aquatic humic materials.

Starner et al. (1999) measured the degradation rates of six pesticides in water samples collected from Sacramento River, California, during April to August, 1996. The pesticide tested wereCarbaryl, Malathion, Atrazine, Simazine, Methidathion and Diazinon. Carbaryl and Malathion were degraded rapidly; Atrazine and Simazine were sTable for all conditions.

Alexander (2000) reviewed the aging of organic environmental pollutants in nature. He reported that biodegradation and bioremediation by microorganisms could reduce the bioavailability of contaminants. The lack of suiTable methods for extraction of DDT, Dieldrin, Heptachlor and other poly chlorinated biphenyl pollutants resulted in over estimation of the contaminants.

Rodriguez-Campos et al. (2014) reviewed the potential of earthworms to accelerate removal of organic contaminants from soil. The survival of earthworms and removal of contaminants from soil were possible at lower concentrations of contaminants like pesticides, herbicides, poly cyclic aromatic hydrocarbons (PAHs) polychlorinated biphenyls (PCBs) and crude oil. The removal of contaminants was due to the activity of microorganisms in their digestive track and adsorption of pollutants by casts.

Rojas et al. (2015) studied the sorption and desorption of Chlorfenvinphos, Chlorpyrifos, Simazineand Trifluralinon sunflower seed shells, rice husk, composted sewage sludge and an agricultural soil. Physicochemical characteristics of the surface of organic matter could have great influence on the adsorption of pesticides. Chlorpyrifos and Trifluralin showed fastest sorption kinetics and capacities when sorbed in all organic waste. Hence organic residues can be used as effective adsorbent for removing pesticides because of their high absorption capacity.

Though much of studies are reported worldwide on the persistence and fate of agrochemicals in various agro ecosystems, both *invitro* and *invivo*, studies pertaining to the impacts of pesticides concerning cardamom ecosystems is less. This has necessitated the present study with the objective of assessing the leaching and dissipation pattern of pesticides like Chlorpyriphos and Quinalphos in cardamom growing soils of Kerala, under controlled conditions.

MATERIALS AND METHODS

Soil samples for soil column and batch experiments were collected from an ideal cardamom plantation in zone B (Santhanpara Village of Udumbanchola Taluk of Idukki District), which lies in between zone A and C. Soil samples required for experimentation was collected from a depth of 15 cm. These were then brought to laboratory; air dried under shade and ground and sifted using a 2 mm mesh sieve (Gaillardon 1996; Fenoll 2011; Marin-Benito et al. 2018; Menon et al. 2004).

Estimation of soil biota

The total microbial population associated with the soil sample was determined using serial dilution and plate method on specific media as per Hirte (1969).

For the estimation of soil biota, homogenized soil sample was spread on a paper to remove plant materials, air dried, sifted with 2 mm mesh sieves and stored at 4 ^{0}C until processing.

Soil suspension was prepared by transferring 10.0 g of soil into 100 mL sterile distilled water and mixed in a rotary shaking machine (260 rpm) for homogenization for 30minutes. The soil suspension was then diluted from 10^{-1} to 10^{-6} times. From each dilution, 10 mL aliquot was transferred to petri dishes containing the following culture media.

1. Nutrient agar medium: for total bacteria
2. Potato dextrose agar medium: for fungi
3. Potato dextrose agar medium modified by the addition of chloramphenicol @ 0.3 g/L: for Trichoderma.

These were then incubated at 25 ^{0}C for 7 days. After this period, the number of colony forming units per 100 g of dry soil (CFU) was calculated.

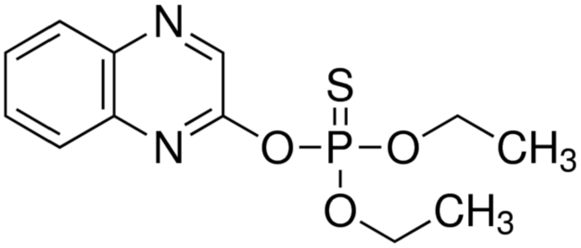
Soil column studies

An unsaturated flow study was conducted using hand packed soil column prepared as per OECD guidelines (2004) for testing of chemicals. For this, a cylindrical glass column having 5cm diameter and 60 cm length was employed (Plate 3). The lower end of the glass column was fitted with a perforated stainless steel plate to retain soil particles and connected to a plexi glass funnel to drain and collect the leachate in an amber coloured bottle. All these arrangements were put vertically by metallic stand and clamps. The column was first packed with one cm layer of prewashed quartz sand and then added untreated air dried and sieved soil up to a height of 50cm. The soil was added to the column in small portions with a spoon and tapped slowly with a gentle vibration until the top of the soil would not sink further. About 1.0 kg soil was used for filling each hand packed column. After packing four such columns, the soil was pre wetted with distilled water and allowed to equilibrate and let excess drain off by gravity.

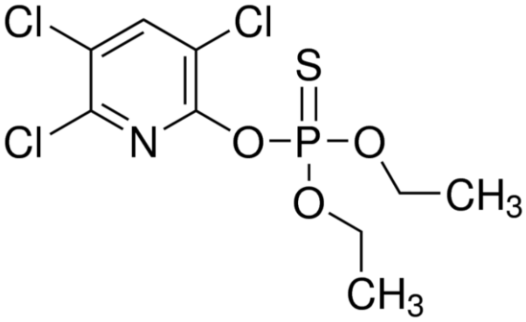
Soil samples used for column studies were initially analysed for soil texture, pH (1:2.5), conductivity and organic carbon, following standard methods (Jackson, 1973). In order to express the final result on dry weight basis, moisture content of all soil segments were determined using gravimetric method.

Ekalux 25 EC and Tricel 20 EC, which are commercial formulations of Quinalphos (*O,O-Diethyl O-quinoxalin-2-yl phosphorothioate*) and Chlorpyriphos (*O,O-Diethyl O-(3,5,6-trichloro-2-pyridyl) phosphorothioate*) (figure.4) respectively, were taken for the study. These pesticides are generally sprayed for the management of trips and borer in various stages of cardamom cultivation. The purity of these commercial formulations was determined using gas chromatograph by serial dilutions (figure.5). The quantity of Chlorpyriphos (drenching of 0.04% a.i. ha^{-1}) and Quinalphos (spraying of 0.025% a.i. ha^{-1}) as recommended in the package of practices for cardamom cultivation (Spices Board of India, 2001) were calculated and applied (4760µg Chlorpyriphos and 525 µg Quinalphos as recommended dose) to the top of each column using calibrated micropipette. The measured quantity of pesticide formulations taken for the study was mixed with 1 g of prewashed and dried quartz sand. For ensuring better distribution of chemicals, the quartz sand containing respective pesticides were applied to the top of the soil column using spatula and kept for equilibration for 2 h. An artificial rain equivalent to 20 mm, which corresponds to the mean precipitation per day of the area under cardamom plantation, was applied slowly to three of the soil columns using separatory funnels fitted at the top of the glass column, for a period of 30 days. The fourth soil column was equipped with a facility for unsaturated flow with 0.01M $CaCl_2$ solution, as described in OECD guidelines (Fenoll et al. 2011). One column without pesticide application was kept as control. All the four arrangements were covered with aluminium foil to avoid photochemical degradation of molecules under observation. After 20 days of such artificial irrigation using distilled water, the two treated soil columns was once again added with recommended dose of Quinalphos and Chlorpyriphos to study the effect of leaching and dissipation of the test chemicals under repeated application in the field. As in early case, subsequent to second round of pesticide application, the same column was again irrigated for 30 days. Leachate collected daily from each column was stored individually in amber coloured glass bottles and kept at 4 ^{0}C. After 30 days, all soil columns, except the columns which received repeated application of pesticides, were allowed to drain off by gravity. Soil column which was treated twice was taken out 30 days after the second application. In field condition, when farmers lose control over root grub/thrips, there will be repeated application of these chemicals.

