DETERMINATION OF PESTICIDE RESIDUES IN CABBAGE AND LADY'S FINGER COLLECTED FROM CUMILLA

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JUNE, 2018

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A Thesis
Submitted to the Department of Agricultural chemistry
Sher-e-Bangla Agricultural University, Dhaka, in partial
fulfillment of the requirements
for the degree
of

MASTER OF SCIENCE
IN
AGRICULTURAL CHEMISTRY

SEMESTER: JANUARY-JUNE, 2018

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CERTIFICATE

This is to certify that the thesis entitled **"DETERMINATION OF PESTICIDE RESIDUES IN CABBAGE AND LADY'S FINGER COLLECTED FROM CUMILLA''** submitted to the Department of Agricultural Chemistry, Faculty of Agriculture, Sher-e-Bangla Agricultural University, Dhaka, in partial fulfillment of the requirements for the degree of **MASTERS OF SCIENCE (M.S.)** in **AGRICULTURAL CHEMISTRY**, embodies the result of a piece of bonafide research work carried out by **AFSAR HOSSAIN**, Registration No. **12-04988** under my supervision and guidance. No part of the thesis has been submitted for any other degree or diploma.

I further certify that any help or source of information, received during the course of this investigation has been duly acknowledged.

June, 2018
Dhaka, Bangladesh

_____

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Dedicated to
My
Beloved Parents

ACKNOWLEDGEMENT

All praises to the **"Almighty Allah"** who enable to complete a piece of research work and prepare this thesis for the degree of Master of Science (M.S.) in Agricultural Chemistry.

Author feels much pleasure to express his gratefulness, sincere appreciation and heartfelt liability to my venerable research supervisor **Dr. Md. Tazul Islam Chowdhury**, **Associate Professor,** Department of Agricultural Chemistry, Sher-e-Bangla Agricultural University, for his scholastic guidance, support, uninterrupted encouragement, valuable suggestions and constructive criticism throughout the study period.

Author also expresses his gratitude and thankful to reverend co-supervisor **Dr. Mohammad Dalower Hossain Prodhan**, Senior Scientific Officer, Pesticide Analytical Laboratory, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipur for his constant inspiration, valuable suggestions, cordial help, heartiest co-operation and supports throughout the study period.

Author also expresses his gratitude and thankful to **Dr. Md. Sirajul Islam Khan** Chairman, Department of Agricultural Chemistry, Sher-e-Bangla Agricultural University, for his scholastic guidance, support, uninterrupted encouragement, valuable suggestions and constructive criticism throughout the study period.

The author would like to express his gratefulness to all teachers of the Department of Agricultural chemistry for their constructive suggestions and advice during the study period.

The author desires to express his cordial thanks to Md. Kamal Hossain and other office staffs of Pesticide Analytical Laboratory, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipur for their assistance and co-operation during the period of research work.

The author deeply acknowledges the profound dedication to his beloved Father, Mother, Sister and Brother for their moral support, steadfast encouragement and continuous prayer in all phases of academic pursuit from the beginning to the completion of study successfully.

Finally, the author is deeply indebted to his friends and well-wishers for their kind help, constant inspiration, co-operation and moral support which can never be forgotten.

The Author

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Abstract

A study was conducted to analyze pesticide residues in two common vegetables (cabbage and lady's finger) collected from five local markets of Cumilla district during January 2018 to May 2018. The collected samples were carried to the Pesticide Analytical Laboratory, Entomology Division of Bangladesh Agricultural Research Institute (BARI), Gazipur on the same sampling day. The collected samples were analyzed using Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) extraction technique and Gas Chromatography (GC) coupled with Flame Thermionic Detector (FTD) for the determination of pesticide residues in 40 samples of cabbage and 40 samples of lady's finger. Among the 40 analyzed samples of cabbage, 5 samples (12.5% of the total number of samples) contained residues of dimethoate and diazinon where 1 sample contained multiple residues and 5 samples contained residue above the maximum residue limits (MRLs). Out of 40 samples of lady's finger, 4 samples (10% of the total number of samples) contained residues of dimethoate and diazinon, where 2 samples contained multiple residues and 4 sample contained pesticide residues above MRL. This study reflects the overall scenario of pesticide residue remain in cabbage and lady's finger collected from local markets of Cumilla district, which will help the consumer to be aware of their health and safety.

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LIST OF ABBREVIATIONS

ADI	Acceptable Daily Intake
AOAC	Association of Analytical Communities
BARI	Bangladesh Agricultural Research Institute
CCD	Central Composite Design
CSN	Committee for Standardization
DAS	Days After Spraying
DLLME	Dispersive Liquid–Liquid Microextraction
d-SPE	dispersive solid phase extraction
ECD	Electron Capture Detector
et al	*et alibi* (and others)
etc	*et cetra* (and so on)
EU	European Union
FAO	Food and Agriculture Organization
FTD	Flame Thermionized Detector
GC-MS	Gas Chromatograph-Mass Spectrometry
HPLC	High Performance Liquid Chromatography
HRI	Hazard Risk Index
LC-MS	Liquid Chromatography-Mass Spectrometry
LOD	Limit Of Detection
LOQ	Limit Of Quantifications
MDQ	Minimum Detectable Quantity
MRL	Maximum Residue Limit
PDI	Potential Daily Intake
PSA	Primary Secondary Amine
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
RSM	Response surface methodology
RTL	Retention Time Locked
SAU	Sher-e-Bangla Agricultural University
SBSE	Stir Bar Sorptive Extraction
TOTAD	Through Oven Transfer Adsorption Desorption
UHPLC-MS/MS	Ultra-High-Performance Liquid Chromatography-Tandem Mass Spectrometry
WHO	World Health Organization

Chapter I

Introduction

CHAPTER I

Introduction

Vegetables are one of the most important classes of food item which provide carbohydrate, vitamins, minerals, fiber and other kinds of important element. It helps to maintain our healthy life. Vegetable provide many kinds of vitamins, which helps invasion improvement (Omale and Ugwu, 2011). Vegetables fulfill nutritional requirements and they also provide antioxidants that can be extracted from bark, stalk, fruits, roots, flowers, fruit peels and seeds. These antioxidants prevent human diseases like cardiac disorders, inflammation, neuro degenerative diseases, diabetes mellitus and cancer (Kalpna *et al*., 2011).

Cabbage (*Brassica oleracea var. capita*), a highly nutritive exotic vegetable is one of the most consumed vegetables. It is eaten raw in salad or boiled or in stews (Norman, 1992). It is an excellent source of vitamin C and vitamin k. It contains more than 20% of the daily Value (DV) for each of these nutrients per serving (USDA, 2014). It is also a good source of vitamin B6 and folate, protein, carbohydrate, calcium, iron, carotene, thiamin, riboflavin, niacin, as well as vitamin C (De Lanny, 1992). Purple cabbage contains anthocyanin which are potential for anti-carcinogenic properties. It is also a good source indole-3-carbinol, a chemical substance under basic research for its possible properties (Wu *et al*., 2010). Besides this, cabbage has been used historically as a medicinal herb for a variety of health benefits. The Ancient Greeks used cabbage as a laxative (Wright, 2001). The enormous benefits of cabbage to the growth and development of humans, but production of the crop are beset with insect pests attack. Pest infestation normally causes reduction in market value and in some cases total crop failure.

Lady's finger (*Abelmoschus esculentus* L.) is the most important summer vegetable. It belongs to family Malvaceae. Lady's finger plant grows in tropical, subtropical and warm temperate regions around the world. It is cultivated during spring to rainy season. Lady's finger's pods are eaten as a fresh fruit and it provides a healthy source of iron, minerals, iodine, carbohydrates, protein and vitamins (Benchasri, 2012). Under hot and humid conditions causes heavy economic losses to vegetable growers by insects and pest infestation (Benson, 2004, Lantican, 2000). This crop is attacked by over 37 insect pests throughout its life cycle from germination till harvest. The major insect pest of okra is leafhopper, *Amrasca*

biguttulabiguttula (Ishida), spotted ballworms Earias spp. Jassids and thrips, white fly etc. (Nayyar *et al.,* 1996). Leafhopper and shoot and fruit borer had caused 32.06 to 40.84% and 50% respectively (Singh *et al.,* 1994). For control of these pests a number of insecticides are recommended (Anonymous, 2008).

Devloping country like Bangladesh, agriculture plays a key role in the economic performance of the country, contribution to gross domestric production (GDP, 20.01%) foreign exchange earnings and providing employment (47.3%) to a large segments of the population, particularly for the poor (BER, 2010). But damage caused by the pests to agricultural crops , yield often decline below subsistance level which have adverse effects on the national economy. To control the pest and insect, pesticide application in Bangladesh has increased manifold from 758 metric tons in 1960, and 3028 metric tons in 1980 to over 19000 metric tons in 2000 (Kabir *et al.,* 2008) and in 2008, the applied amount of pesticide is 48690 metric tons. Insecticide are account for 76% of the pesticides applied in year (BBS, 2009).

Most of the farmers of Bangladsh spray insecticide and a little amount of herbicides, fungicides, acaricides and rodenticides in the form of granules, liquid and powder in the vegetable crop fields (Gain *et al.,* 1998).). It has been reported that bangladeshi farmers use 18 fungicides, 2 rodenticides in their crops field (Sattar *et al.,* 1985). Depending upon the invading pests in Bangladesh, most of pesticide are cypermethrin, dichlorvos, malathion, carbofuran, mancozeb and diazinon. . Besides, farmers use many restricted or banned pestcide list under international agreements (NOVIB, 1993). Farmers use pesticides in their vegetable and crop fields from harmful pests, particularly in vegetables such as cabbage, lady's finger, potato, tomato, eggplant, cauliflower and cucumber and these vegetables are affected more than rice or other crops. According to PAB, (Pesticides Association of Bangladesh) 2002-2003, use of pesticide for growing vegetables was six times higher than for the rice (1.12 kg/ha for vegetables while it was only 0.20 kg/ha in rice). Per crop cycle, farmers spray on their vegetables 17-150 times (Ali *et al,* 2002). DAE reported that around 95 percent farmers do not wait for pre-harvesting interval (PHI) after application of pesticides in their crops. (The Daily Prothomalo, July 20 & 21, 2008). Another study reported that pesticides (cypermethrin, diazinon, quinalphos, fenotrothion and malathion) residue is found in number of vegetables such as brinjal, hyacinth bean, cauliflower and yard long bean samples which are collected from farmers' fields and markets of different regions which was above Maximum Residue Limits (MRL) (Rahman *et al.,* 2010).

Farmers and workers of Bangladesh spray pesticides in crop fields without taking any safety measures. As a results they unawarely absorb the toxic items by inhalation and many other different ways. Our farmers spray pesticides without wearing masks, gloves and others proper clothes. Even making spraying pipe clear, they often blow air by mouth. While applying pesticides over 87% farmers use little or no protective measures (Dasgupta *et al.,* 2005). During and after application, pesticides can enter into human body in different ways. The rate of dermal absorption of pesticide residues of different body parts are scalp (3.7%), forehead (4.2%), ear canal (5.4%), abdomen (2.1%), forearm (1.0%), palm (1.3%), genital area (11.8%) and ball of foot (1.6%)(Ogg *et al.,* 2006).

A pesticide which is a modern chemical input and has become established global practice. Pesticides are used to control pests in order to meet the growing demands of vegetable. Pesticides are the poisonous chemical substances which are used in certain circumstances to kill specific target pests (Wassemann, 1972). Insecticides play a major role in the management of these insect pests. Pest control still depends on the use of different groups of pesticides such as organophosphate which causes bad effects on human health (Gajbhiye *et al*., 1985 and Rai *et al*.,1980). WHO reported that an annual three million cases of acute and severe pesticide poisoning worldwide with some 220,000 deaths (WHO, 1990). Pesticide residue refers to the pesticides that may remain on or in food after they are applied to food crops. WHO (2016), define pesticide residue as any substance or mixture of substances in food for man or animals resulting from the use of pesticide and includes any specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance. Pesticide residue is the remaining of pesticide active ingredient, its metabolites or breakdown products present in the environment after its application, spillage or dumping (Dasika *et al.,* 2012). The presence of pesticide residue is a concern for the human consumer as it is a potential harmful effect on other non-target organism than pest and disease (Krikothaile and Spanoghe, 2011).

Oraganophosphates, organochlorine and carbamates and many others pesticide residues affect central and peripheral nervous system by their toxic effects. During adult, childhood or in utero exposure pesticide show long-term or short-term acute or chronic effects and it lead to very chronic nervous disorders like parkinson disease (Keifer *et al.,* 2007). Pesticide also cause leukemia in some children if mothers are expose to pesticide during their pregnancy period. Less than one year old child have seven time more chances of leukemia if they exposed to permethrin pesticide. Children also are caused by leukemia whose mothers are

exposed during pregnancy period. It is reported that time from pregnancy to 11 month they have two times more chances of leukemia if they exposed to pesticides (Ferreira *et al.,* 2009). It also reported that 5 pesticides such as bitertanol, propiconazole, cypermethrin, malathion and terbuthylazine have high level of exposure in the endocrine disruption in human (Rossana *et al.,* 2013). Pesticide use might cause a potential health risk from both occupational and non occupational exposures though it is recognized as important for food production. Different pesticides cause neurotoxicity, endocrine disruption, immune impacts, genotoxicity, mutagenicity and carcenogenesis though consumption of dietary residues. Some people, especially infants and children are more vulnerable than others to pesticide impacts. Infants and children are more susceptible than adults. People with asthma may have severe reactions with organophosphate, carbamate. These pesticide chemical substances are consumed by a human being which is remained in the harvested crops. An experiment was conducted for several studies in Kerela had led to conclude that the direct health effect of pesticide residues entering the human system, though contaminated food is much more serious than the indirect effects though food chain and environment (Babu *et al*., 1996, Methew, 2012).

Pesticide exposure is harmful for both adults and young children and fetus developmental period which are more vulnerable to pesticides because of their weak and inactive immune system. Exposure of fetus in mother womb cause congenital anomalies, genetic diseases onset due to disruption of their DNA development and endocrine disruption side effect seen both during and after birth. For both adults and children, the most harmful effect of pesticides are due to their carcinogenic effects. This type of exposure cause leukemia, bladder, clone, thyroid and brain cancer in exposed childhood and adult persons (Asghar *et al.,* 2016). In human body, very common effects of pesticide residues are nausea, vomiting, blurred vision, coma, difficulty in breathing, deficit hyperactivity disorder, disorder in fetuses and children (EPA, 1999). Many pesticide residues are also known to be contributory factors in several diseases like cancer, heart diseases, Alzeheimer's and Parkinsonism (Khaniki, 2007). WHO reported that an annual three million cases of acute and severe pesticide poisoning worldwide with some 220,000 deaths (WHO, 1990).

Now a day's pesticide residue in food has become a consumer issue and the people have the right to know how much pesticide is incorporated in the food they eat. At present, in Bangladesh many research works on pesticide residues in vegetables and other matrices have been conducted in the pesticide Analytical Laboratory, Entomology Division of Bangladesh

Agricultural Research Institute (BARI), Gazipur (Prodhan *et al*., 2018; Aktar *et al.,* 2017; Rasan 4 *et. al*., 2017; Kabir *et al*., 2007; Islam *et al*., 2014; Kabir *et al*., 2008; Prodhan *et al.,* 2009; Prodhan *et al.,* 2010).

Cumilla district of Bangladesh is very famous for vegetable cultivation and the farmers of Cumilla are using pesticides indiscriminately to control the insect pests of vegetables. So, it is essential to find out the actual scenario of pesticide residues present in vegetables collected from Cumilla district. Keeping this view, the present study was initiated with the following objectives:

Objectives:

- To identify pesticide residues in cabbage and Okra collected from different markets of Cumilla district.
- To quantify the level of detected pesticide residues (mg/Kg) remain in the selected vegetables collected from different markets of Cumilla district.
- To compare whether the level of detected insecticide residues is above the Maximum Residue Limit (MRL) or not.

Chapter II

Review of Literature

CHAPTER II

REVIEW OF LITERATURE

An effort has been made to review the available literatures to extend our knowledge regarding the present status of research and information on pesticide residues remain in different vegetable and food matrices. Available and accessible sources of relevant information have been systematically reviewed and summarized with essential comments as appropriately as possible. Although the review could not be made so comprehensive because of limited scope and facility, it is hoped that most of the relevant information available in and around Bangladesh was collected and reviewed. It is discovered that most of the information on the aspects searched as mentioned above are mostly available from research station, different types of journal and information of farmers' field condition are scanty. However, a significant number of study-reports on pesticide residues in vegetable crops conducted under farmers' field conditions are available. The studies on the quantification of detected insecticides residues below or above the Maximum Residue Limit (MRL) of vegetables in Bangladesh are rarely reported. With this background, the information collected from different sources have been reviewed and presented below:

Hadian *et. al.,* (2019) conducted a study with forty-eight pesticide residues from different chemical structures including organochlorine, organophosphorus, organonitrogen, dicarboximides, strobilurin, triazine, pyrethroids, and other chemical groups. By GC-MS, 85 fruits and vegetables were determined and confirmed. The pesticide was extracted with ethyl-acetate and then the extracts cleaned using high performance gel permeation column chromatography (GPC) and solid phase column (SPE). Between 81 and 136% were the mean recoveries of the pesticides. The reproducibility of the relative standard deviation values was 2.1% and 14.8%. Pesticide residues of fruit were (65.5%) and vegetables (26.7%). The limits of detection and quantification of pesticide residues for the method were ranged from 0.003 to 0.06 μg/g and between 0.01 to 0.1 μg/g respectively. The analyzed samples did not contain residues from the monitored pesticides that were higher than the accepted maximum residue limits (MRLs) as adapted by the FAO/WHO Codex Alimentarius Commission.

Maciej, (2019) developed a modified quick, easy , cheap, efficient, rugged and safe (QuEChERS) method coupled to gas chromatography with electron capture detector (GC-ECD) for simultaneous determination of selected electronegative pesticides in fruits and

vegetables with high water content. In fruit and vegetable crops, the chosen compounds and some of their metabolites have even been found in human urine and some of them are known or suspected carcinogens according to the International Agency for Research of Cancer. In accordance with 'green chemistry' principles, extraction and clean up parameters were optimized, thus the original QuEChERS method was modified to decrease solvent usage. The proposed methodology was validated in terms of selectivity , specificity , linearity , precision and accuracy . For all investigated pesticides, the obtained limits of detection (LODs) ranged from 5.6 $\mu g \cdot kg^{-1}$ to 15 $\mu g \cdot kg^{-1}$ and limits of quantification (LOQs) from17 $\mu g \cdot kg^{-1}$ to 45 $\mu g \cdot kg^{-1}$. The obtained data showed the good reproducibility and stability of the procedure in the testedconcentration range up to 10 $mg \cdot kg^{-1}$, with relative standard deviations (RSDs) lower than 10%. For spiked pear samples, recoveries at LOQ level for each pesticide were from 90% to 107% with RSDs lower than 9.6%. The suitability of the developed procedure was tested on various fruit and vegetable samples available on the market at different seasons.

Hakme *et. al.,* (2018) performed a study on "Analysis of pesticide residues in olive oil and other vegetable oils".Pesticide residue analysis in olive oil presents difficulties due to the high amount of co-eluted compounds resulting in high matrix effect. Different extraction/clean-up methods including gel permeationchromatography, liquid/liquid extraction, solid-phase extraction and other extraction methods areapplied to overcome these difficulties. Recent approaches such as the addition of the freezing-out stepand the application of Enhanced Matrix Removal-Lipid sorbent (EMR-Lipid) are reported. Gas chromatography and liquid chromatography coupled to mass spectrometry are considered the gold standardtechnologies covering a wide scope of pesticides. This review recapitulates the methods most widelyused for the determination of pesticide residues in vegetable oils. As a continuation of previous reviews,the work conducted is an update review of methods from 2006 in thisfield, evaluating their strengthsand limitations. Main analytical parameters of the different extraction procedures and detection methodsare discussed in terms of recoveries, robustness, limit of quantification, and matrix effect.

