DETERMINATION OF PESTICIDE RESIDUES IN COUNTRY BEAN AND EGGPLANT COLLECTED FROM BARISHAL DISTRICT OF BANGLADESH

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DETERMINATION OF PESTICIDE RESIDUES IN COUNTRY BEAN AND EGGPLANT COLLECTED FROM BARISHAL DISTRICT OF BANGLADESH

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CERTIFICATE

This is to certify that the thesis entitled ***"DETERMINATION OF PESTICIDE RESIDUES IN COUNTRY BEAN AND EGGPLANT COLLECTED FROM BARISHAL DISTRICT OF BANGLADESH"*** *submitted to the Faculty of Agriculture, Chemistry, Sher-e-Bangla Agricultural University, Dhaka, in partial fulfillment of the requirements for the degree of* ***MASTER OF SCIENCE*** *in* ***AGRICULTURAL CHEMISTRY****, embodies the result of a piece of bona fide research work carried out by* ***Umme Salma Nisha****, Registration No.* ***18-09150*** *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, as has been availed of during the course of this investigation has duly been acknowledged.

December, 2020
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Dedicated to
My
Beloved Parents

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ABSTRACT

The study was carried out to analyze pesticide residues in two common vegetables (country bean and eggplant) collected from five different locations of Barishal district during November 2019 to February 2020. The collected samples were analyzed using Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) extraction technique and Gas Chromatography (GC) coupled with Electron Capture Detector (ECD) for the determination of residues of acetamiprid, cypermethrin, lambda-cyhalothrin, and thiram in 30 samples of country bean and 30 samples of eggplant. Among the 30 analyzed samples of country bean, 5 samples (17% of the total number of samples) contained residues of acetamiprid and cypermethrin, and out of 5 contaminated samples, only one sample contained residue of acetamiprid, which was above the maximum residue limits set by European Union (EU-MRLs). While, in the case of eggplant, out of 30 analyzed samples, 4 samples (13% of the total number of samples) contained residues of cypermethrin and acetamiprid, where 1 sample contained residue of acetamiprid, which was above the EU-MRLs. None of the sample was found contaminated with thiram and lambda-cyhalothrin residues for both of the analyzed vegetables. This study reflects the overall scenario of pesticide residues remain in country bean and eggplant collected from different markets of Barishal district, which will help the consumer and policy makers 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
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 Thermionic 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 Quantification
MRL	Maximum Residue Limit
ND	Not Detected
PDI	Potential Daily Intake
PSA	Primary Secondary Amine
QuEChERS	Quick, Easy, Cheap, Effective, Rugged and Safe
RSM	Response Surface Methodology
RTL	Retention Time Locked
RSD	Relative standard deviation
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

Vegetables are significant food crops playing a superior role in food trade. Bangladesh's diverse climatic conditions certify availability of all diversities of vegetables for consumption and throught the year. There are varieties of vegetables available used as edible roots, stems, leaves, fruits or seeds. Every single group contributes to diet in its own approach (Robinson, 1990). It is considered important in dietary guidance because of their great concentrations of dietary fiber, vitamins, minerals, electrolytes, phytochemicals, especially antioxidants (Slavin and Lloyd, 2012). In addition, it has been stated that greater consumptions of vegetables may reduce consumption of minor calories, proliferation of satiety and help manage weight (Boeing *et al*., 2012). Vegetables are the fresh and edible parts of herbaceous plants, contain valuable food components which can be successfully applied to build up and repair the body. Vegetables are valuable in conserving alkaline reserve of the body. Consumption of vegetables has been fortified not only to prevent consequences due to vitamin deficiency but also to diminish the occurrence of leading diseases such as cancer, cardiovascular diseases and obesity.