Figure.4. Chemical structure of (a) Quinalphos, (b) Chlorpyriphos

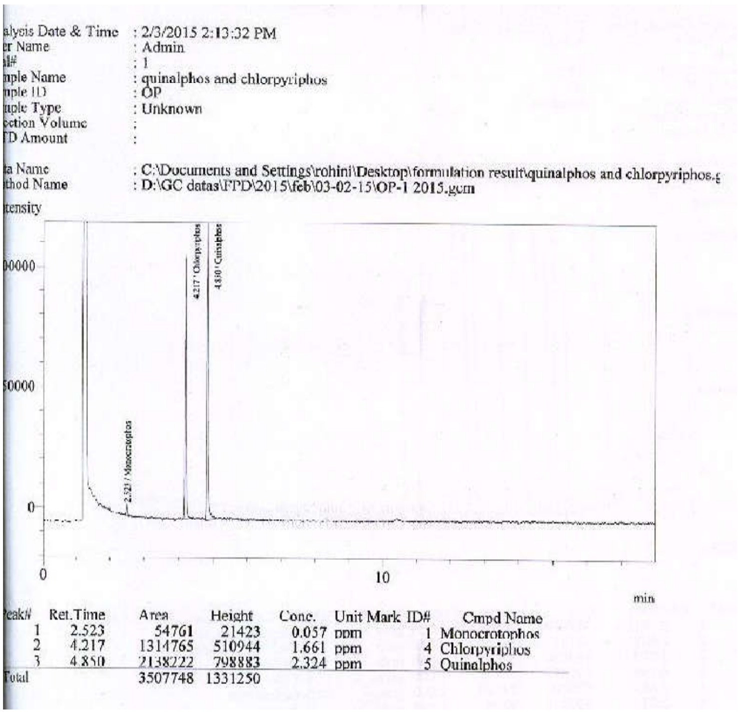


(a)



(b)

Figure.5. Chromatogram of commercial pesticides taken for column studies



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eak#	Ret.Time	Area	Height	Conc.	Unit	Mark	ID#	Cmpd Name
1	2.523	54761	21423	0.057	ppm		1	Monocrotophos
2	4.217	1314765	510944	1.661	ppm		4	Chlorpyriphos
3	4.850	2138222	798883	2.324	ppm		5	Quinalphos
Total		3507748	1331250					

PLATE 3

Schematic Representation of Soil Column Experiment

The soil columns, after stipulated time, were pulled out and cut into 10 segments at 5 cm apart. The soil segments were analysed for soil moisture content using gravimetric method and pesticide residues was extracted (Kumari et al. 2008) using multi residue method and estimated using gas chromatograph equipped with FPD. The pooled leachate from each soil columns were also analysed for pesticide residues using GC –FPD method.

Sorption studies (Batch method)

Soil samples collected for column experiments were taken for sorption studies. A schematic representation of experiment carried out is depicted in plate 4. 100 g of soil sample was treated with 6% hydrogen peroxide and kept overnight for complete oxidation of the organic matter. After frothing was over, the residual particles were dried over a water bath and finally in a hot air oven at 110 ^{0}C for 5h to evaporate all moisture from the soil. Similarly, oxidised soil was prepared from another 100 g soil by oxidizing with 6% hydrogen peroxide and kept overnight for complete oxidation of the organic matter. After frothing was over, it was mixed thoroughly and kept undisturbed for half an hour and decanted the supernatant soil solution. The supernatant solution was dried over water bath and finally in a hot air oven. After drying soil, oxidized soil was powdered using mortar and pestle and passed through 0.5 mm sieve for sorption studies.

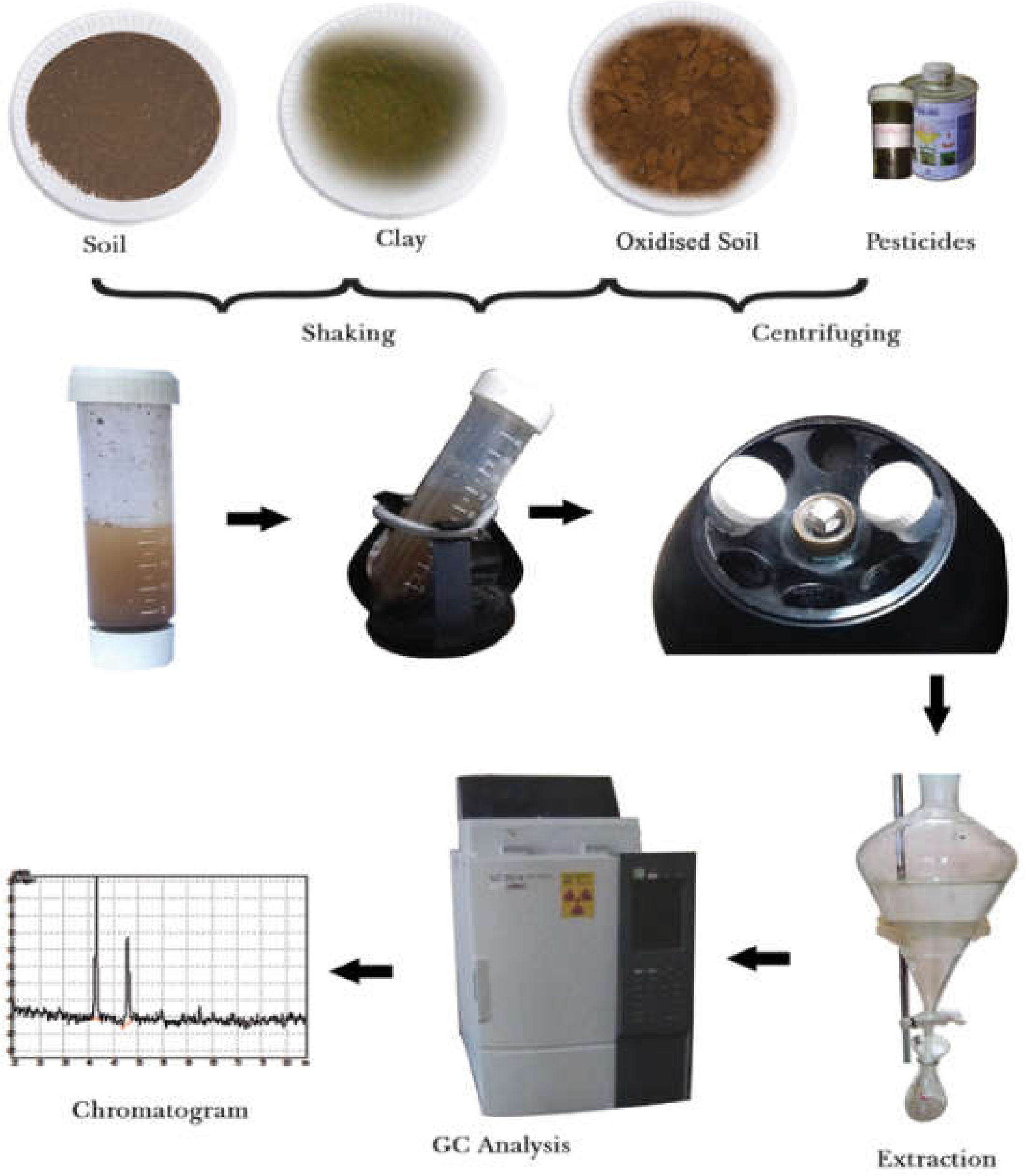
Tricel and Ekaux, the commercial formulations of Chlorpyriphos and Quinalphos used in column studies, were also used as the source of pesticides in sorption studies. Their purity was estimated using Gas Chromatography by serial dilutions. Tricel contained 166,000 µg/mL of Chlorpyriphos and Ekalux had 233,000 µg/mL of Quinalphos. The concentration calculated for Chlorpyriphos in soil drenching was5 µg/mL and for foliar application of Quinalphos was 0.5 µg/mL. In order to avoid error during pesticide transfer to soil and other adsorbents, following concentrations were applied using calibrated micropipette.