Liang *et. al*., (2018) performed surveillance of pesticide multi-residues in vegetables. By using gas chromatograph, 420 vegetables samples of 10 different types of fresh vegetables were analyzed for their pesticide multi-residue contents and NY/T 761-2008 pesticide multi-residue screen methods. The pesticide residues that exceeded MRLs of forbidden pesticides found were: carbofuran 0.110 mg/kg (kidney bean) and methamidophos 0.037 /kg (celery),

methamidophos 0.037 mg/kg (tomato), aldicarb 0.013mg/kg (kidney bean) in September 2009, omethoate 2.200 mg/kg (celery) in November 2009, carbofuran 0.052 mg/kg (green pepper) in April 2010, parathion 0.056 mg/kg (celery) and carbofuran 0.030 mg/kg (celery) in July 2010. Also, chlorpyrifos used as unforbidden pesticide was most frequently found above MRL, rape (0.820 mg/ kg) and celery (0.365 mg/kg) in January 2009, celery (0.330 mg/kg) in May 2009, lettuce (0.298 mg/kg) in September 2009, rape (0.910 mg/kg) in April 2010 and lettuce (0.230 mg/kg) in July 2010. In addition, cypermethrin used as unforbidden pesticide was found above MRL only once in rape (1.270 mg/kg) in May 2009 and none of unforbidden pesticides above MRL was found in November 2009 and January 2010. Most of the samples (96%) were up to the national standard.

Ibrahim *et. al*., (2018) conducted a study on "Determination of Organochlorine Pesticide Residues in Pumpkin, Spinach and Sorrel Leaves Grown in Akwanga, Nasarawa State,Nigeria" they collected leafy vegetable samples of pumpkin leaves, spinach leaves, and sorrel leaves were collected from a farm in Akwanga and were tested for the presence of residues of organochlorine pesticides. By using GC/MS, the concentrations of all the pesticide residues in the vegetable samples were determined. Among all the samples organochlorine pesticide p,p'-DDT was detected in pumpkin (0.75 mg/kg), spinach (0.319 mg/kg) and sorrel (0.219 mg/kg). ∂-BHC and ɣ-BHC were detected only in pumpkin leaves (0.359 mg/kg and 0.647 mg/kg respectively). Dieldrin was detected in spinach and sorrel (0.124 mg/kg and 0.053 mg/kg respectively). Endrin was detectedin pumpkin (0.732 mg/kg) and Aldrin in sorrel (0.095 mg/kg). All these values were above the maximum residue limit (MRL) value of the pesticides. Endosulfan II was detected in sorrel (0.306 mg/kg) below the MRL. The pesticide residues found in vegetables were above the maximum residue limits (MRLs) that callfor laws to regulate the use and circulation of such chemicals. Routine monitoring of pesticide residues in this study area is necessary for the prevention,control and reduction of environmental pollution, to minimize health risks.

Hayat *et al*., (2018) conducted a study in the Department of Entomology, University of Sargodha, Sargodha, Pakistan during the year 2015. to evaluate the residual level of insecticides. For the simultaneous screening of roughly 22 insecticides in fruits, vegetables, pollen, nectar and water samples in three zones of Punjab Pakistan, optimized analytical methods gas chromatography–mass spectrometry (GC–MS) and high performance liquid chromatography (HPLC) were adopted. 50 samples (34.96%) were found positive for one or more insecticides, out of total of 143 samples analyzed (59 fruits & vegetables, 36 pollen, 36

nectar and 27 water samples). Fruits and vegetables 24(40.67%), pollen 8(22.22%) and nectar 6(16.66%) and water 18(66.67%) samples were found pesticide residue. therteen insecticides were detected in 27 water-samples of three zones of Punjab (Pakistan) ranging from 0.02 to 0.8 µg/L. Different insecticides (carbosulfan, profenofos, cypermethrin, endosulfan sulfate and chlorpyriphos-methyl) were frequently detected in the fruit and vegetable samples. The results suggest that consumers of Punjab province are exposed to the lower concentrations of insecticides that can cause long-lasting disorders.

Fang *et. al*., (2018) investigated the sources of vegetables consumed by farmers, their perception of pesticide related food safety risks and the behaviors they engage into protect themselves, and explores the implications for the social co-governance (shehui gongzhi) of food safety emphasized by China's recent Food Safety Law. The investigation site is a county in Yunnan Province where vegetable cultivation is the major source of income and livelihood for local farmers. They surveyed 417 farmers and collected 776 vegetable samples from 377 surveyed farmer households and tested them for organophosphate and carbamate pesticide residues using PR-12N Rapid Detection Instrument for Pesticide Residues. The results indicated that farmers know about the risks caused by pesticides used in vegetables and they avoid these risks by consuming vegetables planted in home gardens or private plots that use little or no pesticides. These private plots vegetables had the lowest positive rate of pesticide residues (6.10%), compared with vegetable samples from commercial farmland (13.73%) and markets (12.66%), and the difference was statistically significant ($X2=9.69$, $0.005<P<0.010$). Thisindicate that the efforts of farmers to protect themselves from pesticide-related food safety risks . However, the effect is limited due to the environmental pollution caused by the massive use of pesticides in commercial vegetable growing. But this have a negative impact on the social co-governance of food safety set out in the new Food Safety Law.

Prodhan *et. al.*. (2018) conducted a research on the variability of pesticide residues in eggplant units collected from a field trial and marketplaces in Greece. In total, 120 samples from a trial field and 142 samples from different marketplaces in Thessaloniki, Greece, were collected to estimate the variability of pesticide residues in eggplant units. They were extracted by the QuEChERS method and the residues were determined by LC–MS/MS. For the field samples, the level of estimated cypermethrin and deltamethrin residues were 0.01-0.349 mg/Kg and 0.01-0.097 mg/Kg, respectively; and the unit-to-unit variability factors

(VFs) obtained for cypermethrin and deltamethrin residues were 2.54 and 2.51, respectively. The mean residue levels of both pesticides were higher in the composite samples than in the individual samples. The average VFs for the marketplace samples was 3.89. The eggplant units exposed to pesticides were higher in residues than the non-exposed units.

Prodhan *et. al.*, (2018a) conducted a study to determine the pre harvest interval (PHI) for quinalphos in Eggplant, Cabbage and Yard long bean; malathion in Eggplant, Yard Long bean and Cauliflower; cypermethrin in Tomato and Yard long bean; and diazinon in Eggplant and Yard long bean depending on Maximum Residue Limit (MRL) set by FAO/ WHO. Five supervised field trials were conducted and sprayed with the field dose (2 ml/L of water) of each pesticide except cypermethrin (1 ml/L of water). Samples were collected at 0, 1, 3, 5, 7, 10, 12, 15 and 18 days after spray. The collected samples were analyzed using Gas Chromatography (GC) coupled with Flame Thermionic Detector (FTD) and Electron Capture Detector (ECD) for the determination of pesticide residues. The level of residues were above MRL up to 10 DAS for quinalphos in Cabbage, 7 DAS in Eggplant, 5 DAS in Yard long bean; for malathion 5 DAS in Yard long bean and Eggplant, 7 DAS in cauliflower; for diazinon 5 DAS in Yard long bean and Eggplant; and 3 DAS for cypermethrin in Yard long bean and Tomato. The determined PHI for quinalphos were 12 DAS in Cabbage and 10 DAS in Eggplant and 7 DAS in Yard long bean; For malathion 7 DAS in Yard long bean and Eggplant and 10 DAS in cauliflower; For diazinon 7 DAS in Yard long bean and Eggplant; For cypermethrin 5 DAS in Yard long bean and Tomato.

Prodhan *et. al.*, (2018b) conducted a study to quantify the residue loss of Quinalphos, Diazinon and Fenitrothion from eggplant and Malathion from Yard long bean through washing and cooking procedures. Samples were collected from the Research field of Entomology Division of Bangladesh Agricultural Research Institute (BARI). The samples were analyzed using a simple Gas Chromatographic technique. Washing with water reduced 34% Quinalphos, 28% Diazinon and 41% Fenitrothion and heating with water at 100 ^{0}C reduced 95% Quinalphos, 84% Diazinon and 100% Fenitrothion from eggplant. Washing with water reduced 45% Malathion and heating with water at 100 ^{0}C reduced 100% Malathion from Yard long bean. Effect of O_3 sterilizer in reducing pesticide residues from eggplant was also investigated in this study and found that O_3 sterilizer reduced 79.00% Diazinon and 62.50% Quinalphos while washing with only water reduced 60.50% Diazinon and 40.00% Quinalphos from eggplant.

Prodhan *et. al.*, (2018c) has been developed and validated a simple and efficient multiple organochlorine pesticide residues analytical method using quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction technique and Gas Chromatography coupled with Electron Capture Detector (ECD) for the determination of 19 organochlorine pesticides (Alpha BHC, Delta BHC, Beta BHC, Gama BHC, Heptachlor, Aldrin, Heptachlor Epoxide, Gama Chlordane, Alpha Chlordane, Alpha Endosulfan, 4,4 DDE, Dieldrin, Endrin, 4,4 DDD, Beta Endosulfan, 4,4 DDT, Endrin Aldehyde, Endosulfan sulphate, Methoxychlor, and Endrin Ketone) in shrimp. The method was validated by evaluating the accuracy, precision and linearity limit of detection (LOD) and limit of quantification (LOQ). The average recoveries of the selected pesticides ranged from 84% to 106% with RSDr ≤ 14% in four fortification levels of 0.05, 0.1, 0.2 and 0.3 mg/Kg. The linearity was ≥0.996 for all of the selected pesticides with matrix matched calibration standards. The LOD ranged from 0.003 to 0.009 mg/Kg and the LOQ was 0.05 mg/Kg. This method was applied successfully for the residue analysis of 40 shrimp samples collected from different market places in Bangladesh.

Yolando Pico *et. al*., (2018) performed an experiment to determine pesticide residues in fruits from Saudi Arabia and influence in potential risk associated with exposure. The pesticide residues in fruits were determined by a method for 62 analytes and a wide scope screening method against a database of 500 pesticides. Limits of quantification (LOQs) were from 0.5 to 119 μg kg−1 for the non- and target from 0.5 to 6.3 μg kg−1 for the target method. 30 samples (dates, apples, oranges, tangerines, lemons and grapefruits) were selected due to their high consumption, except lemons and grapefruits that were to cover all citrus fruits. Out of 62 pesticides (organophosphorus, carbamates, pyrethroids, chloroacetanilides, triazines, triazoles, imidazoles, etc.),15 compounds (mostly insecticides and fungicides) were detected by using the target method. 80% of the samples contained at or below maximum residue limits (MRLs),as well as 20% above. Non-target method detected several additional pesticides (cypronil, fludioxonil, boscalid and pyraclostrobin in apples).

Yu-Han Chiu *et. al.,* (2018) conducted research to estimate of pesticide residue intake from fruits and vegetables with urinary concentrations of pesticide biomarkers. A pesticide residue burden score (PRBS) was developed based on a food frequency questionnaire and surveillance data on food that contains pesticide residues to characterize dietary exposure over the past year. Fruit and vegetable (FV) intake was classified as low (PRBS<4) or high (PRBS≥4) pesticide residues for 90 men from the EARTH study. Of them two urine samples per man were analyzed for seven biomarkers of the herbicide 2,4-dichlorophenoxyacetic acid

and organophosphate and pyrethroid insecticides. To analyze the association of the PRBS with urinary concentrations of pesticide biomarkers, they used generalized estimating equations. Though Urinary concentrations of pesticide biomarkers were positively related to high pesticide FV intake, inversely related to low pesticide FV intake. The molar sum of urinary concentrations of pesticide biomarkers was 21% (95% confidence interval (CI): 2%, 44%) higher for each one serving/day increase in high pesticide FV intake, and 10% (95% CI: 1%, 18%) lower for each one serving/day increase in low pesticide FV intake.

Joseph *et. al*., (2018) conducted a study that evaluated the residues of 99 pesticides in 72 samples of 12 agricultural products collected in the region, using QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method extraction, and analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS) and gas chromatography with electron capture detection (GC-ECD). This method was suitable for detecting the targeted compounds: For 81 pesticides by LC-MS/MS, the limit of quantification (LOQ) was between 0.0004 and 0.0537 mg/kg; and for 18 halogenated pesticides by GC-ECD, it ranged from 0.0012 to 0.2180 mg/kg. The samples contain residues of 62 pesticides, including 12 banned compounds . The most prevalent group were insecticides (39.7%) with all the samples containing at least one pesticide. Of them twenty-one pesticides (34.4%) exceeded their European Union MRLs (maximum residue limits) and 22 pesticides (34.4%) were found in all 6 sampling locations. Almost all the samples and sampling sites were found malathion and DDT. Food items that contained the highest rates of residues were chili pepper (23.2%), white pepper (20.2%), kidney beans (17.3%), and soybeans (17.2%). 38% samples cotained residues above MRLs were chili pepper (6.4%) and kidney beans (5.5%) were found to have the most residues above their MRLs. The most critical food commodities were kidney beans, soybeans, chili pepper, and maize. This results presents scientific evidence that investigation into continuous monitoring and good regulation of pesticide usage in Cameroon is needed, and paves the way forhealth risks analysis.

Arain *et. al.,* (2018) conducted a study in order to determine the residual concentration of Chlorpyrifos organophosphorus pesticide in surface water, ground water and vegetables (Okra, potato). Five samples of surface water, ground water and each vegetable were randomly collected from the eight union council (UCs) of tehsil Mehrabpur district. For the extraction and clean-up of pesticide residues, USEPA 3510C and USEPA 3620C the standard analytical methods were used. The Gas Chromatography-Flame Ionization detector (GC-FID) was used to analyse the samples. Results showed that in ground water samples the selected

pesticide residual concentration was not more than MRL (maximum residual limit), the minimum value 6.6µg/L was found in UC2 while maximum was 11.2µg/L in UC5. In vegetable samples the concentration pesticide residues were found in 20% of potato samples and 15% of okra samples were within MRL values and rest were found above MRL. On the other hand, the higher residual concentration was found in surface water samples having minimum and maximum values 43.46 µg/L and 79.7 µg/L, respectively Chlorpyrifos pesticide residue present in surface water and vegetables samples which pose harmful effect to the peoples who depend on these sources of water and food.

Şeyda *et. al.,* (2018) use a gas chromatography-tandem mass spectrometry (GC-MS/MS) which has been widely used in recent years and has high separation power, selectivity and ability to identify pesticides. In this analytical method QuEChERS methodology is used. By this method, 123 pesticide residues as well as their degradation products were quantitatively assayed by GC-MS/MS and method validations in tomatoe, lemon, lettuce, almonds, raisins, honey, green pepper, milk and flour. As potential reference matrixes for the target tomatoe was selected. The steps of concentration and solvent exchange were performed in the resultant extracts for the purpose of improving analytical performance in terms of recovery, precision, linearity, of reducing the amount of coextracts. To identify and quantify the pesticides, Multiple reaction monitoring (MRM) was used. The samples were extracted with 1% acetic acid in acetonitrile, anhydrous magnesium acetate, anhydrous magnesium sulfate and clearing agent. For all pesticides, good linear calibrations with coefficients (R2) ≥0.99 for nearly all of the analytes were obtained. Quantitation limit of most of the pesticides were in the range of 5-10 ng/g, and recovery of the method validationaccuracy parameter was done at two different concentrations 10 ng/g and 50 ng/g were 88.6 -99.7% and CV 1.60 – 14.0%.

Golge *et. al.,* (2018) described levels of 170 pesticide residues in green pepper and cucumber marketed in Turkey. By liquid chromatography coupled to tandem mass spectrometry (LC-MS /MS) total 725 sample of vegetables were analysed for residues of 170 distinct pesticides. The in-house validation data fulfilled the requirements of the European SANTE/11945/2015 Guide line. The limit of quantifications (LOQs) varied from 0.003 to 0.016 mg /kg. Recoveries ranged from 80.5 to 118.2%, within ter-day precisions of 0.7–19% relative standard deviation (RSD). Of them 12.9% of green peppers and 13.5% of cucumbers contained at least one detectable residue which were below the EU legal limits. The Hazard Quotients (HQs) for identified pesticides in green peppers and cucumbers ranged from 0.0003 to 0.0143% ,and from 0.0001 to 0.0103%, respectively for adults. Propamocarb and

chlorpyrifos were the major contributors to hazard index (HI) for green pepper and cucumber. The results indicate that there is no reason to be concerned about cumulative exposure to residues from greenpepper and cucumbers for Turkish population.

Lozano *et. al.,* (2018) determined the multiresidue pesticide analysis of baby foods in full-scan mode by of GC coupled with quadrupole Orbitrap MS . The criteria of determination were studied following SANTE guidelines (retention time, mass accuracy, and ion ratio), comfortably complying with the values established, even at 0.003 mg/kg. Method validation was carried out on 15 selected GC amenable pesticides covered by Commission Directive No. 2006/125/EC in three different baby food matrixes. For all the pesticides assayed, recovery studies were performed at 0.003 and 0.006 mg/kg, with 96% of the cases falling within the 70–120%range and with RSDs <15%. Linearity over 3 orders of magnitude was verified, with residuals <16% and correlation coefficient values >0.995. Generaly, matrix effect values were >100%. The limit of quantification was 0.003 mg/kg for 97% of the cases. The validated method was applied to 20 real baby food samples from Spain and to the European Union Proficiency T est FV-BF01 sample, in which the z-scores obtained were <1, thus demonstrating that this instrumentation has good quantitation capabilities.

Xiaomin *et. al.,* (2018) investigated the concentrations of residues of four groups of pesticides in the People's Republic of China: organophosphorus, carbamate, pyrethroid, and triazine pesticides. By using gas chromatography–tandem mass spectrometry and liquid chromatography tandem mass spectrometry twenty-six pesticides were examined in 2,169 samples of 12 typical vegetables collected from 15 provinces in China. The results showed that 41.9% (908 samples) samples were positive, with 6.1%(133 samples) exceeding the legal limit in China. Fruits and root vegetables showed less positive rates than leafy vegetables. Organophosphorus, carbamate, pyrethroid, and triazine pesticides were found in 1 1.8%, 7.7%, 13.9%, and 10.9% of the samples, respectively. The positive samples, a slight violation rate of 1.9% for the organophosphorus pesticide category exceeded China's maximum residue limits.

Frederick *et. al.,* (2018) conducted the study to assess the level of organochlorine pesticide (OCP) residues in fruits and to determine the potential health risks associated with the exposure to these pesticides. 120 fruits samples (watermelon, pineapple, and banana) were collected from five communities and a local market and analyzed for organochlorine pesticide residues. The results showed that the concentrations ranged from ND (not

detectable)–48.22 ng/g for DDTs, ND–19.03ng/g for HCHs, ND–4.10 ng/g for CHLs, ND–22.84 ng/g for Aldrin, and ND–11.53 ng/g for other OCPs. In watermelon, levels of methoxychlor, Aldrin and gamma-hexachlorocyclohexane (HCH) exceeded the maximum residue limits. Aldrin in watermelon could pose potential toxicity to the consumer revealed by estimated health risk. Estimated averagedaily intake for Aldrin was above the acceptable average daily intake.

Abubakar *et al.,* (2018) developed quick, easy, cheap, effective, rugged and safe technique (QuEChERS) coupled with dispersive solid-phase extraction (dSPE) to overcome the setback challenges experienced by the previous technologies for determination of pesticide residue. Conclusively, the reviewed QuEChERS-dSPE techniques and the recent cleanup modifications justifiably prove to be reliable for routine determination and monitoring the concentration levels of pesticide residues using advanced instruments such as high-performance liquid chromatography, liquid chromatography–mass spectrometry and gas chromatography–mass spectrometry.