Country bean (deshi shim), a winter vegetable, *Lablab niger*, is grown all over the country. It is commonly called country bean in Bangladesh, but it has a variety of names at different regions of the country like ‘sheem, ‘chhoi, ‘uri, ‘deshi sheem etc. Internationally also the crop has various other names e.g., hyacinth bean, bonavist bean, Dolichos bean, Indian bean, Egyptian kidney bean, Lima bean, faba bean etc. (Jadhav *et al*., 1987). It is primarily grown in rabi season for pods, which are cooked as vegetable; dry seeds are also used in preparing various dishes (Hossain, 2015). It is very rich in carbohydrate, protein, fat, vitamins and minerals. In the past years, it was a homestead vegetable in Bangladesh but recently it is cultivated commercially as field crop in flood free high land.

Eggplant (*Solanum melongena* L.) is an important solanaceous vegetable in many countries of Asia and Africa. It is a good source of minerals and vitamins in the tropical diets (Kumar *et al.* 2008). A serving of eggplant can provide at least 5% of a person's daily requirement of fiber, copper, manganese, B-6, and thiamine. It is also a

source of antioxidants, which are molecules that help the body eliminate free radical's unstable molecules that can damage cells if they accumulate in large amounts. Foods that contain antioxidants may help prevent a range of diseases. Foods containing certain flavonoids, including anthocyanins, helps reduce inflammatory markers that increase the risk of heart disease (Walter, 2009).

Like other crops, fruits and vegetables are attacked by pests and diseases during production and storage prominent to injuries that decrease the quality and the yield. In order to decrease the loss and sustain the quality of fruits and vegetables harvest, pesticides are used together with other pest management techniques during cropping to destroy pests and prevent diseases. Pesticide application is a vital part of modern crop production technology (Kabir *et al*., 1996). Their practice has been contentiously increasing over the past decades. Pesticide use in Bangladesh exceeds the recommended doses in some cases (cereals, fruit and vegetables) which lead to adverse impact on human health (Rahman *et al*., 2014). The Pakistan, the pesticides application is at extreme on cotton crop compared to fruits and vegetables (Usman *et al*., 2009). Insecticides, herbicides and fungicides are frequently used for crop protection all over the country but the overdose of pesticides makes the residue problem. It might pollute our food and be unsafe for our health (Hossain *et al*., 2000).

Acute health problems may occur in workers who handle pesticides, such as abdominal pain, dizziness, headaches, nausea, vomiting, as well as skin and eye problems. In China, an estimated half million people are poisoned by pesticides each year, 500 of whom die. Pyrethrins, insecticides commonly used in common bug killers, can cause a potentially deadly condition if breathed in. The effects of pesticide exposure on the risk of leukemia, lymphoma, brain, kidney, breast, prostate, pancreas, liver, lung, and skin cancers. This increased risk occurs with both residential and occupational exposures. Increased rates of cancer have been found among farm workers who apply these chemicals. A mother's occupational exposure to pesticides during pregnancy is associated with an increases in her child's risk of leukemia, Wilms' tumor, and brain cancer. Exposure to insecticides within the home and herbicides outside is associated with blood cancers in children. Evidence links pesticide exposure to worsened neurological outcome (Kumar *et al*. 2012).

Pesticides can contaminate soil, water, turf, and other vegetation. In addition to killing insects or weeds, pesticides can be toxic to a host of other organisms including birds, fish, beneficial insects, and non-target plants. Insecticides are generally the most acutely toxic class of pesticides, but herbicides can also pose risks to non-target organisms.

Due to indiscriminate use of pesticides by the unqualified persons, only a small portion of applied pesticides reaches the targeted species; residue may enter in food chain and is sometimes indirectly delivered on to human beings (Yadav, 2010). Amongst food items, fresh fruits are the most exposed part of the diet. Because of their frequently consumption directly after picking as compared to vegetables and grains that are cooked which in turn decreases and metabolizes the pesticide residues. A world vegetable survey revealed that 402 vegetable crops are cultivated worldwide, signifying 69 families and 230 genera (Kays and Dias, 1995; Dias, 2011).