Treatments	Chlorpyriphos		Quinalphos	
	(µg)	(ng)	(µg)	(ng)
C1	0.830	830	1.165	1165
C2	1.660	1660	2.330	2330
C3	4.980	4980	4.660	4660

Exactly 1.0 g soil sample was transferred to 50 mL polypropylene centrifuging tube with lid. Each dilution was replicated thrice. The estimated quantity of commercial formulations of Chlorpyriphos and Quinalphos were added and mixed thoroughly in a vortex mixer under closed condition. After 10 minutes, the lid was opened and 25 mL deionised water was added separately to each centrifuging tube. The tubes were shaken with rotary agitator (60 rpm) for 6 hrs at 25 ^{0}C. After agitation, the centrifuging tubes were taken and centrifuged at 5000 rpm for 30 min. Then, the supernatant solution was decanted carefully into a glass bottle, analyzed for pesticide residues as per extraction method for multi residue (Kumari et al. 2008). Desorption experiments were conducted immediately after the sorption experiment. To the centrifuging tube containing residual soil, 25 mL of deionized water was added again and shaken for 6 h as per the above procedure and centrifuged. The supernatant was analysed separately for estimating desorbed pesticide residue from various adsorbents (Kumari et al. 2008). After extraction of residues, the final solution was made up to 1 mL using iso-octane and injected in GC-FPD.

PLATE 4

Adsorption/ desorption studies



Temperature regime of GC

Pesticide concentrations were measured using Shimadzu GLC 2014 equipped with Flame Photometric detector and a RESTEK 30 m x 0.25 mm RTX-5 fused silica capillary column with 0.25 μm film of Phenyldimethylpolysiloxane. The injector was kept at 290 ^{0}C throughout the analysis within a split ratio of 1:10.The column head pressure of carrier gas, nitrogen was maintained at 169.7 kPa. The oven temperature was initially maintained at 200 ^{0}C for 1 min and then increased to 290 ^{0}C at 10 ^{0}C for 1 min, and held at 290 ^{0}C for 15 min. Pesticide residue (μg/g) in soil and water were calculated as per George et al. (2013). Further the soil extract was analysed using GC-MS (Shimadzu QP 2010S) in scan mode under identical temperature and pressure regime of GC.

RESULTS AND DISCUSSION

Cardamom is a high value spice crop, cultivated mostly in Idukki district of Kerala. In recent times, lot of unsystematic practices are followed in these plantation systems, which include application of over concentrated spray solutions, application during off seasons as well as other unscientific prophylactic measures. Quinalphos is one of the most widely used systemic pesticides for the management of various insect pests such as cardamom thrips and shoot/panicle/capsule borers (George et al. 2013; Mohanan, 2006). Quinalphos is also used for the management of various insect pests such as mealy bugs, scale insects and rice pests (George et al. 2013). Chlorpyriphos is another pesticide used for the control of root grub. These agrochemicals, apart from the target, undergo adsorption, retention, dissipation or leaching in associated environments, which may lead to serious health effects. Hence their mobilization needs to be monitored periodically to evaluate their presence and persistence in associated environments. Solute transport of pesticides in such systems can be systematically studied by diverse methods like in situ / ex situ lysimeters, adsorption kinetics in various soil components or by isotopic studies using radioactive tracers.

The present study has been carried out to assess the leaching and dissipation pattern together with the sorption characteristics of Chlorpyriphos and Quinalphos in cardamom growing soils from Idukki district of Kerala under controlled laboratory conditions. The study has been carried out during March-July 2015.The physico-chemical and biological properties of soil taken for both column studies and sorption experiments are depicted in Table 19. It is noted that the acidic soils (4.97) from the study sites were of sandy clay loam type, belongs to Pampadumpara series (sand 41.7%, silt 12.86% and clay 36.43%) having electrical conductivity 0.387±0.38, cation exchange capacity 18.72±1.53 meq/100g soil and high organic matter content (5.5%). Generally, for annual fertilizer recommendation for cardamom, organic carbon content above 2% in soil plough layer is considered as high and accordingly the quantity of nitrogenous fertilizer will be reduced for better and sustainable yield. The soil was porous and had particle density of 2.76 ± 0.52 and maximum water holding capacity of 66.5 ± 8.96. The pore space and volume of expansion of the soil was high due to greater quantity of organic matter content. Soil used for the leaching studies was quantitatively analysed for soil microbial population (Gil et al.2009) and found that it is rich in soil beneficial microorganisms like bacteria, fungi and Trichoderma.

Similarly soil moisture content of each 5cm layer of soil column after unsaturated flow studies for 30 days was determined as per Handa et al. (1999). Even though the soil column was maintained at field capacity, soil moisture content was found to be different in each 5 cm layers (Table 20). Soil water content in each layer was taken to express the final quantity of Chlorpyriphos and Quinalphos, uniformly on dry weight basis. None of the pesticides used in the experiment were detected in leachate and in any of the 5 cm soil layers of the column kept as control (R_0).

Table 19.Results of the physico-chemical and biological properties of soil taken for soil column studies.

Sl. No	Parameters	Results
1	pH	4.97 ±0.09
2	Moisture content (%)	12.21±1.38
3	Organic Carbon content (%)	3.2 ±0.35
4	Bulk density (%)	1.14 ±0.07
5	Particle density (%)	2.76 ±0.52
6	Maximum water holding capacity (%)	66.5 ±8.96
7	Pore space	63.42 ±5.35
8	Volume of expansion	6.45± 2.3
9	Cation Exchange capacity(meq per 100 g soil)	18.72± 1.53
10	Electrical conductivity (dS/cm)	0.387±0.038
11	Sand (%)	38.78± 2.54
12	Silt (%)	8.92± 3.79
13	Clay (%)	35.45± 3.27
14	Total Bacteria (CFU per100g)	$124x10^5$
15	Pseudomonas	$3x10^5$
16	Total Fungus	$34x10^5$
17	Trichoderma	$1x10^5$

Table 20.Soil moisture content (%) in various layers of soil column before extraction.