Willem *et. al*., (2018) developed augmentative biological control (ABC), in which, invertebrate and microbial organisms are seasonally released in large numbers to reduce pests. The current popularity of ABC is due to (1) its inherent positive characteristics (healthier for farm workers and persons living in farming communities, no harvesting interval or waiting period after release of agents, sustainable as there is no development of resistance against arthropod natural enemies, no phytotoxic damage to plants, better yields and a healthier product, reduced pesticide residues [well below the legal Maximum Residue Levels (MRLs)], (2) professionalism of the biological control industry (inexpensive large scale mass production, proper quality control, efficient packaging, distribution and release methods, and availability of many (>440 species) control agents for numerous pests), (3) a number of recent successes showing how biological control can save agricultural production when pesticides fail or are not available, (4) several non-governmental organizations (NGOs), consumers, and retailers demanding pesticide residues far below the legal MRLs, and (5) policy developments in several regions of the world aimed at reduction and replacement of synthetic pesticides by more sustainable methods of pest

management. propose to move to "conscious agriculture", which involves participation of all stakeholders in the production and consumer chain, and respects the environment and resource availability for future generations. Were "conscious agriculture" to be considered a serious alternative to conventional farming, ABC would face an even brighter future.

Shou *et. al*., (2018) synthesized magnetic multiwalled carbon nanotubes (MMWCNTs) and used as adsorbent for preconcentration of chiral pesticide residues (including epoxiconazole, tebuconazole, and metalaxyl) in lettuce, cabbage, and apple. Several parameters affecting the treatment efficiency were investigated, including extraction solvent and absorption solvent. Under the optimal conditions, all three chiral pesticides showed decent enantiomeric separation (Rs > 1.48).The average recoveries of the three spiked levels were 73.4% to 110.9% with repeatability (RSDr) less than 7.6%, and the limit of quantification of the method was 0.10 to 0.25 mg·kg−1. The results indicated that MMWCNTs had a good purifying effect, which can be applied as an effective pretreatment tool for the determination of residual chiral pesticides in fruits and vegetables.

Magali *et. al*., (2018) developed A fast ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC-MS/MS) method for quantitative determination of pesticide residues in pear. A fast modified acetate QuEChERS method without clean-up was used for sample preparation. Validation was performed according to SANTE guideline. Matrix effect results were significative for most part of compounds and thus a matrix-matched calibration was employed. The linear range of the method was from 2.5 to 100 μg kg^{-1}. Recoveries were between 70 and 120% with precision ≤ 20%. Limit of quantification was 2.5 μg kg^{-1} for most compounds. Uncertainty results ranged from 22 to 49%. In real sample analyses, 21 compounds were quantified in concentrations between 3.3 and 1427 μg kg^{-1}. Method proved to be simple, robust and effective to be applied in routine analysis.

Chen *et. al.,* (2018) developed rapid resolution liquid chromato-graphy triples quadrupole tandem mass spectrometry (RRLC-QqQ-MS/MS) for simultaneous determination of pyridaben, dinotefuran, DN and UF in eggplant ecosystem. Matrix-matched

external calibrations were introduced to check matrix effects. Limits of quantification (LOQs) of pyridaben, dinotefuran, DN and UF in eggplant were 0.2, 0.2, 1.0 and 1.0 μg kg^{-1}, and 0.2, 0.2, 5.0 and 1.0 μg kg^{-1} in soil, respectively. Limits of detection (LODs) of four pesticides were below 0.41 μg L^{-1}. The mean recoveries (n = 5) of these insecticides varied from 79.4% to 103%, and the relative standard deviations (RSDs) ranged from 2.1% to 15.3% at three levels. This method was applied to Chinese open-field samples from two representative locations, which were previously treated with these insecticides at the doses of 210–315 g a.i. ha^{-1} twice or three times. The dissipations of pyridaben and dinotefuran in eggplant and soil followed first-order kinetics with the half-lives of 3.65–11.4 d. The residues of pyridaben and total dinotefuran (calculated as sum of dinotefuran parent, DN and UF) in eggplant were below 0.0311 mg kg−1 at the pre-harvest interval (PHI, 7 d). Presently, no maximum residue limit (MRL) of pyridaben and dinotefuran in eggplant was recommended by China, Codex Alimentarius Commission (CAC) or European Union (EU).

Anna *et. al*., (2018) invented a Suspect Screening Strategy for Pesticide Metabolites in Fruit and Vegetables by UPLC-Q-Tof-MS for the detection of pesticide metabolites in fruit and vegetable samples. Based on a retrospectively created accurate mass compound database, a suspect screening approach was established for pesticides of high concern applied to a wide scope of plant-derived commodities. The metabolite database contained a total of 648 pesticide metabolites originating from 58 active compounds. In 500 samples from daily routine analysis, 96 samples with positive detects for a total of 26 pesticides were re-analyzed for the occurrence of corresponding metabolites. Forty-seven different phase-I and phase-II metabolites were identified, respectively. The developed metabolite database can be applied for a suspect screening approach for pesticide metabolites identification in all kinds of fruits and vegetables.

Prodhan *et. al.,* (2018) Determined the organochlorine pesticide residues in shrimp which is very important to ensure the consumer's safety and to fulfill the importer's demand. A simple and efficient analytical method using quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction technique and Gas Chromatography coupled with Electron Capture Detector (ECD) has been developed and validated for the determination of 19 organochlorine pesticides (α- BHC, δ- BHC, β- BHC, γ- BHC, Heptachlor, Aldrin, Heptachlor Epoxide, γ-Chlordane, α- Chlordane, α- Endosulfan, 4,4 DDE, Dieldrin, Endrin, 4,4 DDD, β-

Endosulfan, 4,4 DDT, Endosulfan sulphate, Methoxychlor, and Endrin Ketone) in shrimp. The method was validated by evaluating the accuracy, precision, linearity, limit of detection (LOD) and limit of quantification (LOQ). For the selected pesticides the average recoveries ranged from 84% to 106% with RSDr ≤ 14% in four fortification levels of 0.05, 0.1, 0.2 and 0.3 mg kg^{-1}. for all of the selected pesticides, the linearity was ≥ 0.996 with matrix matched calibration standards. The LOD ranged from 0.003 to 0.009 mg kg^{-1} and the LOQ was 0.05 mg kg^{-1}. This method was applied successfully for the residue analysis of 40 shrimp samples collected from different regions in Bangladesh.

Kumari *et. al.,* (2018) determined pesticide residues in fruits and vegetables by Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method and assure the safety of food. The main objectives were to optimize the method for multi-residue pesticide analysis, to develop calibration curve to detect concentration of pesticides and to determine prevalence of five pesticide residues in locally grown vegetables tomato, cabbage and capsicum in Puttalum, Dambulla and Nuwara Eliya districts. By Gas Chromatography with Mass Spectrometry after multi residue extraction procedure (QuEChERS method) pesticide residues were determined . The QuEChERS method was validated using five pesticides named Diazinon, Chlopyrifos, Fipronil, Prothiofos and Tebuconazole and their retention times in minutes were15.948, 19.566, 20.342, 22.308, and 26.201 respectively. Coefficient of detection was obtained near 0.99 for all tested standard pesticides confirming the accuracy of the test method. Among 45 vegetables samples, 15 samples were detected with pesticide residues, either Chlopyrifos, Prothiofos or Tebuconazole. However, for all the tested pesticides pesticide, residual values were less than MRLs (Maximum Residual Levels) . Tebuconazole was the mostly detected pesticide residue with 0.128 ppm and 0.052 ppm in tomato and cabbage collected from Matale and Puttlum districts respectively. So it is important to collect samples while obtaining farmer details including the type of pesticide applied, harvesting interval and frequency and application rate of pesticide for further study.

Liang Fu *et. al.,* (2018) collected 420 samples of 10 diffrent types of fresh vegetables and analyzed for their pestiide multiresidue contents using gas chromatograph and NY/T 761-2008 pestiide multiresidue screen methods. The residues exceeded MRLs of forbidden pestiides found were: carbofuran 0.110 mg/kg (kidney bean) and methamidophos 0.037 mg/kg (celery) in January 2009, methamidophos 0.037 mg/kg (tomato) in May 2009, aldicarb 0.013 mg/kg (kidney bean) in September 2009, omethoate 2.200 mg/kg (celery) in November 2009, carbofuran 0.052 mg/kg (green pepper) in April 2010, parathion 0.056 mg/kg (celery)

and carbofuran 0.030 mg/kg (celery) in July 2010. Also, chlorpyrifos used as unforbidden pestiide was most frequently found above MRL, rape (0.820 mg/kg) and celery (0.365 mg/kg) in January 2009, celery (0.330 mg/kg) in May 2009, lettce (0.298 mg/kg) in September 2009, rape (0.910 mg/kg) in April 2010 and lettce (0.230 mg/kg) in July 2010. In additin, cypermethrin used as unforbidden pestiide was found above MRL only once in rape (1.270 mg/kg) in May 2009 and none of unforbidden pestiides above MRL was found in November 2009 and January 2010. Most of the samples (96%) were up to the natinal standard.

Freitas *et.al.,* (2018)conducted a study based on matrix solid-phase dispersion (MSPD) extraction and gas chromatography with electron-capture detection (GC-ECD) is employed to determine pesticide residues in the following tropical fruits: banana, mango, melon, papaya and pineapple. C18, silica gel and ethyl acetate presented the best results in the extraction, clean-up and elution steps, respectively in the MSPD proposed method. To minimize the matrix effect in the chromatographic determination spiked blank samples were used. The validation process was conducted at three different concentration levels of spiked samples (0.50-2.50 µg g-1) in within-a-day and in among days assays. The limits of detection for the pesticides ranged from 4.0 to 23 µg kg-1. The method showed acceptable selectivity, coefficients of correlation higher than 0.997, and recovery between 76-105%. The within-a-day precision was assessed through the relative standard deviation (2.8-19%) for the different levels of spiked samples tested.

Zhijuan *et. al.,* (2018) developed a method for the determination of 50 pesticides in fruits by gas chromatography-tandem mass spectrometry (GC-MS/MS) . The three QuEChERS methods (the original one without buffer, the one with acetate buffer and the one with citrate buffer) were compared. The purification effects of primary secondary amine (PSA) and SinChERS-Nano column were also investigated. The results showed that the acetate buffer and the citrate buffer had positive influence on the extraction compared to the original method without buffer, and there was no significant difference between the two methods using buffers. As the extraction method, the QuEChERS method using acetate buffer was chosen finally. SinChERS-Nano column was revealed to have a better cleaning effect by comparing the purification effect images and the total ion current (TIC) chromatograms and was chosen for cleanup. The recoveries of methamidophos, acephate, omethoate, chlorothalonil and dicofol were in ranged of 71.2%-129.2%, the other 45 pesticides were ranged from 79.1% to 122.3%. The limits of detection (LODs) were 0.3-3.0 µ g/kg and the

limits of quantification (LOQs) were 1.0-10.0 μ g/kg. The method is rapid and suitable for the screening of the 50 pesticide residues in citrus, grapes and other fruit samples.

Akhtar *et. al.,* (2018) conducted a study to determine selected pesticides namely bifenthrin, difenoconazole, paraquat, dimethomorph, imidacloprid, deltamethrin residual in fruit (guava) and vegetables (egg plant and round guord) collected from shops in commercial market, Lahore. For detection of pesticide residues the samples were prepared and subjected to high pressure liquid Chromatography (HPLC) . The results showed that concentration of bifenthrin, difenoconazole, paraquat, diomethomorph and imidacloprid in Guava fruit were 5.13, 81.5, 6.6, 0.48 and 1.65 mg/kg respectively. Bifenthrin, difenoconazole, paraquat, diomethomorph and deltamethrin detected residues in Egg Plant sample were 3.53, 5.62, 4.58, 0.25 and 0.005 mg/kg respectively while imidacloprid residues were not detected. In Round Gourd, the amount of bifenthrin, difenoconazole, paraquat, diomethomorph residues were 3.87, 61.53, 5.01 and 0.15 mg/kg respectively. Yet pesticide residues are left in fruits and vegetables which can pose potential health risks to the consumers. Therefore, need of continuous pesticide residue monitoring is highly recommended.

Mahugija *et. al.,* (2017) determined the levels of pesticides and metabolites in vegetables from major markets in Dar es Salaam city, Tanzania. Cabbage, spinach, and onions samples collected from the markets and were analysed for pesticide residues. By using acetone followed by dichloromethane : cyclohexane mixture extraction was performed and the extracts were cleaned up using Florisil. The compounds were determined by gas chromatography-mass spectrometry (GC-MS). In about 72.2% of the samples pesticides and metabolites were detected . The detected pesticide residues and their highest mean concentrations were *p,p′*-DDT 4.00×10^{-3} mg/kg, *p,p′*-DDD 6.40×10^{-1} mg/kg, *o,p′*-DDD 1.00×10^{-2} mg/kg, *α*-endosulfan 6.00×10^{-1} mg/kg, *β*-endosulfan 2.10×10^{-1} mg/kg, chlorpyrifos 3.00 mg/kg, and cypermethrin 4.00×10^{-2} mg/kg. The most frequently detected compounds were *p,p′*-DDD and chlorpyrifos. Among samples and sampling sites, there were no significant variations in concentrations of pesticide residues which indicated similarities in contamination patterns. The concentrations of contaminants were above the MRLs (Maximum Residue Limits) in 33.3–50% of the samples. The findings indicated risks and concerns for public health.

Aktar *et. al.,* (2017) conducted a study to determine the pesticide residue in vegetables the local markets of Mymensingh Sadar, Mymensinghfrom December 2015 to June 2016. 50 samples of eggplant were collected from 10 markets of Mymensingh Sadar, Mymensingh

which were analyzed by a simple and efficient multiple pesticide residue analytical method (QuEChERS extraction) and gas chromatography-flame thermonized detector (GC-FTD) were used for the determination of pesticide residues. Out of the 50 analyzed samples, 11samples (22% of the total number of the samples) contained pesticide residues of diazinon, dimethoate, quinalfos, and chlorpyrifos, of which, 2 had multiple pesticide residues and 5 samples contained residue above the European Union maximum residue limit (EU-MRLs). Chlorpyrifos was detected as the most used pesticide in eggplant in that area. Eggplant samples collected from K.R market did notcontain any residues of pesticides.

Kumari *et. al.*, (2018), conducted a study to determine pesticide residues in fruits and vegetables by the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method and assure the safety of food. The aim of this study were to optimize the method for multi-residue pesticide analysis, to develop calibration curve to detect concentration of pesticides and to determine prevalence of five pesticide residues in locally grown vegetables tomato, cabbage and capsicum. Pesticide residues were determined by Gas Chromatography with Mass Spectrometry after multi residue extraction procedure (QuEChERS method). The QuEChERS method was validated using five pesticides named Diazinon, Chlopyrifos, Fipronil, Prothiofos and Tebuconazole and their retention times in minutes were15.948, 19.566, 20.342, 22.308, and 26.201 respectively. Among 45 vegetables samples, 15 samples were contained with pesticide residues, either Chlopyrifos, Prothiofos or Tebuconazole less than Maximum Residual Levels for all the tested pesticides. Tebuconazole was the mostly detected pesticide residue with 0.128 ppm and 0.052 ppm in tomato and cabbage collected from Matale and Puttlum districts respectively.

Hadian et. al.,(2019) conducted a study about forty-eight pestcide residues from diffrent chemical stuctures including organochlorine, organophosphorus, organonitrogen, dicarboximides, stobilurin, triazine, pyrethroids, and other chemical groups. In 85 fruits and vegetables were determined and confimed by GC-MS. By using ethyl-acetate, then, the extracts cleaned using high performance gel permeation column chromatography (GPC) and solid phase column (SPE), the pestcide was extracted . The mean recoveries of the pestcides were between 81 and 136%.The reproducibility of the relative stndard deviation values was 2.1% and 14.8%. Pestcide residues were more frequently found in vegetables (65.5%) than in fruits (26.7%). The limits of detection and quantifiation of pestcide residues were ranged from 0.003 to 0.06 µg/g and between 0.01 to 0.1 µg/g respectively. The analyzed samples did not contain residues from the monitored pestcides that were higher than the accepted maximum residue limits (MRLs) as adapted by the FAO/WHO Codex Alimentarius Commission.

Lin *et. al*., (2018) developed a rapid and economical method using modified QuEChERS sample pretreatment coupled with high-sensitivity gas chromatography/triple quadrupole mass spectrometry to determine ten pyrethroid pesticides in fruits and vegetables. All pesticides were detected within 20 min of one injection. Concurrent backflushing provided column protection, greatly facilitating instrument maintenance. For quantitation, matrix-matched calibration was used to compensate for signal-enhancement effects and to ensure the precision of the method. The limit of detection (LOD) was in the range of 0.3–4.9 μg/kg. The recovery rate was from 78.8 to 118.6%, with relative standard deviation (RSD) below 14.8%. The developed method is suitable for rapid and sensitive multi-residue analysis of pyrethroid pesticides in fruits and vegetables.

Lakshani *et al*.,(2017) conducted a research on "Pesticide residues in selected vegetables in several growing areas by gc/ms using quechers technique". His study aimed to evaluate the Maximum Residue Levels (MRL) of selected vegetables in the open market in three locations .A total of 90 samples of vegetables including tomato (*Solannumlycopersicum*), capsicum (*Capsicum annuum*) and cabbage (*Brassica olerecea*) were collected during the period of 2016 March to 2016 November from different vegetable markets in NuwaraEliya, Puttlam and Matale districts for the evaluation of pesticide residues. The collected samples were extracted according to the QuEChERS, AOAC code 2007.01 by application of a single step buffered acetonitrile extraction and salting out liquid-liquid partitioning from the water in the sample with MgSO4 and clean-up is done by dispersive solid phase extraction. These concentrated samples were analyzed by GC/MS in Selective Ion Mode (SIM) and presence of pesticides was confirmed with Retention Time (RT) and Mass Spectrum (MS). About 30 samples were contaminated with pesticide residues; out of 90 samples tested. The results provide most important information about contamination of pesticide residues in tomato, capsicum and cabbage available at different markets. It should be recommend that monitoring studies should be expanded to other districts in order to come out with a strong national policy on safer use of pesticides in vegetable cultivation in Sri Lanka.

Manakla, (2017) conducted a study to determine the presence of pesticide residues in fresh vegetables on local markets and supermarkets in Klongluang, PathumThani. 150 of cabbage, tomato, broccoli, coriander, spring onion, Chinese cabbage, Chinese kale, Chinese morning glory, Thai eggplant and celery, were determined Organophosphorus and Carbamates group

pesticide residues. By enzyme cholinesterase inhibition-based colorimetric technique, they were non-quantitative determined. No residues were detect in 5.33% of the vegetables samples and 79.34% of the samples was detected pesticide residues at low-level (≤50% inhibitory concentrations), and 15% of the samples was detected pesticide residues at high-level (>50% inhibitory concentrations), exceeding a safety threshold. The percentage of high-level contaminated samples was high for three different vegetables: Chinese cabbage (33.33 %), broccoli (33.33%) and spring onion (26.33%).

Mustapha *et. al*., (2017) conducted a study on "Monitoring of pesticide residues in commonly used fruits and vegetables in Kuwait" The aim of his study was to assess the level of pesticide residues in commonly consumed fruits and vegetables in Kuwait. A total of 150 samples of different fresh vegetables and fruits were analyzed for the presence of 34 pesticides using the quick easy cheap effective rugged and safe (QuEChERS) multi-residue extraction, followed by gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-tandem mass spectrometry (LC-MS/MS). Pesticide residues above the maximum residue limits (MRL) were detected in 21% of the samples and 79% of the samples had no residues of the pesticides surveyed or contained residues below the MRL. Multiple residues were present in 40% of the samples with two to four pesticides, and four samples were contaminated with more than four pesticide residues. Of the pesticides investigated, 16 were detected, of which imidacloprid, deltamethrin, cypermethrin, malathion, acetamiprid, monocrotophos, chlorpyrifos-methyl, and diazinon exceeded their MRLs. Aldrin, an organochlorine pesticide, was detected in one apple sample, with residues below the MRL. The results indicate the occurrence of pesticide residues in commonly consumed fruits and vegetables in Kuwait, and pointed to an urgent need to develop comprehensive intervention measures to reduce the potential health risk to consumers. The need for the regular monitoring of pesticide residues and the sensitization of farmers to better pesticide safety practices, especially the need to adhere to recommended pre-harvest intervals is recommended.