For determining the extent of pesticide contamination in the food stuffs, programs entitled 'Monitoring of Pesticide Residues in Products of Plant Origin in the European Union' started to be established in the European Union since 1996. In 1996, seven pesticides (acephate, chlopyriphos, chlopyriphos-methyl, methamidophos, iprodione, procymidone and chlorothalonil) and two groups of pesticides (benomyl group and maneb group, i.e. dithiocarbamates) were analysed in apples, tomatoes, lettuce, strawberries and grapes. An average of about 9700 samples have been analysed for each pesticide or pesticide group. For each pesticide or pesticide group, 5.2% of the samples were found to contain residues and 0.31% had residues higher than the respective MRL for that specific pesticide.

Lettuce was the crop with the highest number of positive results, with residue levels exceeding the MRLs more frequently than in any of the other crops investigated. The highest value found in 1996 was for a compound of the maneb group in lettuce which corresponded to a mancozeb residue of 118 mg/kg. In 1997, 13 pesticides (acephate, carbendazin, chlorothalonil, chlopyriphos, DDT, diazinon, endosulfan, methamidophos, iprodione, metalaxyl, methidathion, thiabendazole, triazophos) were assessed in five commodities (mandarins, pears, bananas, beans, and potatoes). Some 6000 samples were analysed. Residues of chlorpyriphos exceeded MRLs most often (0.24%), followed by methamidophos (0.18%), and iprodione (0.13%). With regard to

the commodities investigated, around 34% contained pesticide residues at or below the MRL, and 1% contained residues at levels above the MRL. In mandarins, pesticide residues were most frequently found at levels at or below the MRL (69%), followed by bananas (51%), pears (28%), beans (21%) and potatoes (9%). MRLs were exceeded most often in beans (1.9%), followed by mandarins (1.8%), pears (1.3%), and bananas and potatoes (0.5%) (Akter *et al*, 2009).

Pesticide residue in food has become a consumers' safety issue and the consumers have the right to know how much pesticide get incorporated in the food they eat. The identification and quantification of pesticide in the food are becoming the public interest. Several researchers analyzed pesticide residues in fruit and vegetables in different countries of the world including Bangladesh that have been published in the reputed journals (Nahar *et al*., 2019; Dasika *et al*., 2012; Prodhan *et al*., 2009; Prodhan *et al*., 2010; Prodhan *et al*., 2018; Prodhan *et al*., 2018a; Prodhan *et al*., 2016; Prodhan *et al*., 2015; Prodhan *et al*., 2015a; Kabir *et al*., 2007; Kabir *et al*., 2008; Kabir *et al*., 2008a; Islam *et al*., 2019; Islam *et al*., 2014; Aktar *et al*., 2017; Hasan et al., 2017; Hossain *et al*., 2014). However, a very limited work has been conducted on the presence of pesticide residues in the samples of vegetables collected from southern part, especially from Barishal district of Bangladesh. Therefore, more research work is needed to find out the actual scenario of pesticide residues present in vegetables collected from Barishal district of Bangladesh. Keeping this view, the present study was initiated with the following objectives.

1. To identify the level of selected pesticide residues present in country bean and eggplant collected from different market places in Barishal.
2. To quantify whether the level of detected pesticide residues (mg/kg) were above the Maximum Residue Limit (MRL) or not.

CHAPTER II

REVIEW OF LITERATURE

In this chapter challenge has been made to assessment literatures for updating the information regarding the existing status of research and knowledge about the determination of pesticide residues in fruits and vegetables. Available and accessible sources of information have been systematically reviewed and summarized with essential comments as appropriately as possible. In spite of the fact, there have been inadequate source of information, 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 and information of farmers' field condition are scanty. However, a significant number of study-reports on insecticides 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:

Determination of pesticide residue

Nahar *et al.* (2020) conducted a study to assess the health hazards associated with the residual effect of pesticides in two common vegetables (cauliflower and tomato) collected from five different markets of a northern city of Bangladesh. A total of 80 samples (i.e. 40 of each vegetable) were collected for the analysis of seven major organophosphorus insecticides namely acephate, chlorpyrifos, diazinon, dimethoate, fenitrothion, malathion and quinalphos used in that region. Modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction technique and GC-FTD (Gas Chromatography coupled with Flame Thermionic Detector) used for the analysis of the samples. Results indicate that 11 (6 cauliflower,5 tomato) analyzed samples contained residues which is about 14% of the total number of samples. Most of the samples contaminated diazinon at a level above EU-MRLs. However, health risk assessment based on ADI, the contaminated samples were safe. Continuous

monitoring together with a sample traceability system is suggested to protect consumers' health from the cumulative effects of other contaminated dietary products. Tonoli *et al.* (2020) conducted a study for the analysis of 100 pesticide residues using LC-MS/MS method based on triple quadrupole technology capable of detecting concentrations at 5 ng/g. Confirmatory analysis is performed using data-dependent acquisition that compares full MS/MS spectra of candidates to a fast library interrogation within the same injection. A comparison on more than 200 samples of fruits and vegetables (representing principal types: normal, pigmented, and fatty) with preexisting workflow based on single MRM analysis per compound was performed to validate this approach. A fast turnaround time was demonstrated due to more-unambiguous identification suppressing the need for reinjection to confirm candidates. The automated library searching and confirmation only of putative hits also allowed focusing on the manual verification and validation steps just for putative candidates which hence also increased overall throughput and results quality. Superior robustness of the method due partially to a reduced volume injected was also one of the key points achieved using this methodology. An interesting feature is also the capability to enrich the library and the number of pesticides screened with ease.

Bian *et al.* (2020) performed a study where they found that analytes could be quantified with decent recoveries of 90–101%, with relative standard deviations (RSDs) of 3.0–10.1%. The terminal residues of azoxystrobin in cucumber were all < limit of quantification (LOQ) (0.02 and 0.05 $mg\,kg^{-1}$). The half-lives of meptyldinocap and azoxystrobin were 0.8–1.1 and 1.2–2.8 days, respectively. The processing factors (PFs) for washing were all < 1, but the removal rate for washing was < 29.0%. Peeling had a significant effect on the removal of pesticide. The largest residue reductions were noticed through the pickling process, but special care should be taken regarding residues in the pickling solution as pesticides could transfer to them from cucumber. A more interesting finding was that the degradation of two pesticides was accelerated by the addition of calcium oxide. Pesticide residues on cucumber decreased after these processes. These results enable the health-risks from dietary exposures to pesticide residues to be characterized. They enable maximum residue limits (MRLs) to be established for pesticide residues in food products. They also assist the optimization of food processing with regard to pesticide residue dissipation.

Ramadan *et al.* (2020) conducted a study to determine pesticide residues in 10 different vegetable commodities from the Asir region, Saudi Arabia. They evaluated 211 vegetable samples, collected from supermarkets between March 2018 and September 2018, for a total of 80 different pesticides using ultrahigh-performance liquid chromatography–tandem mass spectrometry (UHPLC-MS/MS) and gas chromatography–tandem mass spectrometry (GC-MS/MS) after extraction with a multi-residue method (the QuEChERS method). The results were assessed according to the maximum residue limit (MRL) provided by European regulations for each pesticide in each commodity. All lettuce, cauliflower, and carrot samples were found to be free from pesticide residues. A total of 145 samples (68.7%) contained detectable pesticide residues at or lower than MRLs, and 44 samples (20.9%) contained detectable pesticide residues above MRLs. MRL values were exceeded most often in chili pepper (14 samples) and cucumber (10 samples). Methomyl, imidacloprid, metalaxyl, and cyproconazole were the most frequently detected pesticides. Based on the results of this study, they recommend that a government-supported program for the monitoring of pesticide residues in vegetables be established to promote consumers' health and achieve sustainable farming systems.