Column depth (cm)	Control (R_0) (DW)	Recommended dose (R_1) (DW)	Double the recommended dose (R_2) (DW)	Recommended dose (R_3) (0.01M $CaCl_2$)
0-5	22.41	20.58	18.58	19.67
5-10	21.14	16.17	20.97	20.31
10-15	24.71	17.0	21.4	21.70
15-20	23.06	16.93	23.45	22.93
20-25	23.52	16.55	27.07	23.70
25-30	25.22	15.83	28.09	24.77
30-35	25.99	15.89	27.55	25.80
35-40	26.28	17.06	28.09	26.89
40-45	28.72	16.44	25.24	28.66
45-50	27.06	14.99	26.92	28.44

Distribution of Chlorpyriphos in soil column

Soil column studies were carried out as per standard procedures cited in materials and methods, and depicted in plate 3. The residues of Chlorpyriphos extracted from each layer of soil column are presented in Table 21.

Table .21. Residues of Chlorpyriphos in various layers of soil column on dry weight basis

Column depth (cm)	Relative concentration of Chlorpyriphos (C/C_0) in soil layers		
	Recommended dose (R_1) (DW)	Double the recommended dose (R_2) (DW)	Recommended dose (R_3) (0.01M $CaCl_2$)
0-5	0.4334	0.4381	0.0738
5-10	0.0032	0.0079	0.0108
10-15	0.0006	0.0006	0.0003
15-20	0.0005	0.0001	0.0003
20-25	0.0004	0.0003	0.0001
25-30	0.0003	0.0001	0
30-35	0.0002	0.0001	0
35-40	0.0003	0.0002	0
40-45	0.0003	0.0001	0
45-50	0.0002	0.0002	0

While analysing results, residues of Chlorpyriphos were detected in all 5 cm soil segments in column experiments, which were treated with recommended dose of Chlorpyriphos and simulated with 20 mm rain for 30 days. The soil column, which was treated with recommended dose of Chlorpyriphos (R_1) and leached with distilled water, had retained 43% of total Chlorpyriphos applied in soil column. Moreover, the top 5 cm layer of soil column retained about 99% of the total quantity of extracTable Chlorpyriphos detected in whole soil. There was a drastic decline in the concentration of

Chlorpyriphos content from down the 10 cm layer. The relative concentrations of extracTable residue of Chlorpyriphos from the first 5 cm soil segment to others were also reduced. Pesticide leaching from soil has been reported to be decreasing with increasing time in lysimeter studies on leaching of pesticides like Azoxystrobin, Chlorotoluron, Cyanazine and Bentazone at an irrigation interval of 1, 3, 7, 14 and 28 days. The decline in the amount of pesticide in leachate is related to more strongly sorbed pesticides (van Beinum et al. 2006). Similar results were obtained in leaching experiments of Chlorotoluron, Isoproturon and Triasulfuron. Rapid decline in leached loads of Chlorotoluron and Isoproturon from the site of application was noticed by Renaud et al. (2004).The residue of Diuron was found in 0-20 cm soil layer in undisturbed field lysimeter in Gharb area, Morocco (Imache et al. 2009). High soil moisture content enhanced rate of sorption of Diuron and Isoproturon in clay loam and therefore moisture content in soil is a key factor in sorption process of pesticides (Gaillardon, 1996). Similarly, in the present study, where recommended dose of chemical was applied and eluted using distilled water, Chlorpyriphos was dissipated more than 50% within a month and remaining portion of applied chemical was retained in top 5 cm layer of soil column.

The second column which received double the recommended dose of pesticides (R_2) also retained similar quantity of extracTable Chlorpyriphos in top 5 cm layer of soil column as in the case of R_1. Irrespective of applied concentration, the relative concentration (C/C_0) of Chlorpyriphos in both the soil columns, which received simulated rain events with distilled water, was the same. This is adding to the apprehension of repeated application of Chlorpyriphos through soil drenching in cardamom plantations of Idukki district, which would contribute much on the persistence of this pesticide in the soil concerning this agro-ecosystem. These results show light on the influence of water flow and excess application of pesticides on mobility of

Chlorpyriphos. Thus with respect to Chlorpyriphos, under unsaturated flow regime, the trend of leaching of applied chemical to groundwater sources are limited.

Conductivity observed for soil–0.01M $CaCl_2$ (1:5) solution (R_3) was 1.794 dS/cm, whereas that of soil water solution was only 0.387 dS/cm. There was a fivefold decrease in total extracTable Chlorpyriphos residue in soil column treated with 0.01 M $CaCl_2$ than other two. In lower layers of 0.01 M $CaCl_2$ leached column, the relative concentration of Chlorpyriphos has also diminished from top to bottom. Thus factors such as stability, low water solubility and strong adsorption of Chlorpyriphos to soil particles might have significantly influenced in decreasing their leaching potential (Chishti et al. 2013; Babu et al. 2011). In the present study, it was evident that since leaching with distilled water was mimicking precipitation, there was less possibility of leaching of Chlorpyriphos from ploughed layers to ground water sources in the agro ecosystems having cardamom cultivation.

Distribution of Quinalphos in soil column

After analyzing the residue of Quinalphos in soil, the ratio of residue in each 5 cm layer to initially applied concentration was determined and presented in Table 22.

Table 22.Residue of Quinalphos in various layers of soil column on dry weight basis.

Column depth (cm)	Relative concentration (C/C_0) of Quinalphos in soil layers		
	Recommended dose (R_1) (DW)	Double the recommended dose (R_2) (DW)	Recommended dose (R_3) (0.01M $CaCl_2$)
0-5	0.1384	0.14	0.0321
5-10	0.0229	0.005	0.0057
10-15	0.0189	0.004	0.0006
15-20	0.0272	0.003	0
20-25	0.0209	0.004	0
25-30	0.0243	0.002	0
30-35	0.0212	0.001	0
35-40	0.0218	0.002	0
40-45	0.0222	0.003	0
45-50	0.0149	0.002	0

While analyzing the pattern of distribution of residues Quinalphos, it could be observed thatthe concentration of the residue was more in the lower portion of the soil column. The ratio of residue to applied level (C/C_0) was appeared to be similar, irrespective of initial concentration. Quinalphos moved vertically in soil column (R_1), proved by its presence in the leachate (0.286 µg/L). The distribution of Quinalphos in different layers of soil column treated with recommended dose of pesticide has ranged from 1.45 µg/g to 0.156 µg/g. The concentration of residue of Quinalphos was doubled (2.939 µg/g) when doubled the initial level. The relative concentration of Quinalphos in top soil layer remained same (0.14) in both concentrations. Quinalphos was also proved as mobile molecule as it was detected in all layers of soil column. The reduction in relative concentration of Quinalphos in double dose could be attributed to the dissipation of Quinalphos in soil due to aging. Quinalphos is proved as more mobile than Chlorpyriphos, the leaching pattern and relative concentration of their residue were different from Chlorpyriphos.