Njoku *et. al*., (2017) conducted a investigated study on "Assessment of Pesticide Residue Levels in Vegetables sold in some Markets in Lagos State, Nigeria". His study showed pesticide residue levels in the two vegetables commonly eaten in Lagos state Nigeria. They collected the vegetable samples from six markets (Oyingbo, Mile 12, Mushin, Ajah, Agege and Festac) in Lagos.The pesticide residue levels were determined by using gas chromatography/mass spectrometry. Obtained data were statistically analysed using graphpad

prism 6.0 software and were compared with WHO limits. The vegetables were collected from all the markets contaminated with pesticide residue level above the WHO lower limit (0.02 mg/kg). From all the collected samples two vegetables samples from Oyingbo and Mile 12 markets had total pesticide residue levels above the WHO upper limit (0.7 mg/kg). T. occidentalis from Oyingbo market had the highest total pesticide residue level (2.35mg/kg) and the highest number of pesticides while C. argentea from Agege market had the least total pesticide residue level (0.08mg/kg). Aladrinpesticide was found in the two vegetables from all markets and generally more pesticide residue was found in the tissues of T. occidentalis than in the tissues of C. argentea. Significant differences ($P<0.05$; $P<0.01$) were found between some pesticides in T. occidentalis from Oyingbo and some pesticides in the vegetable samples collected from the other markets. The hazard quotient and hazard index values (being less than 1 and 0.2 respectively) show that there will be no health risk in consuming the vegetable, although some of pesticides residues were above the maximum residue levels. The presence of pesticides in the vegetables calls for strict regulation of the application of the pesticides in farms and this will help in preventing some of the diseases and many other problems associated with pesticide accumulation.

Mohammed *et. al*., (2017) conducted a research on "Evaluation of pesticide residues in tomato (*Lycopersicum esculentum*) and the potential health risk to consumers in urban areas of Ghana." His study conducted to assess the concentration of various pesticide residues in tomatoes, obtained from three market centers (namely Bantama, Central, and Ayigya Markets) in Kumasi, dealing with potential health risks for the consumers.Analyzed samples have showed high percentage of organophosphorous pesticide residues (45%) in Ayigya market with Bantama market recording high percentage of organochlorines and pyrethroid. Laboratory analysis of tomato samples for various pesticides residues has indicated that all the pesticide residues pose no threat to human's health along with all estimated hazard indices being below 1; however, heptachlor (HI=0.85) and dieldrin (HI=0.74) have shown the highest risk levels in children. The study also showed that there is some need for strict monitoring of heptachlor and dieldrin in tomato, especially in case of children.

Hazer *et. al.,* (2017) developed a method to determine pesticide residues in fruit and vegetable extracts with short time analysis. By using binary mobile phase consisting of methanol: water; 95:5, v/v and fluorescence detection (λEx and λEm set at 280 and 340 nm, respectively), An optimum results were achieved. The dynamic range was between 0.100 to 10 mg L-1with relative standard deviation less than 0.45%, (n=4). Limits of detection and recoveries forcarbendazim and chlorpyrifos were 0.073 mg L-1(84.2-106.5%) and 0.062

mg L-1 (85.7-90.3%), respectively. The results show that the concentrations of carbendazim and chlorpyrifos residue in all samples were below than the EU legal limit.

ZhiXu *et. al*., (2017) devloped a sensitive and effective method, using gas chromatography (GC) and an electron capture detector (ECD), for the simultaneous quantitative determination of bifenthrin, chlorothalonil, cyfluthrin,cypermethrin, difenoconazole, fenvalerate, procymidone and pyridaben residues in cowpea. Extracting with acetonitrile, purification with a graphitized carbon black/amino solid phase extraction cartridge, and then determining by GC–ECD. Recovery studies were carried out at three spiked levels (0.01, 0.1 and 0.5 mg/kg). With relative standard deviations in the range of 1.2–5.6% for all analytes the average recoveries at the three spiked levels ranged from 76.6 to 107.0 M%. The quantification limit was 0.01 mg/kg for each pesticide and was less than or equal to the relevant RLs set by China, the Codex Alimentarius or the European Union. The developed analyzing method was convenient, time and cost saving, environment-friendly and readily available than the traditional methods.

Akter *et. al.*, (2017) have been identified pesticide residues in eggplant collected from Mymensingh. 22% of the total number of the samples were contaminated with pesticide residues of diazinon, dimethoate, quinalfos, and chlorpyrifos among the 50 analyzed samples of which, 2 had contaminated with multiple pesticide residues and 5 samples contaminated with residue above the European Union maximum residue limit (EU-MRLs). Chlorpyrifos was the most used pesticide which was identified in eggplant in the studied area.

Hasan *et. al*., (2017) have been found two types of insecticides (Dimethoate and Quinalphos) in country bean samples which were collected from different market places of Dhaka. Among the 50 analyzed country bean samples, 10 samples (20%) contaminated with residues of Dimethoate and Quinalphos, of which 5 samples were above the maximum residue limits (MRLs). Most of the samples (8 samples) contained residue of Dimethoate.

Ozcan, (2016) determined the level of pesticide pollution using marrow squash (*Cucurbita pepo* L.), cherry tomato (*Solanum lycopersicum var. cerasiforme*), banana pepper (*Capsicum annuum*), lettuce (*Lactuca sativa* L.), purslane (*Portulaca oleracea* L.), green beans (*Phaseolus vulgaris* L.), cucumber (*Cucumis sativus* L.), and onion (*Allium flavum* L.) in Kirklareli, Turkey. By gas chromatography-mass spectrometry (GC-MS), the concentrations of organochlorine pesticides were determined. Vegetables were prepared for analysis by QuEChERS extraction method. Concentrations of residues of Hexachlorocyclohexane

(ΣHCH), aldrin, heptachlor, dieldrin, endosulfan, methoxychlor and dichlorodiphenyltrichloroethane (ΣDDT) were determined in vegetables collected from different location in Kirklareli. The LOD and LOQ were between 0.02-0.26 and 0.06-0.87 μg/L, respectively. The RSDs of the migration time ranged from 2.4% to 7.7% for the 18 analytes, indicating the good repeatability of the method. Recoveries of the spiked analytes in vegetables ranged from 83% to 104%, respectively. The obtained concentrations for pesticides in all vegetables studied were in the range ND-73.6 μg/kg.

Yohannes *et. al.,* (2016) determine pesticide residue of profenofos in tomato (Solanum lycopersicum L.) had been investigated by using Gas Chromatography technique with Flame Photometric Detector (FPD). The tomato sample was collected from Koto Baru, Tanah Datar, West Sumatera, Indonesia. The samples were divided into unwashedtomato, washed with tap water and washed with detergent. By ultrasonication for 10 minutes with 100 mL ethyl acetate, samples were extracted once. The obtain results showed the unwashed tomato, washed with tap water and washed with detergent contains 0.159±0.0079; 0.070±0.0009 and 0.067 ±0.0016 ppm profenofos pesticide residue respectively. The profenofos residue levels do not exceed the MRL (Maximum Residue Limit) that established by Indonesian National Standard (in ppm). Statistical tests with one-way ANOVA (SPSS 20.0) showed there was decrement in the levels of profenofos pesticide residues significantly between unwashed tomatoes, tomatoes washed with tap water and tomatoes washed with detergent ($P < 0.05$).

Prodhan *et. al.,* (2016) have been found three insecticides (chlorpyrifos, cypermethrin and deltamethrin) and two fungicides (fluopicolide and propamocarb hydrochloride) in the cabbage samples collected from different market places in Thessaloniki, Greece. Among the 132 analyzed samples, 41 (31% of the total no. of samples) had pesticide residues, of which, 2 had multiple pesticide residues and 39 had single pesticide residues.

Prodhan *et al.* (2016a) have also been detected four insecticides (chlorpyrifos, cypermethrin, deltamethrin and indoxacarb) in cauliflower samples collected from different market places in Thessaloniki, Greece. Among the 120 analyzed samples, 48 (40% of the total no. of samples) were found to have pesticide residues.

Prodhan *et. al.,* (2015) conducted a research on ‘‘Determination of Multiple Pesticide Residue in Eggplant with Liquid Chromatography-Mass Spectrometry’’ where a simple and efficient multiple pesticide residue analytical method using quick, easy, cheap, effective,

rugged, and safe (QuEChERS) extraction and liquid chromatography triple quadrupole-mass spectrometry was developed and validated for the determination of ten insecticides and three fungicides in eggplant. The method was validated by evaluating the accuracy, precision, linearity, limit of detection, and limit of quantification. They evaluated matrix effect and it was found that thiamethoxam, cypermethrin, and deltamethrin had pronounced matrix effect (-69, +57, and +93 %, respectively). They applied this method for the residue analysis of 72 fresh eggplant fruit samples collected from different market places in Thessaloniki, Greece. Among the 72 analyzed samples, 34 (47 % of the total no. of samples) had pesticide residues, of which, 5 had multiple pesticide residues and 29 had single pesticide residue. Only one sample contained residue above the EU-MRLs.

Prodhan *et. al*., (2015a), where they use a rapid, precise and efficient method for the determination of seven insecticides (chlorpyrifos, dimethoate, deltamethrin, thiamethoxam, thiacloprid, pirimicarb and indoxacarb) and three fungicides (azoxystrobin, fluopicolide and propamocarb hydrochloride) in melon by employing quick, easy, cheap, effective, rugged and safe extraction method coupled with liquid chromatography triple quadrupole mass spectrometry which was developed and validated by evaluating the accuracy, precision, linearity, limit of detection (LOD) and limit of quantification (LOQ). They evaluated matrix effect and it was found considerable for thiamethoxam and deltamethrin (-53% and +135%, respectively). Finally, this method was applied for the residue analysis of 122 fresh melon samples collected from different market places in Thessaloniki, Greece. Among the 122 analysed samples, 32 (26% of the total no. of samples) were found to have pesticide residues. None of the samples contained residues above the European Union Maximum Residue Levels. The most frequently detected pesticides were fluopicolide and thiamethoxa

Pal *et. al*., (2016) performed a research on "Determination of the organophosphorus pesticide in okra crop, Abelmoschusesculentus (l.) By gas-liquid chromatography in Meerut region."A multi pesticide residues analysis was done for farmgate okra fruits samples from four markets places of Meerut region. Samples were analyzed for monocrotophos, chlorpyriphos, dimethoate. Okra vegetable sampleswas analyzed for pesticide residues using multiresidue analysis by GLC. It was indicated that 39.0% of the samples were contaminated residues below MRL three pesticides. The results indicated that 42% of the samples tested contained residues higher than the MRLs and 19 % BDL. On the basis of observations made in these studies; it is proposed that more extensive monitoring investigations covering Okra from

different farmgate and market Meerut regions of the city be carried out to find the exact position of pesticide residues.

Abdulhamid *et. al.,* (2015) determined the concentration of organochlorine and pyrethroid pesticide residues in Amaranthushybridus (spinach), hibiscus esculentus (okra) and Telfairiaoccidentalis (fluted pumpkin) which were collected from seven farms in Minna, Nigeria by using gas chromatographytriple quadrupole mass spectrometry. The results showed that the presence of cypermethrin in concentration range of 0.51 to 9.95 μg/mL in two samples of spinach. The presence of heptachlor was not confirmed in these samples. None of the pesticides under investigation was detected in any of the okra and fluted pumpkin samples.

Prodhan *et. al.*, (2015) estimated seven insecticides such as chlorpyrifos, dimethoate, deltamethrin, thiamethoxam, thiacloprid, pirimicarb and indoxacarb and three fungicides such as azoxystrobin, fluopicolide and propamocarb hydrochloride in 122 fresh melon samples which were collected from various market in Thessaloniki, Greece . From the selected pesticides the average recoveries of the selected pesticides in the samples ranged from 82% to 106% with RSDr ≤6% in four fortification levels of 0.01, 0.05, 0.1 and 0.2 mg/kg and the correlation coefficient (R2) was ≥0.997. The values of LOD ranged from 0.001 to 0.003 mg/kg, and for all the samples, LOQ was determined at 0.01 mg/kg. From the 122 analysed samples, 32 (26% of the total no. of samples) were found to have pesticide residues at all.

Francisco *et. al*., (2014), performed a study on "Analysis of tomato matrix effect in pesticide residue quantification through QuEChERS and single quadrupole GC/MS". The detection of pesticide in tomato (*Solanum lycopersicum L*.) matrix using Gas Chromatography hyphenated to Mass Spectrometry detector (GC/MS) can affect the sensitivity of the analysis by enhancement or suppression of their chromatography response, the percentages of recoveries and leading to errors in the quantification of the pesticides. In this study, the matrix effect was investigated using nine pesticides, and "Quick, Easy, Cheap, Effective, Rugged and Safe" (QuEChERS)-GC/MS analytical technique was validated for pesticides multiresidue analysis. The matrix effect was determined using not statistical and statistical procedures including ANOVA, with similar results. Strong negative matrix effect was found for the pesticides trifluralin, 4,4'-DDT, and permethrin, resulting in the increment of the chromatogram background and a decrease in their detection responses. Contrary, an enhancement induced by the matrix presence was obtained for carbaryl and azinphos methyl, showing a positive medium matrix effect. While, dimethoate, simazine, 4,4'-DDE, and iprodione did not exhibit matrix effect. The detection limits (LOD) obtained, varied from

0.003 to 0.1 mg kg-1.Reproducibility was less than 20% for each pesticide. Recoveries were found to be between 71% and 121%, except for dimethoate, carbaryl, and azinphos methyl which reached values lower than 70%. Recoveries relative standard deviations were less than 22%. Quechers-GC/MS technique was used for evaluation of fresh commercial tomatoes samples, detecting carbaryl in all of them, but in concentration levels lower than the maximum residue limits according to regulations of Codex.

Chandra *et. al*., (2014) conducted a research on "Analysis of pesticide residue in vegetables local market, Nanded, India". He conducted a research to analysis the residues of chlorpyriphos, cypermethrin and monocrotophos in locally grown vegetables. A total of 288 vegetable samples were periodically collected from local market ,Nanded, India and analyzed by gas chromatography equipped with mass detector. The result showed that the vegetable samples analyzed contained detected level of pesticides residues below the maximum residue limit (MRL). By application of a single-phase extraction of 15 g of sample with acetonitrile containing 1% of acetic acid, followed by a liquid-liquid partion formed by addition of $MgSO_4$ and NaOAc. Cleanup of the extract was carried out with primary secondary amine and MgSO4, the vegetable samples were extracted. The average recoveries of pesticide residues in brijal, capsicum, okra, cauliflower samples were 75.0 to 105.0%. %. The method offers safer and cheaper alternative to typical multi-residue analysis methods for the estimation of pesticides residues in vegetables samples.

Islam *et. al*., (2014) conducted a research on "Detection and quantification of pesticide residues in selected vegetables of Bangladesh". He conducted a survey in intensive vegetable growing area in the Narsingdi district of Bangladesh regarding pesticides used by farmers on three major vegetables like eggplant, cauliflower and country bean. About 23 farmers were interviewed and it was noted that fourteen pesticides belonging to different groups were found to be commonly used on the selected vegetables by the respondent farmers to control the major pests. Two selected locations of Narsinghdi 8.33 to 45.00 percent farmers were recorded in which they apply different pesticides every day and even twice in a day on vegetables in some cases. About 42 samples were collected from fields and different markets and multiple pesticide residue analysis was done by Gas Chromatography (GC) with Flame Thermionic Detector (FTD) and Electron Capture Detector (ECD). 27 samples had pesticide residue, out of 42 samples. Out of these 27 samples, 14 samples had pesticide residues above the Maximum Residue Limit (MRL). The detected pesticides were Malathion, Diazinon , Cypermethrin, Quinalphos, Fenitrothion ,Fenvalerate and Propiconazole.

Sitaramaraju *et. al.,* (2014) conducted a research on impact of pesticides used for crop production on the environment. In his research he found that majority of pesticides are not specily targeting the pest only and during their application they also non target plants and animals. Repeted overtime application leads to loss of biodiversity , increases in pest resistance and its effects on other species can facilitate the pest resurgence. Most pesticides are not easily degradable, they persist in soil, they leach to ground water and runoff can carry peticides into aquatic system and contaminate environment. Sprayed pesticides gives effects other than on their target species, including non target sites. More over intensive pesticide application results in several negative effect in the environment.

Tobin *et. al.,* (2014), conducted a study on "Detection of Pesticide Residues in Organic and Conventional Fruits and Vegetables Available in Ireland Using Gas Chromotography/Tandem Mass Spectrometry (GC-MS/MS) and Liquid Chromotography/Tandem Mass Spectrometry (LC-MS/MS) Detection". In their study , Nine different fruit and vegetable types of organic and conventional origin were sampled from large supermarkets. Analysis for 465 pesticide residues was carried out using GC-MS/MS and LC-MS/MS analysis. Of the 27 organic samples tested, 15 contained one or more detected pesticide residues, with one of these being above the limit of quantification (LOQ) for the method, imazalil in organic onion, 11.13 ng/g. Of the conventional samples 17 of the 27 samples contained one or more residues. Twelve of the residues detected in conventional samples were above the LOQ with concentrations ranging from 9.84 to 154.10 ng/g. A similar number of organic (15) and conventional (17) samples tested positive for detectable residues, however the number of residues detected was higher in conventional (43) than in organic (29), and the concentration of these residues .

Yihua *et. al.,* (2014) determined four pesticide residues (phoxim, chlorpyrifos, imidacloprid and chlorantraniliprole) in bamboo shoot using quick, easy, cheap, effective, rugged and safe (QuEChERS)-matrix solid phase dispersion (MSPD) cleanup and liquid chromatography-mass/mass spectrometry (LC-MS/MS). The sample (5.0 g) was extracted with 20 mL acetonitrile and cleanup with 2.0 g dispersive primary secondary amine (PSA). The results showed the developed QuEChERS-MSPD-LC-MS/MS method is simple, rapid and effective. Average recoveries ranged between 87.5% and 107.2% with RSD values from 5.2% to 12.4% at two concentration levels (20 and 200 µg/kg) and detection limit (LOD) was below the regulatory maximum residue limits for the pesticides were achieved. The sample preparationduration is only 30 min, which is faster than the application of the traditional

standard method (at least 400 min). So the new developed method is more environ- mental friendly due to the less solvent consumption.

Munawar *et. al.,* (2013) determined Cypermethrin, chlorpyrifos and imidacloprid residues in different vegetables. The samples were collected from different six major vegetable markets from Lahore. For extraction Ethyl acetate was used, whattman fluted filter and charcoal was used for cleaning procedure. High performance thin layer chromatography was used for dectetion and quantification of pesticides. By using gas chromatography/mass spectrophotometer, confirmation of results was done . The results showed that different vegetables contain different concentration of pesticides means adsorption rate is different for each pesticide and vegetable. 79% samples were contaminated with cypermethrin, 70% from imidacloprid and 65% samples were contaminated from chlorpyrifos. pumkin, okra, egg plant, cucumber spinach and cabbage were contaminated with pesticides. Peeling of vegetables resulted in less concentration of pesticide.

Corteas *et. al.,* (2013) developed a method for the determination of organophosphorus pesticides in vegetables. Pesticide residues were extracted from vegetable samples with a small amount of ethyl acetate and anhydrous sodium sulfate. Analyses were done by large volume GC injection using the through oven transfer adsorption desorption (TOTAD) interface. The limits of detection for each pesticide injecting 50 μL of extract that is much lower than the maximum residues levels (MRLs). Repeatability studies show a relative standard deviation lower than 10% in all cases. The method was applied of eggplant, lettuce, pepper, cucumber, and tomato to the analysis.

Sachin *et al.,* (2013) performed a research on "Persistence and decontamination of bifenthrin residues in okra fruits". In his study, Residue levels of bifenthrin were determined in unprocessed and processed okra fruits to evaluate the effect of different household processes on reduction of bifenthrin residues. Bifenthrin (commercial formulation) was applied at 25 g a.i. ha-1(single dose T1) and 50 g a.i. ha-1(double dose T2) in field. Okra fruits samples were collected on 0, 1, 3, 7, 10, 15 and 30 days and at harvest (60 days after treatment). Bifenthrin residues were estimated by gas chromatograph- electron capture detector (GC-ECD) system and reached below detectable level of 0.005 mg kg−1on 15 and 30thday in single and double dose, respectively. Half-life period for bifenthrin were found to be 1.58 and 2.18 days at single and double dose, respectively following first order kinetics. Processing was found quite effective in reducing the levels of bifenthrin residues in okra fruits. Maximum reduction

(64.58 to 68.42%) was observed by washing + boiling followed by washing (36.71 to 40.00%).