Reichert *et al.* (2020) initiated a study to validate a multiresidue method for the monitoring of pesticide residues in common beans. Extraction was performed applying QuEChERS approach to ground samples. C18 and PSA were used for clean-up and a solvent exchange step was performed before injection into the GC-MS/MS. Method validation was done analyzing blank samples spiked at 20, 30, 50 and 100 µg kg-1 (n=5). Linearity and linear range were assessed by the analysis of standard solutions at concentrations of 5, 15, 25, 50, 75, 100 and 150 µg L-1.This method was successfully validated for 91 (64.1%) of the 142 compounds studied (139 pesticides and 3 degradation products). LOQs were equal to 20, 30, 50 and 100 µg kg-1 for 18 (12.7%), 17 (12.0%), 21 (14.8%) and 35 (24.6%) compounds, respectively. Fifteen (10.6%) compounds were not detected at any level and 36 (25.4%) did not fulfill requirements for quantitative method. Sixteen common bean samples of South of Brazil were analyzed. Two samples were positive, one for tebuconzole and a second for picoxystrobin, permethrin and cyproconazole. Cyproconazole is not allowed for the crop, consisting of a violation. As demonstrated the validated approach is suitable for pesticide residues determination in common bean. Results of the sample analysis

show that the control of pesticide residues in common bean is necessary to ensure food safety.

Varela-Martínez *et al.* (2020) used a quick, easy, cheap, effective, rugged, and safe official method, together with gas chromatography coupled to a triple quadrupole mass spectrometer for the analysis of 38 multiclass pesticides from dried fruits typically cultivated and exported from Colombia: uchuva (*Physalis peruviana*), lulo (*Solanum quitoense*), guanabana (*Anona muricata*), and pitahaya (*Hylocereus undatus*). The whole method was validated in terms of matrix-matched calibration, matrix effect, and recovery using atrazine-d5 as internal standard, triphenylphosphate for quality control of the injection, and a proper mixture of analytes protectants. Matrix-matched calibration data were found satisfactory for all pesticides and dried fruits, reportingR2values above 0.99. Matrix effect values evidenced the existence of such effect in most cases. The applied procedure gave satisfactory recovery percentages (70–120%) and relative standard deviation values (<20%) for 92% of the 456 combinations pesticide/fruit studied (spiked levels of 25, 200, and 400μg/kg). Finally, 20 real dried fruit samples were analyzed and residues of tebuconazole were found in two samples of uchuva at a concentration below the lowest calibration level of the method for one of them and at 10.8±1.6μg/kg for the other, being below or similar to the general maximum residue level established for monitoring purposes in food applications.

Islam *et al.* (2019) carried out a study for the determination of major organophosphate insecticide residues in cabbage samples from different markets of Dhaka. The study was conducted to analyse 4 organophosphorus pesticide namely chlorpyrifos, diazinon, fenitrothion and quinalphos residues in cabbage. Between September 2016 and March 2017, 50 Cabbage samples were collected from 5 vegetables markets of Dhaka city, namely Rampura kacha bazar, Jatrabari krishi market, Kawran Bazar, Taltola Bazar and Mohammadpur Krishi Market. The collected samples were extracted and analyzed by QuEChERS based Gas Chromatography coupled with Flame Thermionic Detector (GC-FTD) method. Total 6 samples (12%) contained pesticide residues and interestingly all of them were above the MRLs set by EC. Among the four organophosphorus insecticides tested only chlorpyrifos and diazinon were detected above the MRLs. This research represents a snapshot situation of

contamination of pesticides in one of the common winter vegetables available in Dhaka City's local markets linked to consumer safety.