Residues of Quinalphos were detected in all the 5 cm layers of soil column, irrespective of the initial concentration, which indicated that the mobility of Quinalphos is primarily dependent on the chemical property of the solute. The presence of Quinalphos in the leachate also emphasizes this hypothesis. Moreover the interaction of pesticides and soil particles may also vary with solute molecules. Even though Quinalphos is quite a popular pesticide for the control of insect pests of cardamom, ecologically this pesticide causes damage to water bodies due to its mobility to sub-soil layers. The mobility of Imazosulfuron labeled with carbon-14 in lysimeters showed that Imazosulfuron was present in leachate and the main portion of ^{14}C was detected in the 30 cm soil layer (Mikata et al. 2003). Similarly Trifloxystrobin has been reported to have very high potential to leach and most of the applied pesticide had persisted in 80cm depth of topsoil, 16 weeks after application (Dusek et al. 2009).

Further, the soil column irrigated with 0.01M $CaCl_2$ (R_3) showed one forth less extracTable Quinalphos (0.337µg/g) in top layer and its concentration has become BDL beyond15cm. The dissipation of Chlorpyriphos and Quinalphos in soil column treated with $CaCl_2$was 92.6% and 96.8% respectively, whereas those of water treated column were 86% and 56%. Similar results were reported for Sulcotrione and Atrazine in surface (0-5cm) layer of soil column after 15 days of application (Cherrier et al. 2005). Faster dissipation of pesticides under the influence of calcium ions attributes to the ionic interaction between the organic pollutants and calcium ions.

Dissipation affects pesticides that can be extracted by $CaCl_2$ solution (Ciglasch, et al.2008).

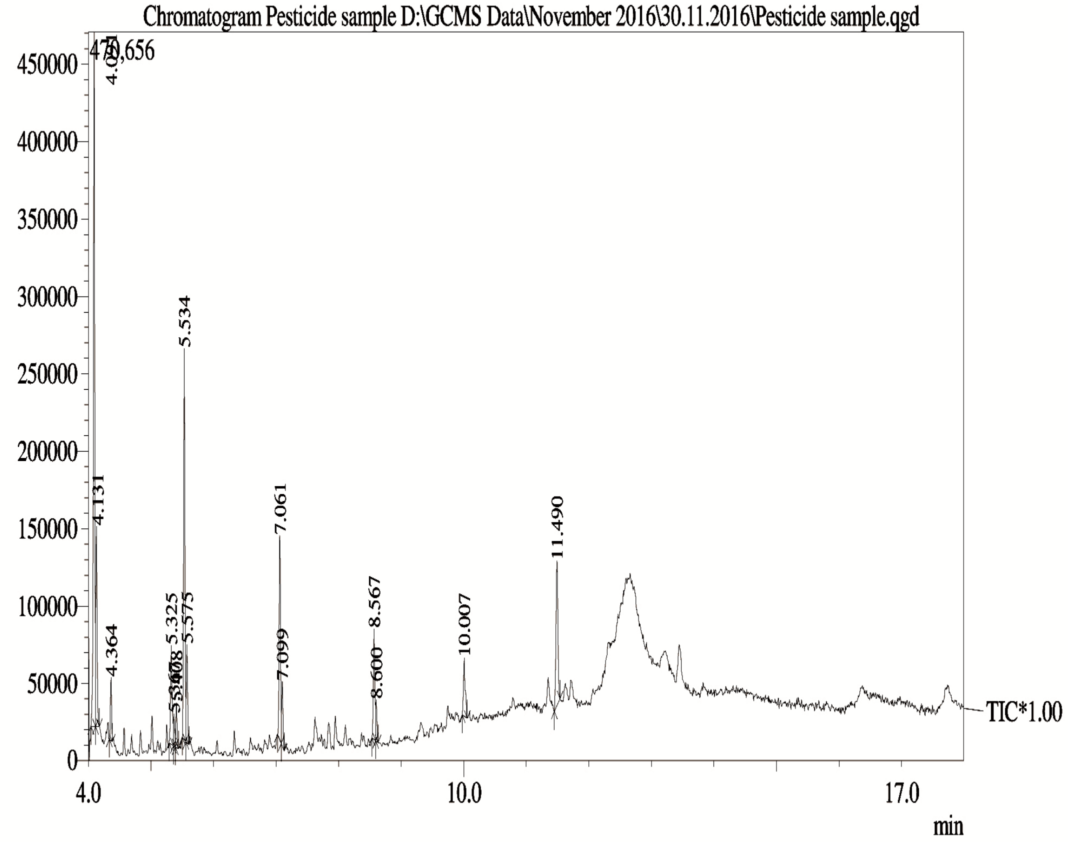
Organic matter fraction of soil influences the transport, reactivity and bioavailability of organic pollutants in soil column (Pignatello, 1998). The nano porous structure of SOM is related to the sorption in the hole-filling domain with low desorption rates. Further, studies of Spark and Swift (2002) revealed the sorption behavior of pesticides such as Atrazine, 2,4-D, Paraquat and Isoproturon in dissolved organic matter fractions, mineral composition and ionic strength of soil. The studies revealed that the sorption behavior of Atrazine, Paraquat and Isoproturon were controlled by solid state soil components. Organic sorbents proved a significant effect on mobility of herbicides like Ethofumemesate and Terbutryn under controlled conditions (Marin-Benito et al. 2018). The study also emphasized the significance of solid state organic fractions and clay minerals on the sorption of pesticides. High order heterogeneity of soil particles and various organic components may also have accelerated the degradation and formation of bound residues of applied chemicals. The present study also highlights immobilization/ degradation of pesticides in the presence of $CaCl_{2,}$ which might be due to the ionic interaction of calcium and organic pollutant as well as retention of organic molecules entrapped in holes.

Electrical conductivity recorded for soil – 0.01 M $CaCl_2$ solutions as recommended in OECD guidelines were higher than that of soil– water solution. The faster dissipation and unavailability of extracTable pesticide residues attributed to the faster hydrolysis at high ionic strength of the eluent. The adsorption-desorption studies conducted with various pesticides showed that more pesticide was desorbed by deionized water than by 1N $CaCl_{2\,,}$which indicates that the mechanism of adsorption is cation exchange of colloid surface (Carringer et al. 1975). FYMalone or in combination with microbial consortium has reduced the residue of Lindane cropped with rice and maize (Bhatia et al. 2012). Sorption on clay minerals is important because it can result in decomposition of certain pesticides (Liu et al. 2000).

GC-MS analysis of the soil extract for pesticide residue in scan mode showed about 14 major compounds (Figure.6). Among these compounds, the second peak at the retention time of 4.13 was a complex of iron and Tricarbonyl [N-(Phenyl-2-Pyridinyl Methylene) Benzamine-N, N]. The pyridinyl ion in this complex might have been evolved from the degradation of Chlorpyriphos. This could be attributed to effective charge transfer between the adsorbed insecticide species and ferric ions from clay particles, which is evidenced from the iron complex detected in the soil extract of the column studies. The high quality of ferric ion in non-tronite and montmorillonite as compared to hectorite could have acted as the efficient energy acceptor for the photostabilisation of adsorbed species (El-Nahhal et al. 2001). Similarly, slight lower rate of photo-degradation was detected for Quinalphos adsorbed on palygorskite than kaolinite in acceptance of the previous view.