Ogah *et. al, .(*2012) determine the concentration of organophosphate and carbamate pesticides in maize samples collected from various markets in Lagos State and compare these values with established safety values. Maize (Zea mays L.) samples were collected from different markets in LagosState were analyzed for residues of organophosphate and carbamate pesticides. Analysis was done with the help of gas chromatograph with mass spectrometric detector (GC-MS) after careful extraction and cleanup. the result shows that all the maize samples contained residues of one or more organophosphate or carbamate pesticides and mean concentrations ranged from 12.0 to 1565.4 µg/kg. Maximum residue limits (MRL) of some of the pesticides were exceeded in up to 10% of samples.

Kapoor *et. al., (*2012), conducted a study on "Analysis of imidacloprid residues in fruits, vegetables,Cereals, fruit juices, and baby foods, and daily intake Estimation in and around lucknow, India". He collected a total of 250 samples including fruits, fruit juices, and baby foods (50 samples each), vegetables (70 samples), and cereals (30 samples) from Lucknow, India, and analyzed for the presence of imidacloprid residues. The QuEChERS method of extraction coupled with high-performance liquid chromatographic analysis were carried out, and imidacloprid residues were qualitatively confirmed by liquid chromatography mass spectrometry. Imidacloprid which was not detected in samples of fruit juices and baby foods. It was detected in 38 samples of fruits, vegetables, and cereals, which is about 15.20% of the total samples. About 22% of fruit samples showed the presence of imidacloprid, and 2% of samples showed residues above the maximal residue limit. Although imidacloprid was detected in 24% of vegetable samples, only 5.71% of the samples showed the presence of imidacloprid above the maximal residue limit. Although 33% of cereal samples showed the presence of imidacloprid, and about 3% of samples were above the maximal residue limit. The calculatation estimated daily intake ranged between 0.004 and 0.131mg/kg body weight, and the hazard indices ranged from 0.007 to 0.218 for these food commodities. It is also indicated that lifetime consumption of vegetables, fruits, fruit juices, baby foods, wheat, rice, and pulses may not pose a health hazard for the population of Lucknow because the hazard indices for imidacloprid residues were below one.

Shinde *et. al*., (2012) study on "Cypermethrin residue in okra leaves and fruits assessed by gc." Cypermethrin is a relatively toxic pesticide and it is used to control moth pests of fruits

and vegetable crops. Gas chromatography is used for determination of cypermethrin residue because it is one of the most powerful method for determination of cypermethrin residue. Cypermethrin were applied separately in three different concentrations 50ppm, 75ppm, 100ppm respectively on okra crops .Extraction of leaves as well as fruits were done by using solvent mixture Petroleum Ether: Acetone(9:1)by standard method and is estimated by GC. In the present times gas chromatography is most frequently used for residue analysis .After the application of Cypermethrin on okra crop the residue were determined 0,1,3,57,9,11,13,15,17,19 and 21 days after application. The results show that the residue below the detectable were found after 17 days.

Anwar *et al*., (2011) conducted a research on "Determination of pesticide residues in fruits of Nawabshah district, Sindh, Pakistan." In this study, eight fruit samples (apple, guava, orange, grapes, pear, persimmon, banana, pear) were collectedfrom the local markets of Nawabshah district, Sindh. Pesticide residue of organophosphate (OP), pyrethroid and organochlorine (OC) (i.e., dichlorvos, fenvalerate, dimethoate, methyl parathion, fenitrothion, cypermethrin, endosulfan, deltamethrin, mevinphos, chlorpyriphos, profenofos and dicofol) were monitored in fruit samples by Gas Chromatography (GC). All the fruit samples were contaminated with pesticide residues except banana and among these only apple samples were found exceeding the maximum residue limits (MRL) of Codex Alimentarius Commission.

Farag *et. al.*, (2011) conducted a research on Monitoring of pesticide residues in some Egyption herbs, fruits and vegetables. He collected one hundred thirty two samples of fruits, vegetables, herbs, and spices collected from Egyptian local markets were for pesticide residues. Contamination with pesticide residues reached 54.55% while contaminated reached 45.45%.from 132 analyzed sample one sample violated the Maximum Residue Limits (MRLs) of the Codex Committee. 72 samples (54.55%) were contaminated, from which 43.18% contaminated with residues from one pesticide residue, 6.06% with 2 residues and 5.3% with more than 2 residues from 132 analyzed samples. On other way, 2 caraway and one fennel samples contained 4 pesticide residues, one sample of marjoram contained 5 pesticide residues and one mint sample contained 6pesticide residues. Of them Six pesticides detected as residues in the analyzed food items which were carcinogens at different levels of assurance.

Parveen *et. al.*, (2011) monitored pesticide residues in 120 different fruits sample (apple, apricot, persimmon, chiku, citrus, grapes, guava, mango, papaya, peach, pulm and pomegranate) collected from different market of Karachi, Pakistan. The fruit samples were

analyzed for multiple pesticide residue using GC/FID and HPLC/UV. They noticed that 62.5% of samples contained pesticide residues of them 22% exceeded the MRL (maximum residue limit) according to FAO/WHO.

Bagyalakshmi *et. al.*, (2011) conducted a research to determine the residue of Dimethoate in leafy vegetables (Spinach) using RPHPLC. They performed the quantification using RP-HPLC for processed (washed, washed and cooked) and unprocessed (fresh) spinach samples. They extracted the sample by benzene. They noticed that unprocessed spinach containsresidue of dimethoate that was slightly more than the tolerance limit but the processed sample contains dimethoate residue within the tolerance limit. The washed samples (3 times under ordinary tap water) showed 28-50 % reduction and the cooked samples (boiling for 15 min) showed 58-71 % reduction compared to the unprocessed samples. In case of greens, it should be washed three times with ordinary water and then cooked (cooked for fifteen minutes) so that the pesticide residue is very much reduced and it will be well within the tolerance limit as specified by Environmental Protection Agency(EPA).

Khan, (2011) conducted a research on "Assessment of Pesticide Residues Selected Vegetables In Pakistan". In his study , he determined the pesticide residues on selected summer vegetables. In a split plot ramdomized complete block design, five vegetable were grown with three replicates. The pesticides residues were extracted from edible leaf portion using anhydrous sodium sulfate and ethyl acetate at maturity stage and adsorption chromatography technique was used for clean up. The extraction was done in high performance liquid chromatography(HPLC) for separation and analysis of the compounds. Highly significance differences($p<0.001$) were observed for the leaf portion where as significance differences($p<0.05$) were found in the pesticides residues on edible portions. The residual level of cypermethrin was highest (16.2 $mgkg^{-1}$) in edible portion of bitter gourd, while Mancozeb and Lambdacyhalothrin residues were detected high (6.26 $mgkg^{-1}$ 4.50 $mgkg^{-1}$) in edible portion of bitter gourd and Cucumber respectively. Mancozeb ,Lambdacyhalothrin residual level was high (1.23$mgkg^{-1}$, and 0.0002 $mgkg^{-1}$) in chili and tomato leaves and Cypermethrin residues were high (1.86 $mgkg^{-1}$) in Okra leaves. In edible and leaf portion of the selected vegetables, Cypermethrin residues were readily detected.

Afful S. *et. al.*, (2010) conducted a research on "Gas Chromatographic Methodology for the Determination of Some Halogenated Pesticides". In his research, gas chromatography (GC) methodology has been validated for the estimation of some halogenated pesticides. Fully separation of the pesticide prepared in ethyl acetate was achieved on Rtx - 1 column with dimension, 30m x 0.25mm x 0.25:m. By using column temperature programmed from 80ºC

(2 min) to 200ºC (15 min) at the rate of 4ºC/min giving a total analysis time of 47 min, the GC equipped with electron capture detector was run. The injector and detector were respectively at temperatures of 225 ºC and 300ºC. The method was validated with respect to precision in terms of reproducibility of retention times and peak heights, linearity and minimum detectable quantity of the pesticides. Diuron eluted first while heptachlor epoxide was the last to elute under the operated GC conditions. The chromatographic detector was more sensitive to endosulfan and endosulfan with Minimum Detectable Quantity (MDQ) of 0.002 ng. The detector was however, less sensitive to captan with MDQ of 0.08 ng. Margins of errors associated with the precision of the method in terms of reproducibility of 11 retention times yielded standard deviation in the range of 0.026-0.063.

Chia-chang *et. al*., (2009) developed a method to determine 19 carbamate pesticides in tea samples. Different parameters was optimized, such as the type of extraction solvents, clean-up cartridges, and elution solvents were carried out. The method used acetonitrile as extraction solvent, amino cartridge for adsorbents and acetone-n-hexane as the eluting solution. 19 carbamate residues were analyzed by high-pressure liquid chromatography (HPLC) with fluorescence detector. The results showed good linearity bycorrelation coefficients of more than 0.9999 for all analyses. Limits of detection and quantification varied from 0.0005–0.023 mgL−1,0.008–0.077 mg L−1,respectively. Recoveries of 16 carbamate pesticides ranged from 65% to 135% at the spiked level of 0.5,1.0 and 2.0 mg L−1. The relative standard deviations were lower than 20% and coefficient of variations were lower than 15%.So the results indicate that the proposed method is an effective multi and trace level screening determination of carbamate pesticides residues for tea samples.

Islam *et al*., (2009) conducted a research on "Residue analysis of difenoconazole, emamectin benzoate and fenazaquin on tomatoes using high pressure liquid chromatography"to study the dissipation rates of three pesticides, difenoconazole (Score 25%EC), emamectin benzoate (Proclaim 5% SG) and fenazaquin (Pride 200, 20% SC) at Shanessa Village, Dhakahlia Governorate, Egypt. The pesticides were sprayed at recommended doses @ 50 Ml/100 liter, 60 g and 300 ml in 100 liters water, for difenoconazole, emamectin benzoate and fenazaquin respectively on the tomato plants after three months of cultivation. The pesticide treated tomato fruits were randomly sampled in triplicates (100g per field replicate) after 1 hr, 1, 3, 6, 10, and 15 days period after application. Samples were extracted, cleaned up, then analyzed using HPLC method. The half-life values were 3.16, 0.6 and 2.4 days for difenoconazole, emamectin benzoate and fenazaquin, respectively. The pre-harvest intervals (PHI) were

determined to be 8, 3 and 1 days for tomatoes treated with difenoconazole, emamectin benzoate and fenazaquinunderprevailed local field conditions, respectively

Islam *et. al.,* (2009) conducted a study on "Analysis of Some Pesticide Residues in Cauliflower by High Performance Liquid Chromatography". In his study reported a method based on High Performance Liquid Chromatography (HPLC)for determination of pesticide residues used in Cauliflower. 4 different pesticides (diazinon, malathion, chlorpyrifos and cypermethrin) at recommended dose and double of recommended dose were analyzed for residual contents. At some days after application of application sample were collected. Commercial cauliflowers sample were collected form market of Dhaka city.) as mobile phase, for the separation, identification and quantification of all these analytes using acetonitrile-water (70:30, v/v) Reversed-phase HPLC system with UV detection was used. Limit of detection was 0.02mgkg-1. Calibration curve show that construction for the analytes spiked into samples followed liner relationships with good correlation coefficient (R^2>0.990). in his analysis vegetable treated with diazinon and chlorpyrifos at recommended and double of recommended dose, residual amounts above respectives MRL value were found.

Polyiem *et. al.,* (2008) developed a method for detecting 20 organophosphate (OP) pesticide residues in vegetable and fruit matrices using gas chromatographic- flame photometric detection. From well-homogenized vegetable or fruit samples OP pesticide residues were extracted using acetonitrile and clean-up with graphite carbon black solid phase extraction. By GC-FPD, the clean OP residues' extract was dissolved in ethyl acetate and analyzed. 20 OP pesticides mean recovery (±SD) was 92.9 (±10.8) % and individual mean ranged from 76.8 % (methamidophos) to 114 % (triazophos). Limits of detection of 20 OP pesticides ranged from 0.0003 mg/kg (diazinon) to 0.015 mg/kg (azinphos-methyl) which are well below the Codex maximum residue limits (MRLs).

Butler *et. al.,* (2008) under took a study on "Analysis of pesticide residues in lettuce using modified quechers extraction technique and single quadrupole GC/MS" to determine pesticide residue in vegetables by a new sample preparation method, QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe), and published recently as AOAC Method 2007.01.1 By using a single step buffered acetonitrile (MeCN) extraction and liquid-liquid partitioning from water in the sample by salting out with sodium acetate and magnesium sulfate (MgSO4), the sample preparation is shortened.1 This technical note describes the application of the QuEChERS sample preparation procedure to determine of pesticide residues in a lettuce matrix using gas chromatography/mass spectrometry (GC/MS) on the

Thermo Scientific TRACE GC Ultr and Thermo Scientific DSQ single quadrupole mass spectrometer. Thermo Scientific Quan Lab Forms 2.5 software was used for data review and reporting. The MeCN extract is solvent exchanged to hexane/acetone for splitless injection with detection by electron ionization and selected ion monitoring . By preparing matrix spikes at 5 ng/g and 50 ng/g, a calibration curve was constructed in iceberg lettuce and then the precision and accuracy of the analytical method were tested.

Iqbal *et. al*., (2007), conducted a research on "Determination of pesticide residues in brinjal fruit at supervised trial." To determine Chlorpyriphos, Acephate, Dichlorovos, Carbofuran and Imidachloprid residues in brinjal by adopting HPTLC method, Supervised field trial was done during May, 2006. Directly these pesticides were sprayed on the brinjal crop. After 0, 3 and 7th day after application data were recorded. These samples were treated with organic solvent ethyl acetate and cleaned up by activated charcoal. All the samples were contaminated with pesticide residues except Imidachloprid. After 0 day the amount of pesticide residues was maximum followed by 3rd day that contained lesser amount of insecticide residue and after 7th day the amount of these residues were negligible in the brinjal fruit. It was concluded that the brinjal fruit was suitable for the consumption of public after three days without posing any hazard to human health.

Mukherjee, (2002) conducted an experiment on "Pesticides residues in vegetables in and around delhi''. His research presents the development of a multiresidue method for the estimation of 30 insecticides, 15 organochlorine insecticides and 6 organophosphorous insecticides, 9 synthetic pyrithoids and 2 herbicides and their quantification in vegetables. His monitoring study shows that though all the vegetable samples were contaminated with pesticides, only 31% of the sample contained pesticides above the prescribed tolerance limit.

Gamon *et. al*., (2001) conducted a research on "Multiresidue Determination of Pesticides in Fruit and Vegetables by Gas Chromatography" to determined the Pesticide residues in fruit and vegetables by gas chromatography/tandem mass spectrometry (GC/MS/MS). Electron impact (EI)/MS/MS and chemical ionization (CI)/MS/MS were 15 developed for 80 compounds(organochlorine, organophosphorus, organonitrogen, and pyrethroids) providing unambiguous spectral confirmation for these complex matrixes. The pesticide residues were extracted from samples with acetone followed by a mixture of dichloromethane petroleum ether. Two injections per sample were needed for determination of the entire pesticide list by EI/MS/MS and CI/MS/MS. Initial steps involving cleanup and concentration of extracts were removed. The excellent selectivityas well as good linearity allowed quantification and identification of low levels of pesticides in the most difficult matrixes.

Chapter III

Materials and Methods

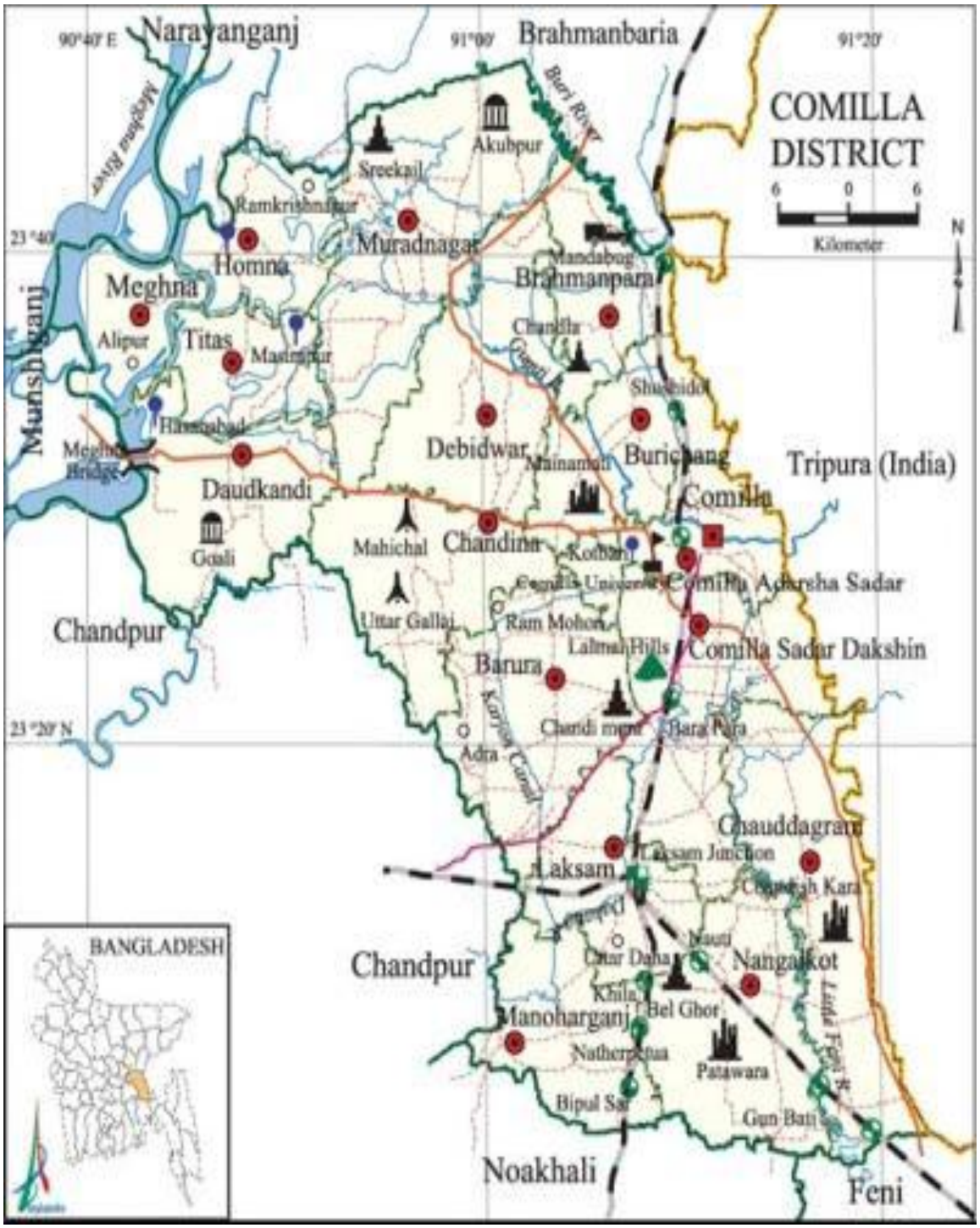
Chapter III

Materials and Methods

The vegetable (cabbage and Okra) samples were collected from different markets of Cumilla district and carried to the Pesticide Analytical Laboratory, Entomology Division, BARI, Joydebpur,Gazipur for pesticide residue analysis during September 2016 to March 2017. From the collection of samples to the final analysis, all way required a number of processes which are described below.