Similarly adsorption and desorption studies were conducted in the soils collected from Santhanpara of Idukki District. Soil and different soil components such as clay and organic matter oxidized soil were used to evaluate the sorption behavior in different concentrations of Chlorpyriphos and Quinalphos using batch and equilibration method (Handa et al. 1999) as described in Plate 4. The concentration of each pesticide in solid phase was calculated from aqueous phase and then processed and analysed using statistical method –ANOVA.

Figure 6 GC-MS data of soil extract



Peak Report TIC

Peak#	R.Time	Area	Area%	Height	Height%	Name	Base m/z
1	4.091	659642	30.52	448508	30.86	1-Heneicosanol	57.05
2	4.131	161554	7.47	129545	8.91	IRON, TRICARBONYL[N-(PHENYL-2-PYRIDINYLMETHYLENE)BENZENAMINE-N,N']	57.10
3	4.364	52958	2.45	41253	2.84	Cyclopropanecarboxylic acid, 1-hydroxy-, (2,6-di-t-butyl-4-methylphenyl) ester	57.05
4	5.325	113006	5.23	63995	4.40	Disulfide, di-tert-dodecyl	57.05
5	5.367	22719	1.05	20722	1.43	Heptane, 3,4-dimethyl-	57.05
6	5.408	35084	1.62	28852	1.99	Oxalic acid, allyl octadecyl ester	57.05
7	5.534	347478	16.08	252697	17.39	n-Tetracosanol-1	57.05
8	5.575	83906	3.88	63637	4.38	OCTADECANE	57.05
9	7.061	202776	9.38	132375	9.11	1-Heptacosanol	57.05
10	7.099	53388	2.47	41641	2.87	OCTADECANE	57.10
11	8.567	118081	5.46	71850	4.94	n-Heptadecanol-1	97.10
12	8.600	26637	1.23	26467	1.82	1-BROMO-8-METHYLHEXACOSANE	57.05
13	10.007	78616	3.64	38035	2.62	(TRANS)-2-NONADECENE	57.05
14	11.490	205560	9.51	93763	6.45	4-Norcaren-2-one, 1,3,5-tri-tert-butyl-3-[(1,3,5-tri-tert-butyl-4-oxo-2,5-cyclohexadien-1-yl)methyl]-	57.05
		2161405	100.00	1453340	100.00		

Sorption studies of Chlorpyriphos

The results of the adsorption and desorption studies of Chlorpyriphos at various concentrations in soil taken for column studies and its components are presented in Table 23.

Table 23. Adsorption - desorption characteristics of Chlorpyriphos in various soil components.

Soil components	ADSORPTION			DESORPTION		
	CI	C2	C3	C1	C2	C3
SOIL	821.31	1635.87	4768.19	62.1	70.03	67.2
CLAY	799.14	1646.41	4894.42	39.39	63.58	29.4
OXIDISED SOIL	749.03	1616.22	4919.24	34.0	2.94	10.15
CD (0.05)	30.81	9.35	80.5	26.13	62.04	23.84

Previous results showed that the physical and chemical properties of soil influences sorption of pesticide in environment. Soil sorption characteristics of each pesticide vary with chemical nature of pesticide molecules and soil characteristics, which determines their fate in soil. The sorption studies of Chlorpyriphos at different concentrations were carried out in various soil adsorbents. Three different concentrations employed in sorption experiment were 0.83, 1.66 and 4.98 µg/g. The lowest concentration applied was 0.83 µg/g. The adsorbent used were soil, clay fraction and oxidized soil. Statistical analysis showed no significant variation in adsorption of Chlorpyriphos with respect to soil and clay fraction. The adsorption between soil and oxidized soil was highly significant ($P < 0.05$).

Adsorption of Chlorpyriphos in soil and clay has showed significant variation ($P < 0.05$), when the concentration of the adsorbate was doubled. A similar pattern was also observed when the concentration of adsorbate has reached the concentration equivalent to that of recommended dose of the pesticide in soil drenching. These results imply that the adsorption of Chlorpyriphos was dependent on the concentration of the adsorbent. In the adsorption of Chlorpyriphos, at controlled condition, there might have certain limiting factors in the adsorption of all molecules of adsorbate to different adsorbents. Moreover, adsorption of Chlorpyriphos was linear to all adsorbents.

Compared to the quantity of adsorption of Chlorpyriphos, desorption was very meager from all adsorbents tested. Desorption of Chlorpyriphos in soil and clay was significant at lower concentration. Desorption of Chlorpyriphos in soil and clay was not significant at higher concentrations. Desorption has significant ($P < 0.05$) effect in soil and oxidized soil in all the concentrations studied. Irrespective of the concentration of adsorbate, desorption of Chlorpyriphos was observed more in soil followed by clay.

While analysing the physical and chemical properties, soil taken for sorption studies was acidic and rich in organic matter (5.5%). Soil physical properties such as bulk density (1.14%), particle density (2.76%), pore space and water holding capacity were favorable for downward percolation of water. The soil physical characteristics showed that it is well drained soil with reasonable content of clay (35%) and organic matter. In soil environment, sorption interaction of pesticides are through mineral or organic, or both. Most chemically active soil components are clay minerals and soil organic matter (Sheng et al. 2001).Particle size of clay minerals are <0.002mm and colloidal in nature. These clay minerals possess high charge density and surface area. Principally clay minerals are alumino- silicates; also contain secondary minerals such as iron oxide (Fe_2O_3), aluminium oxide (Al_2O_3), calcium carbonate ($CaCO_3$) and other salts (Lal and Shukla, 2004). Kaolinite type clay minerals are 2:1 silicate layer and have high surface area and cation exchange capacity. In moist conditions, clay minerals form electrostatic double layer and thus a Zeta potential will be created due to the potential gradient developed between the stationery phase (soil particles) and mobile diffuse layer (water). Electro-kinetic force between clay minerals, dissolved ions (pesticide ions) and water molecules undergo chemical reaction and form bound residues(Barraclough et al. 2005), which has been proved by the formation of complex detected in soil extract of column studies and analyzed using GC-MS. The Iron, Tricarbonyl [N-(Phenyl-2- Pyridinylmethyene) Benzenamine-N,N’] detected from soil column studies proves the formation of new degradation compounds of Chlorpyriphos during downward leaching and natural soil conditions (Bindumol and Harilal, 2017). The incubation studies on Bentazone showed that extracTable quantity of Bentazone become lower and a greater number of desorption series was needed for its release. The quantity of bound residues of Bentazone was enhanced to 65% in clay soil (Boivin et al. 2004). The humification products are associated for binding and remobilization of pesticides in soil (Burauel and BaBmann, 2005). The environmental fate of Chlorpyriphos (O,O-diethyl O-(3,5,6-trichloro–2-pyridyl) phosphorothioate has been studied in various conditions and 3, 5, 6-trichloro-2-pyridinol (TCP) as the major degradation product (Tomlin, 1977; Singh et al. 2005) and 3,5,6-trichloro-2-methoxy-pyridine (Roberts and Hutson, 1999). The identification of new degradation product throws light in to the dissipation bahaviour of Chlorpyriphos in cardamom soils. Highly significant effect on adsorption of Chlorpyriphos in soil and soil components at lower concentration ($P < 0.05$), implies that there is sufficient space available with clay minerals to form linkage with Chlorpyriphos. Thus sorption behavoiur of Chlorpyriphos supports probability in leaching of pesticide molecules to aquatic bodies in the absence of sufficient adsorbents such as clay minerals and organic materials and at favourable environmental conditions.

Sorption studies on Quinalphos

The results of sorption studies conducted with Quinalphos and various soil components were presented in Table 24.

Table 24. Adsorption/ Desorption characteristics of Quinalphos in various soil components

Soil components	ADSORPTION			DESORPTION		
	CI	C2	C3	C1	C2	C3
SOIL	1165.7	2318.7	4541.51	27.56	44.76	29.83
CLAY	1157.7	2321.05	4617.28	14.82	28.75	15.01
OXIDISED SOIL	1136.5	2307.32	4620.59	34	2.94	10.15
CD (0.05)	15.89	8.08	55.35	16.59	21.19	16.73

Sorption study was conducted on Quinalphos (O, O-diethyl O-quinoxalin-2-yl phosphorothioate) at different concentrations *viz,* 1.25, 2.5 and 5.0 µg/g. Even though the recommended dosage of Quinalphos for spraying is 0.5µg/g, to avoid difficulty in extraction of very low concentration of residue from adsorbents and to enhance precision and accuracy, comparatively higher concentration was attempted in the present study.

Adsorption of Quinalphos was significant effect in soil and clay ($P < 0.05$) only at 5.0 µg, where as in soil and oxidized soil adsorption varies in all the three concentrations. The less variation in adsorption of Quinalphos in soil and clay indicated that clay minerals have little effect on binding of Quinalphos molecules to alumino-silicats and other compounds in soil. In the case of oxidized soil, all organic matter was completely removed by oxidation, adsorption was affected significantly. Here, organic matter in any form has influence on the adsorption of Quinalphos residues to soil environment. The parent molecule and identified environmental degradation product of Quinalphos, 2-hydroxyquinoxaline (Tomlin, 1997) was bound to soil organic matter than clays. It was supported by more residues detected in soil than oxidized soil in both lower concentrations. Pesticides can interact with soluble organic matter in soil and the extent and nature of this interaction depends on molecular weight and polarity of pesticide (Spark and Swift, 2002).Partition coefficient on dissolved organic carbon for organic solutes with water varies with the molecular composition of the aquatic humic materials (Chlou et al. 1987). This also supported the findings of increase in the concentration of dissolved organic matter enhancing the mobility of Atrazine (Gao et al. 1997) and DDT (Kan and Thomson, 1990). Adsorption of 2, 4-D on humic acid is suggested to involve physical adsorption perhaps by van der Waals forces and hydrophobic bonding in initial diffusion step and physisorption process (Spark and Swift, 2002). Similar theory can be applicable in adsorption behavior of Quinalphos as it leaches vertically to 50cm length of soil column in natural water flow conditions (Bindumol and Harilal, 2017).

Desorption of Quinalphos in soil, clay and oxidized soil did not varied significantly. Desorption of Atrazine from organic matter was less than from clays (Harris and Warren, 1964). In the present study, enhanced desorption in soil was noted in organic matter than clay or oxidized soil, which can be due to multiple sorption process on organic matter and clays as well as other soil xenobiotic pathways.

SUMMARY AND CONCLUSION

Soil column experiments were conducted to evaluate the dissipation and leachability of Chlorpyriphos and Quinalphos in cardamom growing sandy clay loam from CHR. Different concentrations of Chlorpyriphos and Quinalphos as well as different eluents were tested. The results revealed that at recommended concentration of Chlorpyriphos, the leaching character was limited to top 5 cm layer. More than 50% of Chlorpyriphos has been dissipated within a month. Even though Chlorpyriphos could leach up to 50 cm down the soil column, it was not detected in leachate. Calcium chloride solution (0.01M) could be able to dissipate Chlorpyriphos than distilled water. The dissipation of Chlorpyriphos and Quinalphos in soil column treated with $CaCl_2$was 92.6% and 96.8% respectively, whereas those of water treated column were 86% and 56%. Chlorpyriphos could able to react with soil iron and form new degradation product under laboratory condition. The results of the study revealed that, Quianalphos was more mobile than Chlorpyriphos and was detected in leachate of the soil column study. The concentration of Quianalphos in lower portions of soil column was more than Chlorpyriphos. From this study it could be concluded that, Quinalphos is a potential groundwater contaminant than Chlorpyriphos in cardamom ecosystems.

The adsorption and desorption characteristics of Chlorpyriphos at different concentrations were carried out in various soil adsorbents such as soil, clay fraction and oxidized soil. Three different concentrations employed in sorption experiment were 0.83, 1.66 and 4.98 μg/g. Statistical analysis showed no significant variation in adsorption of Chlorpyriphos with respect to soil and clay fraction. The adsorption between soil and oxidized soil as well as soil and clay were highly significant ($P<0.05$) even at higher concentration. Adsorption of Chlorpyriphos was linear to all adsorbents. Hence adsorption of

Chlorpyriphos was dependent on the concentration of the adsorbent. Thus, adsorption of Chlorpyriphos in soil and its components were due to chemical interaction.

Adsorption and desorption studies have been conducted for Quinalphos at different concentrations *viz,* 1.25, 2.5 and 5.0 µg/g. Adsorption of Quinalphos was significant in soil and clay ($P<0.05$) only at 5.0 µg. Adsorption of Quinalphos in soil and oxidized soil varies in all the three concentrations. The less deviation in adsorption of Quinalphos in soil and clay indicated that clay minerals have little effect on binding of Quinalphos molecules to alumino-silicats and other compounds in soil. Thus Quinalphos is bound to soil organic matter through physisorption. Significant variation was not observed in desorption of Quinalphos from soil, clay and oxidized soil.

BINDUMOL G.P. “STUDIES ON LEACHING AND DISSIPATION OF COMMONLY USED ORGANOPHOSPHORUS PESTICIDES IN CARDAMOM ECOSYSTEMS OF IDUKKI DISTRICT, KERALA”. THESIS. DEPARTMENT OF BOTANY, UNIVERSITY OF CALICUT, 2018.

GENERAL SUMMARY AND CONCLUSION

Kerala, the land of spices is cultivating cardamom, pepper, ginger, turmeric and tree spices for domestic and export purposes. Among them, Cardamom is cultivated mainly in Cardamom Hill Reserve of Idukki district. Since cardamom is a high value spice crop, sufficient care is taken at all stages of plant protection and production. Changes in weather pattern and modern agricultural practices to boost productivity like over application of fertilizers and pesticides have created many ecological issues in these agro ecosystems.