3.1 Study area

The study area included major five markets of Cumilla. The area of Cumilla district is about 3085.17 km, located between 23.27º N and 91.12 º E latitudes. It is under Chittagong Division. There are 10 Municipalities in Comilla named Baruna, Chauddagram, Homna, Comilla, ComillaDakkhin, Nangalkot, Chandina, Daudkandi, Debidawar and Laksham. The number of Upazilla (sub district) in Comilla district is 16, named- ComillaSadar, Homna, Laksham, Muradnagor, Debidar, Barura, Daudkandi, Burichong, Chandina, Chaddagram, Nagolcot, Bhrammonpara, Meghna, Titas, Monohorgonj and SadarDokkhin containing 185 Unions, 2455 Mauzas and 3532 Villages.



3.2 Sample collection

A total of 80 samples (40 cabbages and 40 Okra) were collected for this study. Eight samples of cabbage and Eight samples of lady's finger were collected from each market.

Table 1. Sources and places of collection of cabbage samples

Area of collection	Sample ID
Daudkandi Bazar	CuDaCb-1
	CuDaCb-2
	CuDaCb-3
	CuDaCb-4
	CuDaCb-5
	CuDaCb-6
	CuDaCb-7
	CuDaCb-8
Chandina Bazar	CuChCb-1
	CuChCb-2
	CuChCb-3
	CuChCb-4
	CuChCb-5
	CuChCb-6
	CuChCb-7
	CuChCb-8
Devidar Bazar	CuDeCb-1
	CuDeCb-2
	CuDeCb-3
	CuDeCb-4
	CuDeCb-5
	CuDeCb-6
	CuDeCb-7
	CuDeCb-8
Moynamoti Bazar	CuMoCb-1
	CuMoCb-2
	CuMoCb-3
	CuMoCb-4
	CuMoCb-5
	CuMoCb-6
	CuMoCb-7
	CuMoCb-8
Kongsonagar Bazar	CuKoCb-1
	CuKoCb-2
	CuKoCb-3
	CuKoCb-4
	CuKoCb-5
	CuKoCb-6
	CuKoCb-7

Table 2: Sources and places of collection of cauliflower samples

Area of collection	Sample ID
Daudkandi Bazar	CuDaLf-1
	CuDaLf-2
	CuDaLf-3
	CuDaLf-4
	CuDaLf-5
	CuDaLf-6
	CuDaLf-7
	CuDaLf-8
Chandina Bazar	CuChLf-1
	CuChLf-2
	CuChLf-3
	CuChLf-4
	CuChLf-5
	CuChLf-6
	CuChLf-7
	CuChLf-8
Devidar Bazar	CuDeLf-1
	CuDeLf-2
	CuDeLf-3
	CuDeLf-4
	CuDeLf-5
	CuDeLf-6
	CuDeLf-7
	CuDeLf-8
Moynamoti Bazar	CuMoLf-1
	CuMoLf-2
	CuMoLf-3
	CuMoLf-4
	CuMoLf-5
	CuMoLf-6
	CuMoLf-7
	CuMoLf-8
Kongsonagar Bazar	CuKoLf-1
	CuKoLf-2
	CuKoLf-3
	CuKoLf-4
	CuKoLf-5
	CuKoLf-6
	CuKoLf-7
	CuKoLf-8

3.3 Sample preparation for analysis

The collected samples were carried to the Pesticide Analytical Laboratory, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipur on the day of collection. The whole unit of each sample cut into small pieces and mixed properly. Clean air tight polythene bags were used to store chopped sample in refrigerator at - 20°C until extraction and cleanup process started.

3.4 Chemicals and reagents

The standard of Chlorpyrifos, Acephate, Diazinon, Dimethoate, Quinalphos, Malathion and Fenitrothion were obtained from Sigma-Aldrich (St Louis, MO, USA) via Bangladesh Scientific Pvt. ltd. Dhaka, Bangladesh. Standards of all pesticides contained >99.6% purity.

Methanol, acetone, gradient grade acetonitrile, sodium chloride (NaCl), anhydrous magnesium sulphate ($MgSO_4$) and Primary Secondary Amine (PSA) were purchased from Bangladesh Scientific Pvt. ltd. Dhaka, Bangladesh.

3.5 Analytical Apparatus used

a. Electric balance, Model: AY- 220, Shimadzu Corporation, Japan (Plate 1).

b. Vortex mixer, Model: Maxi max ii, USA (Plate 2)

c. Centrifuge machine, Model: Sigma 3k 30, Germany (Plate 3)

d. GC-2010, Shimadzu corporation, Japan (Plate 4)

Plate 1. Electric Balance

Plate 2. Vortex Mixer

Plate 3. Centrifuge Machine **Plate 4.** (Gas Chromatograph GC)

In addition to the above instruments the following accessories were also used:

- Scissors
- Measuring cylinder
- Conical flask
- Volumetric flask
- Tray
- Knife
- Spatula
- Funnel
- Test tube
- Micro pipette
- Aluminum foil
- Para film
- Centrifuge tube

Some pictorial view related to sample preparation:

Plate 5: Chopping of collected Sample

Plate 6:Homogenization of collected Sample

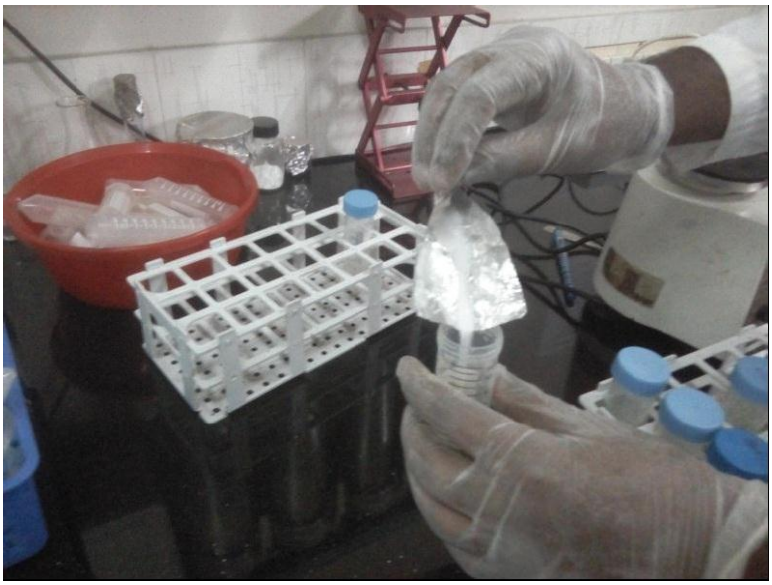


Plate 7: Adding of salt (NaCl and MgSO4)

Plate 8: Centrifuging the sample

Plate 9 : Filtration through PTFE Filter

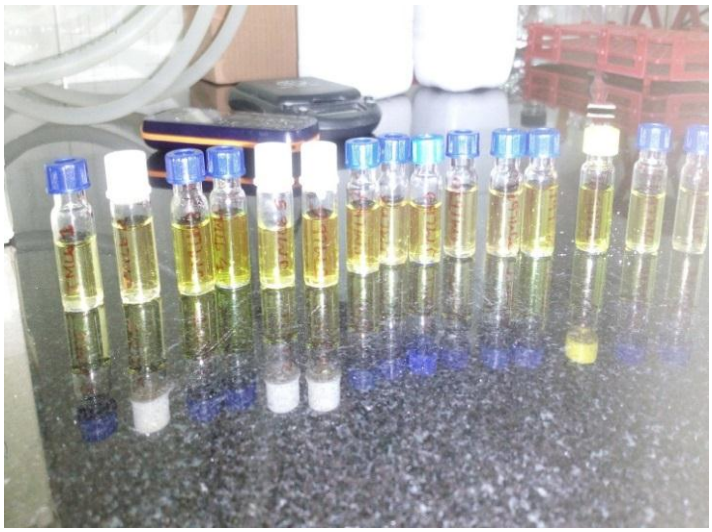


Plate 10. Sample extract ready for injection

3.6 Preparation of pesticide standard solution

Pesticide standard stock solutions of acephate, chlorpyrifos, diazinon, dimethoate, quinalphos, malathion and fenitrothion were prepared separately in acetone at a concentration of 1000 mg/L and stored at -20°C until use. A mixed standard solution of 50 mg/L in acetone containing all the aforementioned pesticides was prepared by adding the appropriate volume of each individual stock solution in a 50 ml volumetric flask and made to volume by addition of acetone. An intermediate mixed standard solution of 10 mg/L in acetone was prepared from the mixed standard solution of 50 mg/L. Then working standard solutions of 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 mg/L in acetone were prepared by transferring the appropriate amount from 10 mg/Lintermediate mixed standard solution into ten separate 10-mL volumetric flasks. All the standard solutions were kept in a freezer at -20°C until use.

3.7 Extraction and clean up

QuEChERS extraction method is one of the latest extraction and clean up techniques for pesticide residue analysis in food matrices which is an anagram for Quick, Easy, Cheap, Effective, Rugged and Safe. This techniques was first introduced by Anastassiades et al. (2003), which is gaining popularity day by day compared to the other existing techniques such as Supercritical Fluid Extraction (SFE), Liquid-liquid extraction (LLE), Solid phase extraction (SPE), Solid phase micro extraction (SPME), Stir bar sorptive extraction (SBSE), and Microwave assisted extraction (MAE). The technique uses a single extraction in acetonitrile and requires a very small amount of(10-15 gm) sample. A large excess of salts or buffers are added to extract to aid in theextraction of both polar and non-polar pesticide. This sample initial step simultaneously extract the pesticide from the samples and prepares it for the next dispersive solid phase extraction (d-SPE), the salts and SPE sorbents chosen for the d- SPE step serve to remove residual water and further remove matrix interference from the sample. The resulting acetonitrile extract is typically analyzed directly by gas chromatography (GC), gas chromatography-mass spectrometry (GC/MS) or liquid chromatography tandem mass spectrometry (LC/MS/MS) with proper dilution (Anon, 2011).

In this study, the QuEChERS extraction technique was used for the extraction and clean-up of samples which was modified by Prodhan et al. (2015). The chopped samples were grounded thoroughly with the fruit blender. A representative 10-g portion of thoroughly homogenized sample was weighted in a 50 mL polypropylene centrifuge tube. Then 10 mL of acetonitrile (MeCN) was added into the centrifuge tube. The centrifuge tube was closed properly and shaken vigorously for 30 s by the use of a vortex mixer. Then, 4 g of anhydrous

MgSO4 and 1 g of NaCl were added into the centrifuge tube, and it was shaken immediately by the vortex mixer for 1 minute to prevent the formation of magnesium sulfate aggregates. Afterwards, the extract was centrifuged for 5 min at 5000 rpm. An aliquot of 3 mL of the MeCN layer was transferred into a 15 mL micro centrifuge tube containing 600 mg anhydrous MgSO4 and 120 mg Primary Secondary Amine (PSA). Then it was thoroughly mixed by vortex for 30 s and centrifuged for 5 minutes at 4000 rpm. (Laboratory Centrifuges, Sigma-3K30, Germany). After centrifuge, a 1 mL

supernatant was filtered by a 0.2 µm PTFE filter, and then it was taken in a clean GC vial for injection.

3.8 Detection and quantification of pesticide residue in samples

The concentrated extracts were subjected to analysis by GC-2010 (Shimadzu) with Flame Thermionic Detector (FTD) for the detection of acephate, dimethoate, diazinon, fenitrothion, malathion, chlorpyrifos and quinalphos. The capillary column was AT-1 length was 30m, ID was 0.25mm and film thickness was 0.25µm. Helium was used as carrier and make up gas for FTD. The identification of suspected pesticide was performed by peak retention times in samples to those of peaks in the pure analytical standards. The instrument conditions are described in Table 2 and Table 3.

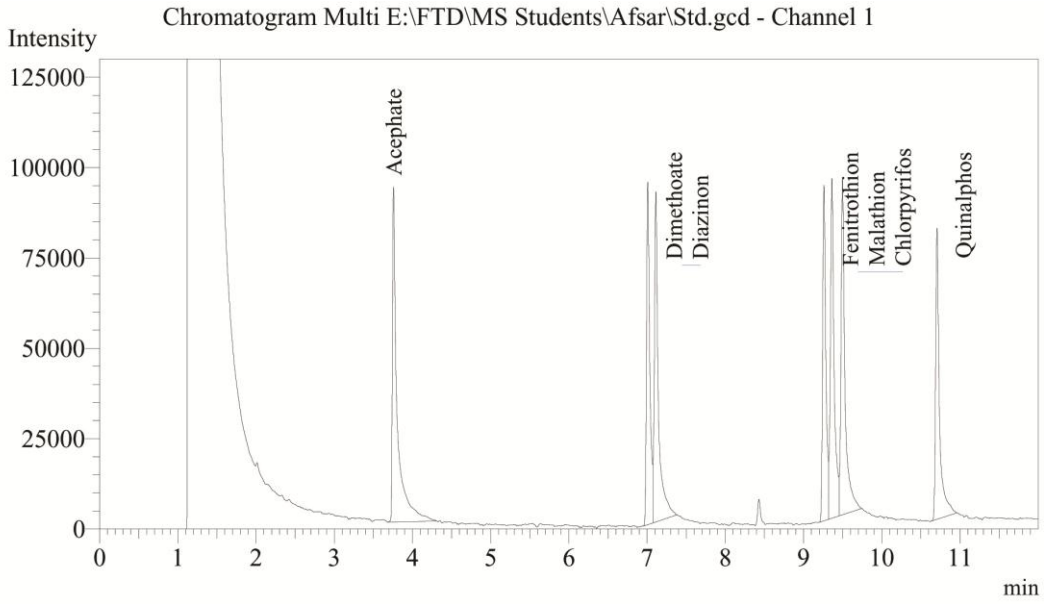


Figure 1:Typical chromatogram of seven organophosphorus insecticide standard run by GC-FTD.

Table 3: The instrument parameters for GC-FTD

Instruments	**Conditions**
Injection port SPL	Injection mode: split; temperature:250°C; flow control mode: linear velocity; split ratio: 30:0
Detector channel 1 FTD	Temperature: 280°C; current: 1.00 Pa; H_2 flow: 1.5 mL/min; stop time: 10 min; make up flow: 30 mL/min; air flow: 145 mL/min

Table 4:Conditions for column oven temperature for FTD

Column oven	Rate	Temperature (^{0}C)	Hold time (min)
Initial temperature: 150°C	**-**	**150**	**1**
	10	**220**	**2**

3.9 Preparation of Calibration curve

Prior to the injection of the sample extract, standard solutions of different concentrations of each pesticide group were prepared and injected with suitable instrument parameters. The samples were calibrated (retention time, peak area etc.) against five pointed calibration curve of standard solution of concerned pesticide (Figure 2-8). Each peak was characterized by its retention time. Sample results were expressed in mg/kg automatically by the GC software.

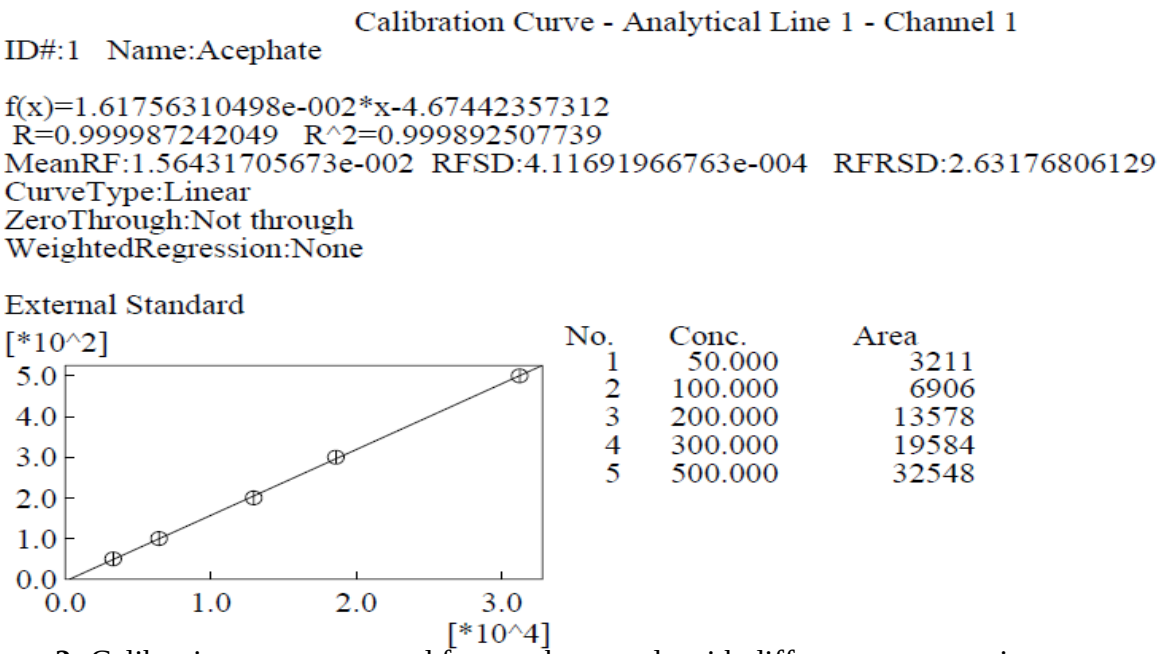
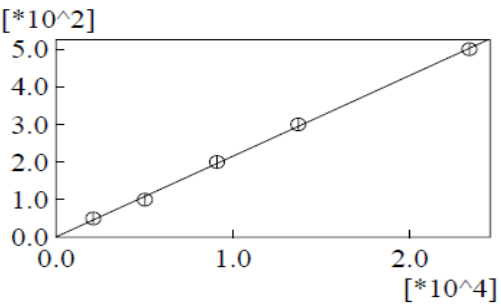


Figure 2: Calibration curve prepared for acephate made with different concentrations ranging from 50 µg/L to 500 µg/L.

ID#:2 Name:Dimethoate

f(x)=2.14476109468e-002*x+1.27409837292
R=0.999894212457 R^2=0.999926113376
MeanRF:2.17625864931e-002 RFSD:1.36709257517e-003 RFRSD:6.28184786586
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard



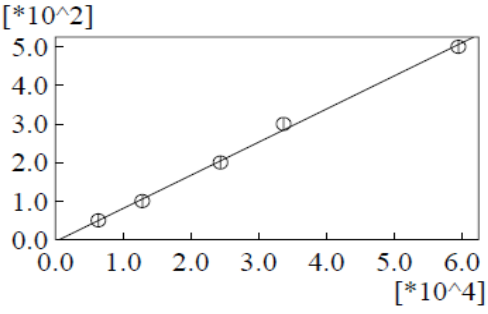
No.	Conc.	Area
1	50.000	2874
2	100.000	5247
3	200.000	9487
4	300.000	14587
5	500.000	22985

Figure 3: Calibration curve prepared for dimethoate made with different concentrations ranging from 50 µg/L to 500 µg/L.

ID#:3 Name:Diazinone

f(x)=8.58182478378e-003*x-4.76864750449
R=0.9989993676 R^2=0.997890349706
MeanRF:8.23177212761e-003 RFSD:4.50915039717e-004 RFRSD:5.47773957694
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard



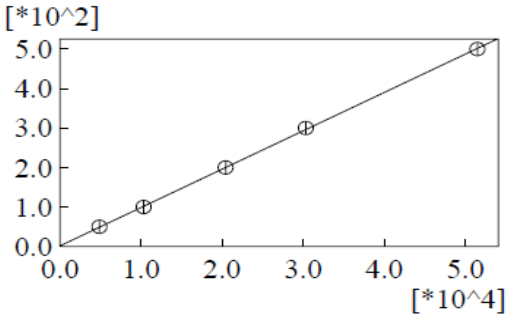
No.	Conc.	Area
1	50.000	6874
2	100.000	13214
3	200.000	23254
4	300.000	32354
5	500.000	58741

Figure 4: Calibration curve prepared for diazinone made with different concentrations ranging from 50 µg/L to 500 µg/L.

ID#:4 Name:Fenitrothion

f(x)=9.69984666697e-003*x+2.01882132141
R=0.999916224021 R^2=0.99983245506
MeanRF:9.85855366395e-003 RFSD:2.34530644934e-004 RFRSD:2.37895590903
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard



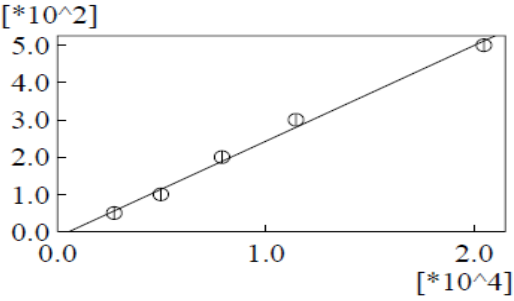
No.	Conc.	Area
1	50.000	4982
2	100.000	11425
3	200.000	21245
4	300.000	32301
5	500.000	50412

Figure 5: Calibration curve prepared for fenitrothion made with different concentrations rangingfrom 50 µg/L to 500 µg/L.

ID#:5 Name:Malathion

f(x)=2.5662119724e-002*x-13.8726059301
R=0.996793718496 R^2=0.993979245023
MeanRF:2.28770289157e-002 RFSD:3.45826768136e-003 RFRSD:15.116769289
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard



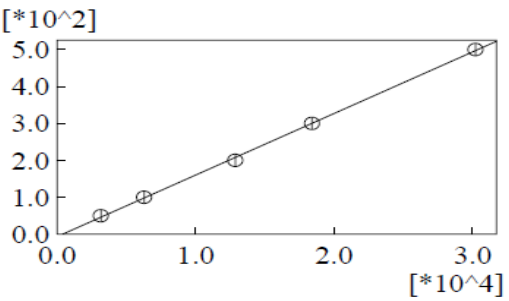
No.	Conc.	Area
1	50.000	2985
2	100.000	4475
3	200.000	7689
4	300.000	12543
5	500.000	21201

Figure 6: Calibration curve prepared for malathion made with different concentrations ranging from 50 µg/L to 500 µg/L.

ID#:6 Name:Chlorpyrifos

f(x)=1.66718969691e-002*x-6.50897807754
R=0.999687866504 R^2=0.999299859839
MeanRF:1.60231310913e-002 RFSD:4.02450756721e-004 RFRSD:2.51168610197
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard



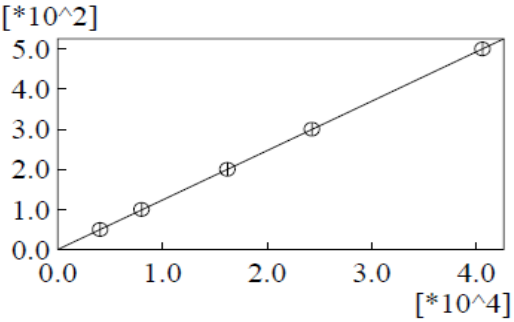
No.	Conc.	Area
1	50.000	3321
2	100.000	6684
3	200.000	13210
4	300.000	18987
5	500.000	31024

Figure 7: Calibration curve prepared for chlorpyrifos made with different concentrations ranging from 50 µg/L to 500 µg/L.

ID#:7 Name:Quinalphos

f(x)=1.2305211624e-002*x+0.670992116044
R=0.999994954248 R^2=0.999989878522
MeanRF:1.23562145806e-002 RFSD:7.05710649982e-005 RFRSD:0.571138227959
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard



No.	Conc.	Area
1	50.000	4248
2	100.000	8325
3	200.000	16895
4	300.000	23985
5	500.000	41002

Figure 8: Calibration curve prepared for quinalphos made with different concentrations ranging from 50 µg/L to 500 µg/L.

Chapter IV

Results and Discussion

CHAPTER IV

RESULTS AND DISCUSSIONS

80 samples of vegetable (cabbage and okra) were collected from 5 different markets of Cumilla (Chindina Bazar, Daudkandi Bazar, Debidwar Bazar, Kangsonagar Bazar and Moynamoti Bazar) of Cumilla district to detect and quantify pesticide residues. The results obtained from this study are presented and described in this chapter using figures and tables.

4.1 Pesticide residues in cabbage

The concentrated extracts of cabbage samples collected from different markets of Cumilla district were analyzed by GC-2010 (Shimadzu) with Flame Thermionic Detector (FTD) with the pre-set parameters. Figure 9-13 shows the chromatograms of the injected extracts of cauliflower sample containing detected pesticides.

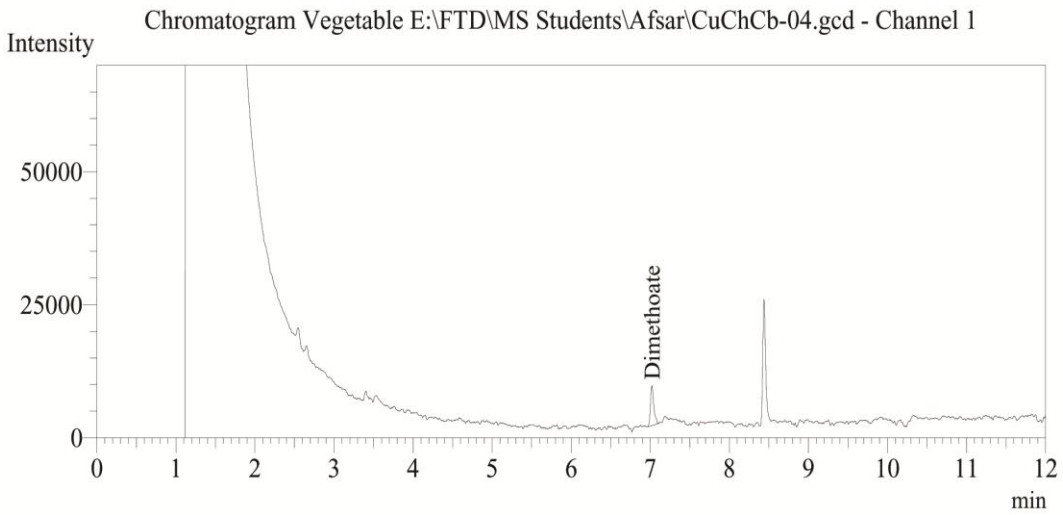


Figure 9: Chromatogram of dimethoate found in one of the cabbage sample (CuChCb-4) collected from Chandina bazar.

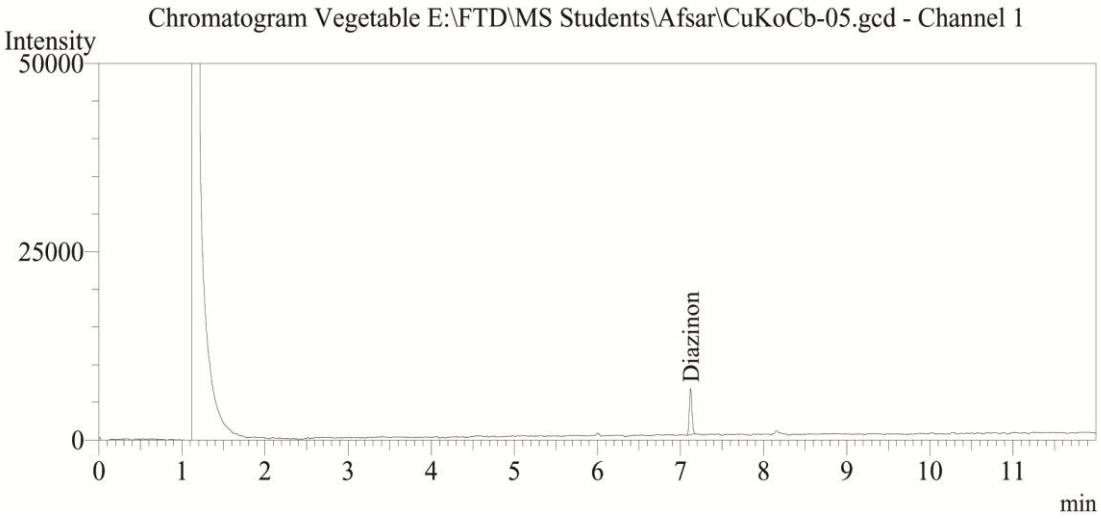


Figure 10: Chromatogram of diazinon found in one of the cabbage sample (CuKoCb-5) collected from kangsonagar bazar.

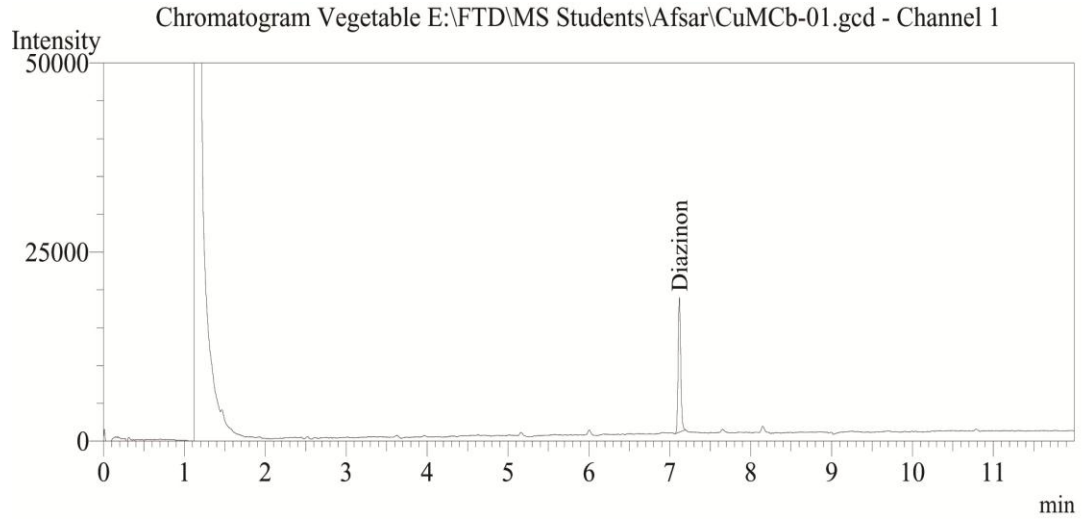


Figure 11: Chromatogram of diazinon found in one of the cabbage sample (CuMoCb-1) collected from Moynamoti bazar.

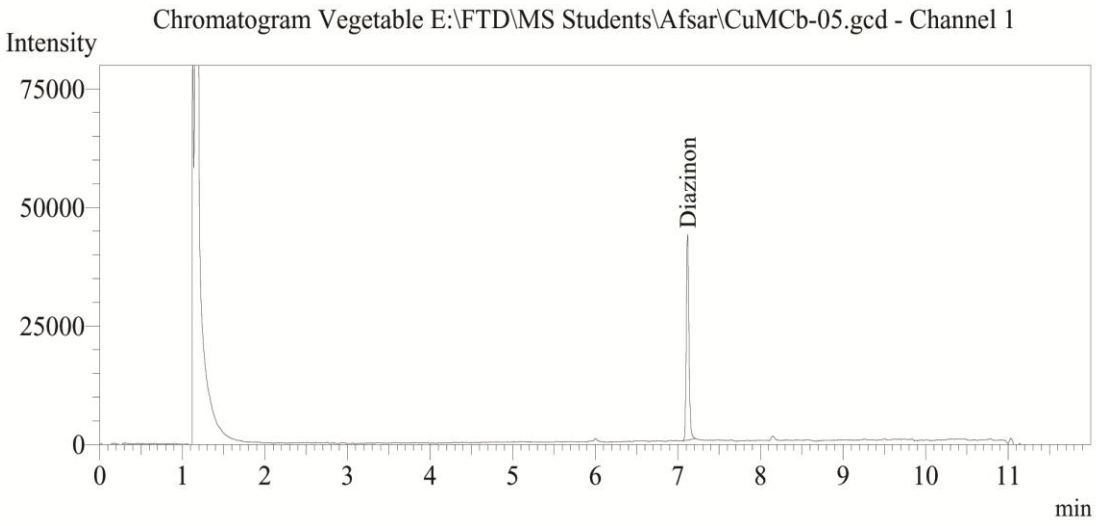


Figure 12: Chromatogram of diazinon found in one of the cabbage sample (CuMoCb-5) collected from Moynamoti bazar.

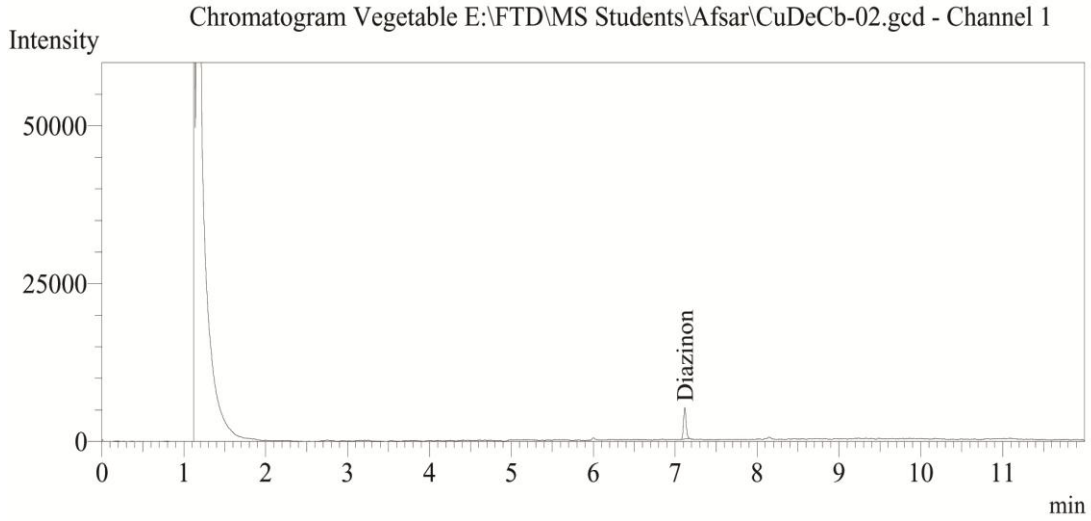


Figure 13: Chromatogram of diazinon found in one of the cabbage sample (CuDeCb-2) collected from Debidwar bazar.

The level of pesticide residues found in the analyzed cabbage samples and their maximum residue levels are outlined in Table 6.

Table 5. The level of residues (mg/kg) of different pesticides found in the analyzed cabbage samples.

Area of collection	**Sample ID**	**Name of detected pesticide**	**Level of residue (mg/kg)**	**MRLs (mg/kg)**
Daudkandi Bazar	CuDaCb-1	ND	-	
	CuDaCb-2	ND	-	
	CuDaCb-3	ND	-	
	CuDaCb-4	ND	-	
	CuDaCb-5	ND	-	
	CuDaCb-6	ND	-	
	CuDaCb-7	ND	-	
	CuDaCb-8	ND	-	
Chandina Bazar	CuChCb-1	ND	-	
	CuChCb-2	ND	-	
	CuChCb-3	ND	-	
	CuChCb-4	Dimethoate	0.163	**0.02**
	CuChCb-5	ND	-	
	CuChCb-6	ND	-	
	CuChCb-7	ND	-	
	CuChCb-8	ND	-	
Debidwar Bazar	CuDeCb-1	ND	-	
	CuDeCb-2	Diazinon	0.059	**0.01**
	CuDeCb-3	ND	-	
	CuDeCb-4	ND	-	
	CuDeCb-5	ND	-	
	CuDeCb-6	ND	-	
	CuDeCb-7	ND	-	
	CuDeCb-8	ND	-	
Moynamoti Bazar	CuMoCb-1	Diazinon	0.217	**0.01**
	CuMoCb-2	ND	-	
	CuMoCb-3	ND	-	
	CuMoCb-4	ND	-	
	CuMoCb-5	Diazinon	0.531	**0.01**
	CuMoCb-6	ND	-	
	CuMoCb-7	ND	-	
	CuMoCb-8	ND	-	
Kangsonagar Bazar	CuKoCb-1	ND	-	
	CuKoCb-2	ND	-	
	CuKoCb-3	ND	-	
	CuKoCb-4	ND	-	
	CuKoCb-5	Diazinon	0.074	**0.01**
	CuKoCb-6	ND	-	
	CuKoCb-7	ND	-	
	CuKoCb-8	ND	-	

Forty samples of cabbage collected from 5 different markets of Cumilla district (Chindina Bazar, Daudkandi Bazar, Devidar Bazar, Konshonagar Bazar and Moynamoti Bazar) and were analyzed to find out the presence of left over residue of seven pesticides (acephate, diazinon, dimethoate, malathion, fenitrothion, chlorpyrifos and quinalphos).

Out of 40 samples of cabbage, 5 samples (12.5% of the total number of samples) contained pesticide residues and 35 samples (87.5% of the total number of samples) contained no detectable residues of the pesticides. The present results can be compared to Islam *et al.* (2014). They have collected 42 samples of brinjal, cauliflower and country bean from fields and markets of Narsingdi district, Bandgladesh, where they found 15 samples (above 68% of total samples) contained no residues of the sought pesticides. The findings of the present study can also be compared with Akter *et al.* (2017). They have been monitored pesticide residues in eggplant collected from Mymensingh district and found that among the 50 analyzed samples, 11 (22% of the total number of the samples) contained pesticide residues of diazinon, dimethoate, quinalfos, and chlorpyrifos, of which, 2 had multiple pesticide residues and 5 samples contained residue above the European Union maximum residue limit (EU-MRLs). Chlorpyrifos was detected as the most used pesticide in eggplant in the studied area.

Pesticide residue status in the samples of cabbage collected from Daudkandi area:

Eight cabbage samples were collected from Daudkandi Bazar area, among them no samples contained detectable pesticide residues.

Pesticide residue status in the samples of cabbage collected from Chandina area:

From Chandina Bazar, eight samples were collected. Of which one sample (CuChCb-4) contained residues of dimethoate (0.163 mg/kg), which was above the EU-MRL (European Commission 2015). But other seven samples contained no detectable pesticide residues.

Pesticide residue status in the samples of cabbage collected from Debidwar area:

Out of eight cabbage sample, one sample (CuDeCb-2) contained residue of diazinon (0.059 mg/kg) which was collected from Debidwar Bazar. But other seven samples contained no detectable pesticide residues. The level of detected residue of dimethoate was above MRL (0.02 mg/kg).

Pesticide residue status in the samples of cabbage collected from Maynamoti area:

From eight cabbage sample of Moynamoti bazar, two sample (CuMoCb-1 and CuMoCb-5) were contained residue of diazinon (0.217 mg/kg and 0.531mg/kg, respectively) which were above the EU-MRL (European Commission 2015).

Pesticide residue status in the samples of cabbabe collected from Kansonagar area:

From eight cabbage sample of Kansonagar Bazar, one sample (CuKoCb-5) was contained residue of diazinon (0.074 mg/kg), which are above the EU-MRL (European Commission 2015).

4.2 Pesticide residues in lady's finger

The concentrated extracts of lady's finger samples collected from different markets of Cumilla district were analyzed by GC-2010 (Shimadzu) with Flame Thermionic Detector (FTD) with the pre-set parameters. Figure 9-13 shows the chromatograms of the injected extracts of lady's finger sample containing detected pesticide

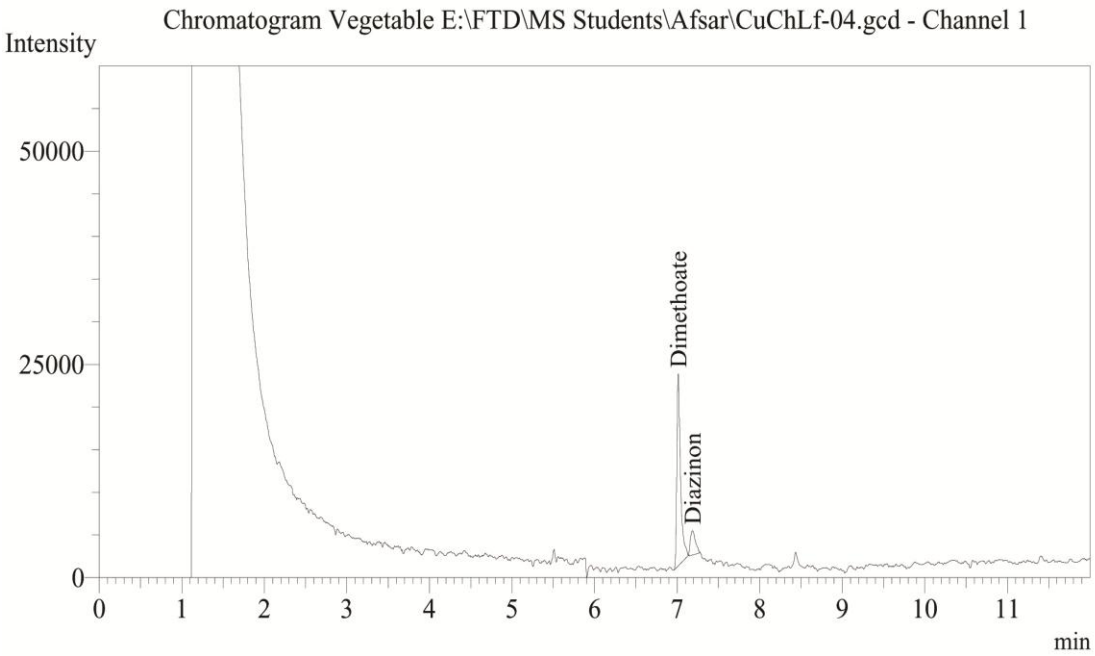


Figure 14: Chromatogram of diazinon and dimethoate found in one of the lady's finger sample (CuChLf-4) collected from Chandina bazar.