The present study envisages the spatio-temporal assessment of commonly used organophosphosrus pesticides like Chlorpyriphos and Quinalphos in cardamom plantations of Kerala. The major objectives outlined are:

- To evaluate the extent of Chlorpyriphos and Quinalphos in soil and aquatic environments associated with cardamom ecosystems of Kerala.
- To study the leaching and dissipation pattern of Chlorpyriphos and Quinalphos in cardamom growing soils under controlled conditions.
- To evaluate the sorption characteristics of Chlorpyriphos and Quinalphos in cardamom growing soils of Kerala.

For fulfilling these objectives, seasonal (pre monsoon, monsoon and post monsoon) and zonal (zone A, B and C) variations in the physico-chemical parameters and pesticide residues in soil and water samples from cardamom plantations were studied for a period of one year. Correlation studies were also carried out to elucidate factors in soil/water responsible for the retention of pesticide residues.

From the analytical results of soil samples, it has been noticed that the cardamom growing soils are acidic. Zonal variation was observed in the pH of soil concerning the study area. Zone A samples recorded low and zone C samples recorded high soil pH. Since cardamom plants are very sensitive to soil moisture and humidity, all plantations were irrigated and maintained with adequate soil moisture. Electrical conductivity of zone A samples were higher than that of zone B and C. Electrical conductivity of soil samples reduced during monsoon. Cardamom growing soils were having moderately high organic matter content. Organic matter content was more recorded in zone C samples. Cation exchange capacity of zone B and C have recorded more than zone A.

Soil physical and hydrological properties such as bulk density, particle density, water holding capacity, pore space and volume of expansion were analyzed. Bulk density of zone B samples was higher than zone C and zone A. Bulk density was less during pre-monsoon season. Zonal and seasonal variation was observed in particle density of cardamom growing soils. Zone A samples had more particle density and water holding capacity than other two zones. Zone B samples were having more pore space than zone A and C. Pore space was high during monsoon and least during pre-monsoon.

In general, soil physical attributes such as bulk density and volume of expansion was in the order of zone C > zone B > zone A, whereas particle density and water holding capacity were in the order of zone A > zone B > zone C. During monsoon soil physical characteristics such as particle density, water holding capacity and pore space were highest. Bulk density was more in pre-monsoon and volume of expansion was high during post-monsoon.

As far as texture of soil concerned, zone A soils were low in sand content, followed by zone C and B. Silt content was more in zone C than other two zones. The average clay content in all the three zones was the same. Seasonal and zonal variation was not noticed in clay content.

Apart from elevation and climate, soil physico-chemical properties have great influence on the growth and yield of cardamom. Cardamom productivity is more in zone A due to soil factors like high electrical conductivity, moderately high organic matter, total phosphorus content and cation exchange capacity as well as high water holding capacity and particle density and low bulk density, volume of expansion and sand content. All these factors have influenced positively in the root proliferation and nutrient uptake than other two zones. Further, these factors have also facilitated the sustainable cultivation and production of cardamom.

Similar to soil, water quality parameters were periodically analysed for samples collected from open wells and streams adjoining cardamom ecosystems. This was significant as both water sources are being used for various purposes, including drinking.

Both essential and general water quality parameters such as pH, total dissolved solids, total hardness, calcium, magnesium, sodium, potassium, alkalinity, carbonates, chloride and sulphate of open well and streams were within the drinking water standards stipulated by IS 10500:2012. Seasonal variation was observed in the quality of water bodies. Nitrate –nitrogen was present in well and stream water samples. However their concentration was higher in well water samples. Average Nitrate nitrogen content was less during monsoon.

The residues of Chlorpyriphos and Quinalphos were detected in all soil samples of the cardamom ecosystem in various quantities. There was seasonal variation in the residue of Chlorpyriphos and Quinalphos in soil. Chlorpyriphos was more in pre monsoon season in zone A and B. The residue of Quinalphos was detected in all soil samples throughout the year. Residues of Quinalphos were detected in both water bodies during monsoon and post-monsoon. Quinalphos was mobile than Chlorpyriphos. Residues of Chlorpyriphos and Quinalphos were not significantly correlated to soil physical and chemical attributes such as bulk density, organic matter, cation exchange capacity, total phosphorus and silt content. Zonal and seasonal correlation was observed for Chlorpyriphos and Quinalphos residues with soil clay. Retention and dissipation of Chlorpyriphos and Quinalphos in soil was influenced by soil physical attributes.

Soil column experiments were conducted to evaluate the dissipation and leachability of Chlorpyriphos and Quinalphos in cardamom growing sandy clay loam from CHR. Different concentrations of Chlorpyriphos and Quinalphos as well as different eluents were tested. The results revealed that at recommended concentration of Chlorpyriphos, the leaching character was limited to top 5 cm layer. More than 50% of Chlorpyriphos has been dissipated within a month. Even though Chlorpyriphos could leach up to 50 cm down the soil column, it was not detected in leachate. Calcium chloride solution (0.01M) could be able to dissipate Chlorpyriphos than distilled water. The dissipation of Chlorpyriphos and Quinalphos in soil column treated with $CaCl_2$ was 92.6% and 96.8% respectively, whereas those of water treated column were 86% and 56%. Chlorpyriphos could able to react with soil iron and form new degradation product under laboratory condition. The results of the study revealed that, Quianalphos was more mobile than Chlorpyriphos and was detected in leachate of the soil column study. The concentration of Quianalphos in lower portions of soil column was more than Chlorpyriphos. From this study it could be concluded that, Quinalphos is a potential groundwater contaminant than Chlorpyriphos in cardamom ecosystems.

The adsorption and desorption characteristics of Chlorpyriphos at different concentrations were carried out in various soil adsorbents such as soil, clay fraction and oxidized soil. Three different concentrations employed in sorption experiment were 0.83, 1.66 and 4.98 µg/g. Statistical analysis showed no significant variation in adsorption of Chlorpyriphos with respect to soil and clay fraction. The adsorption between soil and oxidized soil as well as soil and clay were highly significant ($P<0.05$) even at higher concentration. Adsorption of Chlorpyriphos was linear to all adsorbents. Hence adsorption of Chlorpyriphos was dependent on the concentration of the adsorbent. Thus, adsorption of Chlorpyriphos in soil and its components were due to chemical interaction.

Adsorption and desorption studies have been conducted for Quinalphos at different concentrations *viz,* 1.25, 2.5 and 5.0 µg/g. Adsorption of Quinalphos was significant in soil and clay ($P<0.05$) only at 5.0 µg. Adsorption of Quinalphos in soil and oxidized soil varies in all the three concentrations. The less deviation in adsorption of Quinalphos in soil and clay indicated that clay minerals have little effect on binding of Quinalphos molecules to alumino-silicats and other compounds in soil. Thus Quinalphos is bound to soil organic matter through physisorption. Significant variation was not observed in desorption of Quinalphos from soil, clay and oxidized soil.

BINDUMOL G.P. “STUDIES ON LEACHING AND DISSIPATION OF COMMONLY USED ORGANOPHOSPHORUS PESTICIDES IN CARDAMOM ECOSYSTEMS OF IDUKKI DISTRICT, KERALA”. THESIS. DEPARTMENT OF BOTANY, UNIVERSITY OF CALICUT, 2018.

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