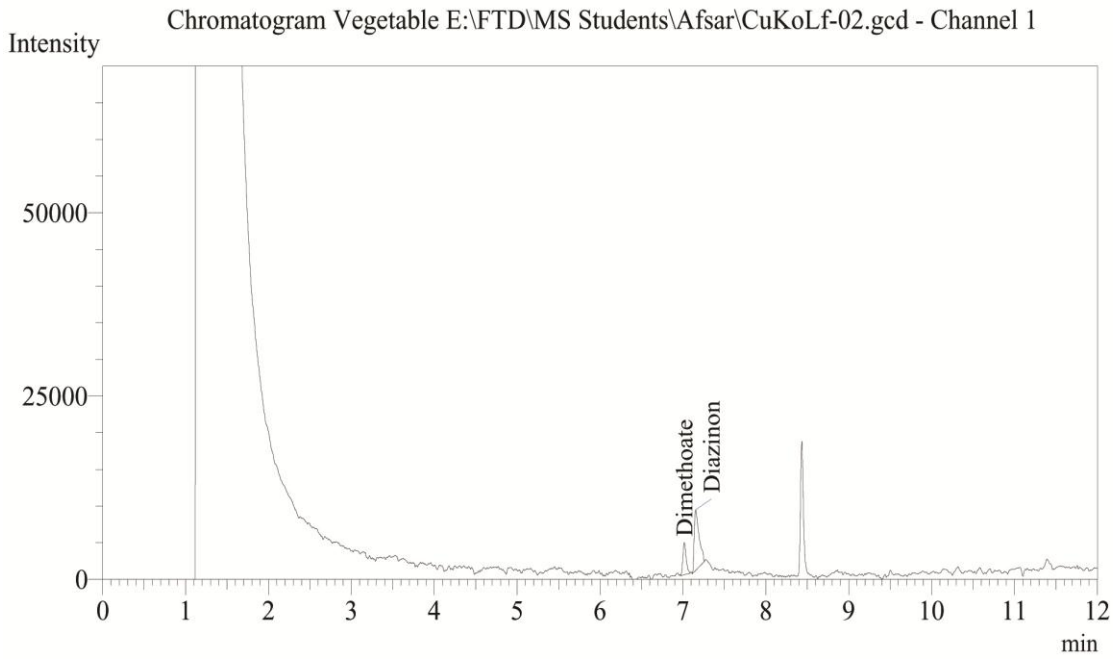


Figure 15: Chromatogram of diazinon and dimethoate found in one of the lady's finger sample (CuKoLf-2) collected from Kangsonagar bazar.

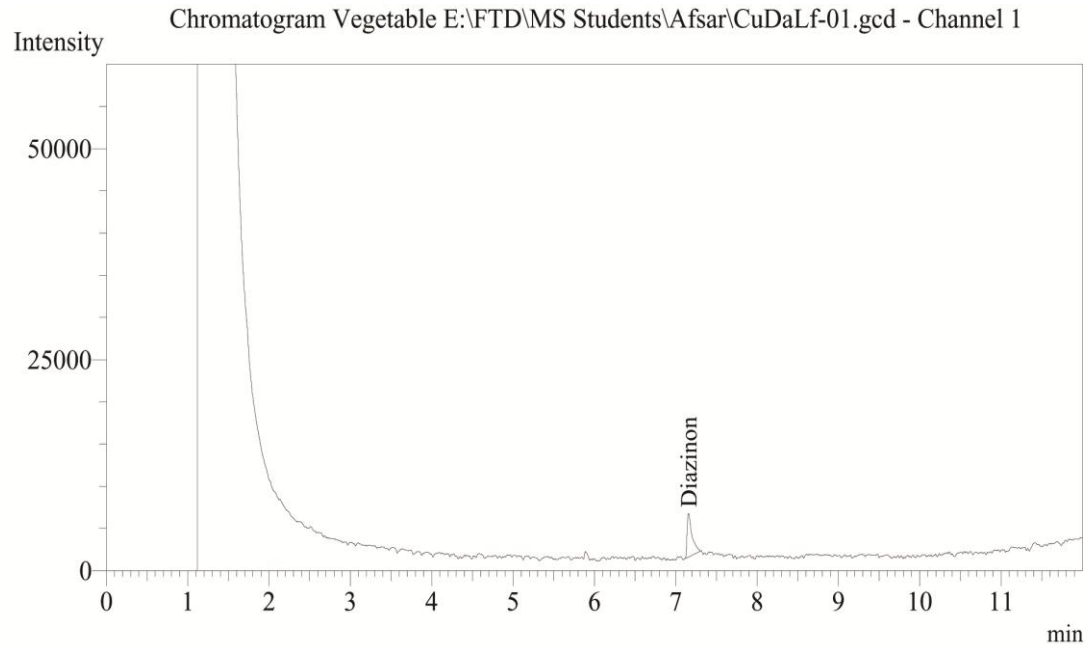


Figure 16: Chromatogram of diazinon found in one of the lady's finger sample (CuDaLf-1) collected from Daudkandi bazar.

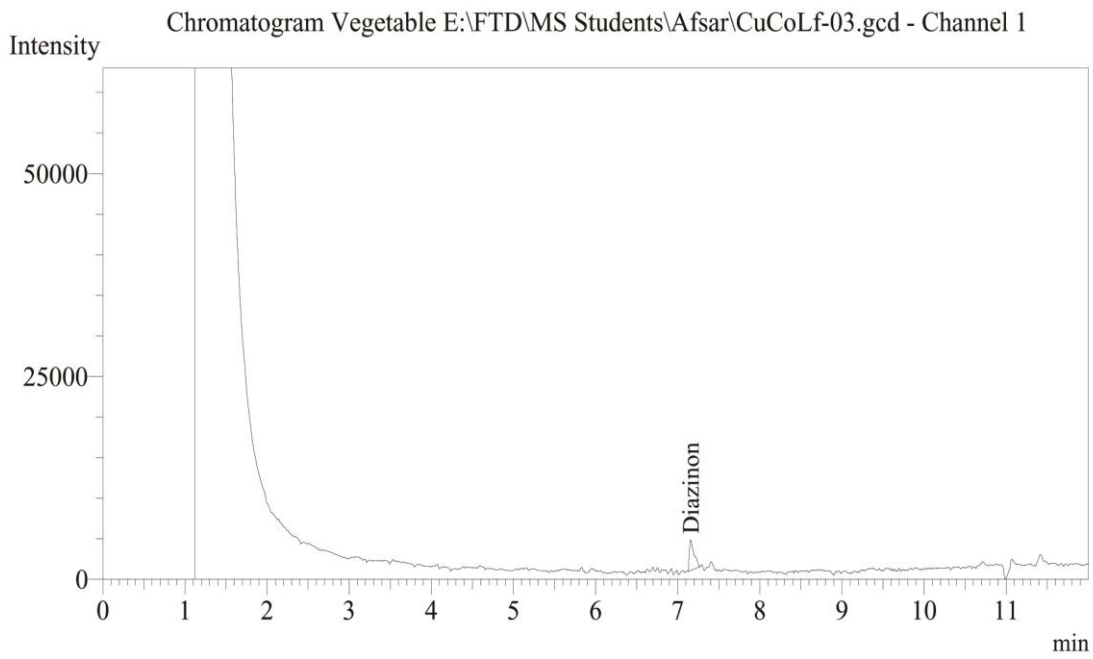


Figure 17: Chromatogram of diazinon found in one of the lady's finger sample (CuMoLf-3) collected from Moynamoti bazar.

The level of pesticide residues found in the analyzed cabbage samples and their maximum residue levels are outlined in Table 7.

Table 6. The level of residues (mg/kg) of different pesticides found in the analyzed lady's finger samples.

Area of collection	**Sample ID**	**Name of detected pesticide**	**Level of residue (mg/kg)**	**MRLs (mg/kg)**
Daudkandi Bazar	CuDaLf-1	Diazinon	0.119	**0.01**
	CuDaLf-2	ND	-	
	CuDaLf-3	ND	-	
	CuDaLf-4	ND	-	
	CuDaLf-5	ND	-	
	CuDaLf-6	ND	-	
	CuDaLf-7	ND	-	
	CuDaLf-8	ND	-	
Chandina Bazar	CuChLf-1	ND	-	
	CuChLf-2	ND	-	
	CuChLf-3	ND	-	
	CuChLf-4	Dimethoate Diazinon	0.518 0.066	**0.02** **0.01**
	CuChLf-5	ND	-	
	CuChLf-6	ND	-	
	CuChLf-7	ND	-	
	CuChLf-8	ND	-	
Debidwar Bazar	CuDeLf-1	ND	-	
	CuDeLf-2	ND	-	
	CuDeLf-3	ND	-	
	CuDeLf-4	ND	-	
	CuDeLf-5	ND	-	
	CuDeLf-6	ND	-	
	CuDeLf-7	ND	-	
	CuDeLf-8	ND	-	
Moynamoti Bazar	CuMoLf-1	ND	-	
	CuMoLf-2	ND	-	
	CuMoLf-3	Diazinon	0.790	**0.01**
	CuMoLf-4	ND	-	
	CuMoLf-5	ND	-	
	CuMoLf-6	ND	-	
	CuMoLf-7	ND	-	
	CuMoLf-8	ND	-	
Kongsonagar Bazar	CuKoLf-1	ND	-	
	CuKoLf-2	Dimethoate Diazinon	0.089 0.184	**0.02** **0.01**
	CuKoLf-3	ND	-	
	CuKoLf-4	ND	-	
	CuKoLf-5	ND	-	
	CuKoLf-6	ND	-	
	CuKoLf-7	ND	-	
	CuKoLf-8	ND	-	

Fourty samples of lady's finger collected from 5 different markets of Cumilla district (Chindina Bazar, Daudkandi Bazar, Devidar Bazar, Konshonagar Bazar and Moynamoti Bazar) and were analyzed to find out the presence of left over residue of seven pesticides (acephate, diazinon, dimethoate, malathion, fenitrothion, chlorpyrifos and quinalphos).

Out of 40 samples of lady's finger, 4 samples (10% of the total number of samples) contained pesticide residues and 35 samples (90% of the total number of samples) contained no detectable residues of the pesticides. The present results can be compared to Islam *et al.* (2014). They have collected 42 samples of brinjal, cauliflower and country bean from fields and markets of Narsingdi district, Bandgladesh, where they found 15 samples (above 68% of total samples) contained no residues of the sought pesticides. The findings of the present study can also be compared with Akter *et al.* (2017). They have been monitored pesticide residues in eggplant collected from Mymensingh district and found that among the 50 analyzed samples, 11 (22% of the total number of the samples) contained pesticide residues of diazinon, dimethoate, quinalfos, and chlorpyrifos, of which, 2 had multiple pesticide residues and 5 samples contained residue above the European Union maximum residue limit (EU-MRLs). Chlorpyrifos was detected as the most used pesticide in eggplant in the studied area.

Pesticide residue status in the samples of lady's finger collected from Daudkandi area:

From Daudkandi Bazar area, eight lady's finger samples were collected, among them one sample (CuDaLf-1) contained residues of Diazinon (0.119 mg/kg) which was above the EU-MRL (European Commission 2015) but other samples contain no detectable amount of pesticide.

Pesticide residue status in the samples of lady's finger collected from Chandina area:

From Chandina Bazar, eight samples were collected. Of which one sample (CuChLf-4) contained multiple residues of dimethoate (0.518 mg/kg) and diazinon (0.066 mg/kg) which were above the EU-MRL (European Commission 2015). But other seven samples contained no detectable pesticide residues.

Pesticide residue status in the samples of lady's finger collected from Debidwar area:

Eight lady's finger samples were collected from Debidwar Bazar area, among them no samples contained detectable pesticide residues.

Pesticide residue status in the samples of lady's finger collected from Maynamoti area:

From eight lady's finger sample of Moynamoti bazar, one sample (CuMoLf-3) were contained residue of diazinon (0.790 mg/kg) which was above the EU-MRL (European Commission 2015).

Pesticide residue status in the samples of lady's finger collected from Konsonagar area:

From Konsonagar Bazar, eight samples were collected. Of which one sample (CuKoLf-2) contained multiple residues of dimethoate (0.089 mg/kg) and diazinon (0.184 mg/kg) which were above the EU-MRL (European Commission 2015). But other seven samples contained no detectable pesticide residues.

Chapter V

Summary and Conclusion

CHAPTER V

SUMMARY AND CONCLUSION

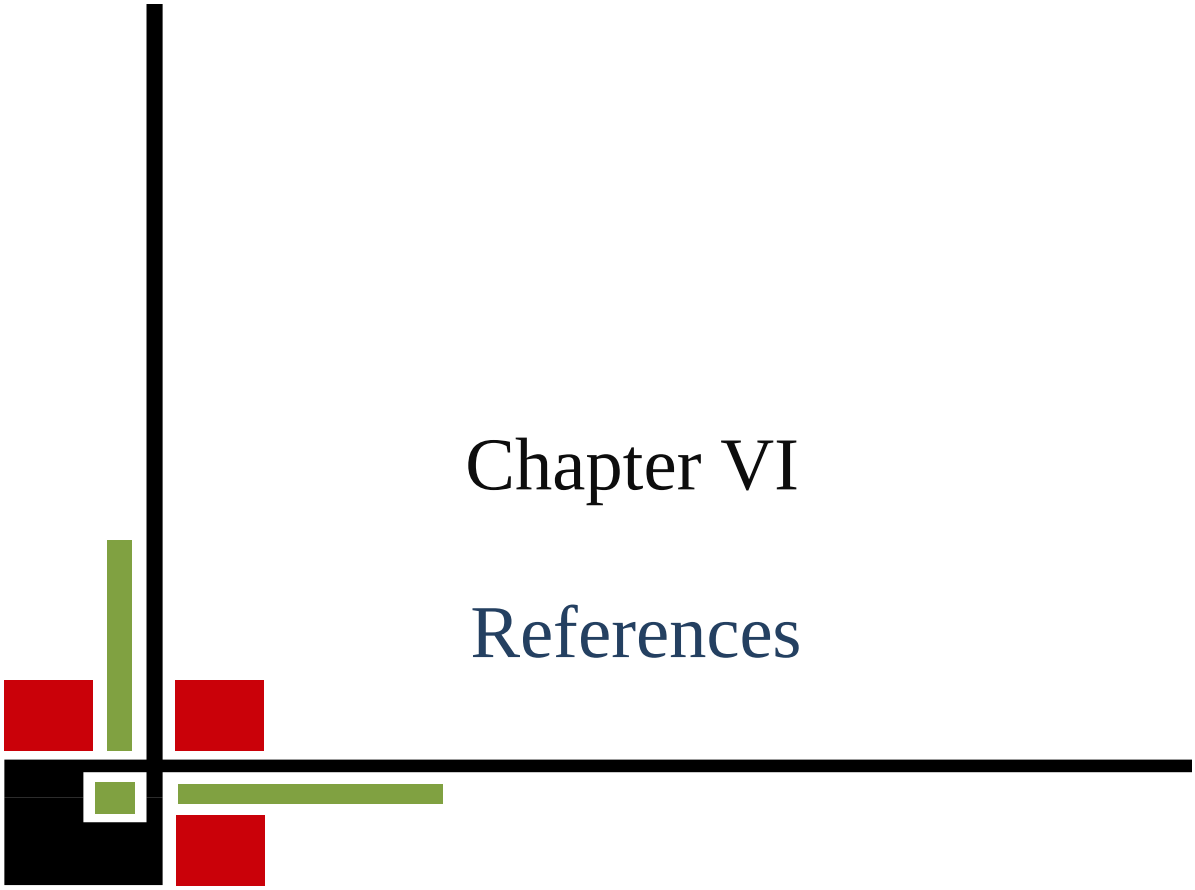
The purpose of this research was to identify and determine of pesticide residue level present in the vegetables collected from different location of cumilla district. For research purpose, forty samples of cabbage and forty samples of lady's finger were collected from five different market of cumilla district such as Daudkandi Bazar, Chandina Bazar, Moynamoti Bazar, Debidwar Bazar and Konsonagar Bazar and these samples were carried to the Pesticide Analytical Laboratory, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipur, Bangladesh. The QuEChERS extraction technique was applied for the extraction and cleanup of the collected sample. Gas chromatography associated with flame thermionic detector (FTD) was used to identify and quantify the level of pesticide residues present in the extracted samples. Seven most commonly used pesticides such as diazinon, chlorpyrifos, acephate, malathion, dimethoate, fenitrothion, and quinalphos were selected for this study.

Among the forty analyzed cabbage samples, 5 samples (12.5% of the total number of samples) contained residue of diazinon and dimethoate. Among the forty lady's finger samples, 4 samples (10% of the total number of samples) contained residue of diazinon and dimethoate where two samples contained multiple residues.

Among the five markets of Cumilla district, samples from of Daudkandi bazar only 6.25% (out of 16 samples only 1 sample) samples contained pesticide residue, samples from Chandina bazar only 12.5% (out of 16 samples only 2 samples) samples contained pesticide residue,samples from Debidwar bazar only 6.25% (out of 16 samples only 1 sample) samples contained pesticide residue,samples from Moynamoti bazar only 18.75% (out of 16 samples only 3 samples) samples contained pesticide residue and samples from Kangsonagar bazar only 12.5% (out of 16 samples only 2 samples) samples contained pesticide residue. From the above findings we can say that Daudkandi and Debidwar bazar is more safe for consumers than other three markets of Cumilla district.

Now a day's the presence of pesticide residue in food especially in vegetables are a great concern and a safety issue for the consumers. The findings of the present study represent the over all condition of pesticide residue load in the selected vegetables which was collected from different market of cumilla district. The results of the present study indicate that the

farmers of Cumilla district are using chlorpyrifos, dimethoate and quinalphos indiscriminately. This study will help to increase public awareness as well.



Chapter VI

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CHAPTER VI

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CHAPTER VII

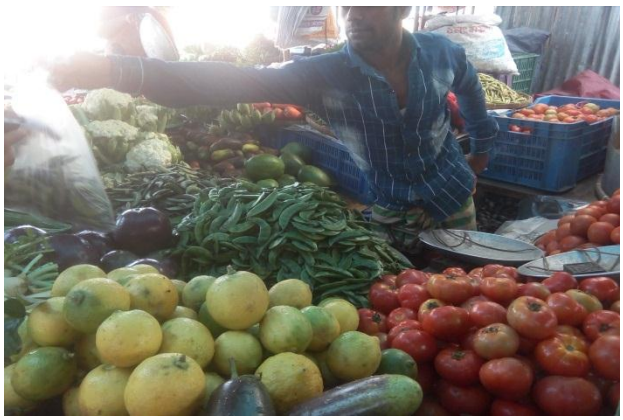
APPENDICES

CHAPTER VI

APPENDICES

Appendix-1: Collection of cabbage samples of different markets of Cumilla District



Appendix-2: Collection of lady's finger samples from different markets of Cumilla district