Islam *et al.* (2019a) initiated a study for the analysis of pesticide residues in bitter gourd using modified QuEChERS extraction coupled with Gas Chromatography. This study was undertaken to monitor the presence of seven organophosphorous pesticide residues like acephate, dimethoate, fenitrothion, chlorpyrifos, quinalphos, diazinon and malathion in bitter gourd. 65 samples were collected from retail markets located at the adjacent area of Jahangirnagar University, Savar, Dhaka, Bangladesh namely Genda bazaar, Savar bazaar, Nayarhat bazaar, Islampur bazaar, Pallibiddut bazaar, Baipayl bazaar and Sreepur bazaar. The samples were extracted by modified quick, easy, cheap, effective, rugged and safe (QuEChERS) method and analyzed by gas chromatography coupled with flame thermo ionic detector (GC-FTD). Among the 65 analyzed samples, eight (12.3% of the total number of samples) were contaminated with pesticide residues and all of them contained residues above Maximum Residue Limit (MRL) set by European Commission (EC). Another fifty-seven samples (87.7% of the total number of samples) contained no detectable pesticide residues of the sought pesticides. The findings from this current study showed the common scenario of pesticide residues in daily consumed vegetables of Savar, Dhaka, Bangladesh that pointed to the imminent health hazards. Therefore, it is suggested to control the overuse of pesticide in vegetable field strictly as well as to increase the awareness of the harmful effect of pesticide residues in vegetables for the growers and the consumers as well.

Islam *et al.* (2019b) established a method for the determination of major organophosphorus pesticide residues in eggplant using modified QuEChERS Extraction and Gas Chromatography. This investigation was undertaken to scrutinize the entity of seven Organophosphorus pesticide residues like acephate, dimethoate, fenitrothion, chlorpyrifos, quinalphos, diazinon and malathion in eggplant. Seventy-eight eggplant samples were collected from retail markets located at the surrounding area of Jahangirnagar University, Savar, Dhaka, Bangladesh namely Genda bazaar, Savar bazaar, Nayarhat bazaar, Islampur bazaar, Pallibiddut bazar, Baipayl bazaar and Sreepur bazaar. The samples were extracted by modified quick, easy, cheap, effective, rugged and safe (QuEChERS) method and analyzed by Gas Chromatography coupled with Flame Thermionic Detector (GC-FTD). Among the seventy eight analyzed

samples, nine (11.5%) were contaminated by pesticide residues. Two of them were exceeded the EU-MRL (EC, 2015). Another sixty nine samples (88.5%) were free from the contamination of the sought pesticides. The findings from this current study showed the subsistence of pesticide residues in daily consumed vegetables of Savar, Dhaka, Bangladesh that pointed to the imminent health hazards. So, public awareness about the pesticides and other related matter should be increased for practicing a pesticide free agriculture as well as gain contaminate free environment.

Pecev-Marinković *et al.* (2019) performed an experiment on a kinetic-spectrophotometric method for atrazine determination and to apply it to determine pesticide in baby-food samples, using solid-phase extraction (SPE) followed by the kinetic-spectrophotometric method and the high-performance liquid chromatography (HPLC) method. This method is based on the inhibition effect of atrazine (the oxidation of sulfanilic acid (SA) by hydrogen peroxide in the alkaline medium in the presence of the Co^{2+} ion). Under the experimental conditions used, atrazine showed a linear dynamic range of 0.5 to 5.0 $\mu g\,mL^{-1}$, and from 5.0 to 70.00 $\mu g\,mL^{-1}$ with relative standard deviations (RSD) from 1.91% to 9.41%. The limit of detection and the limit of quantification were 0.074 and 0.225 $\mu g\,mL^{-1}$, respectively. The kinetic method was successfully applied to determine the atrazine concentration in spiked samples after SPE of samples. High-performance liquid chromatography was used to verify the results.

Huang *et al.* (2019) investigated the excessive or improper use of organophosphorus pesticides (OPPs) using a simple, rapid and effective analytical method for the determination of OPPs and its analogs in different food samples. Under the optimized experimental conditions, five OPPs (quinalphos, triazophos, parathion, fenthion and chlorpyrifos-methyl) exhibit a good linearity within a range of 0.02 to 2.0 $\mu g\,mL^{-1}$. The detection limit range was 3.0 to 10.0 $\mu g\,L^{-1}$ (signal-to-noise ratio = 3). The method was successfully used to detect and quantify the residues of quinalphos and its analogs in tomato, cabbage, barley and water samples; all spiked samples gave satisfactory recovery rates for the target analytes of between 82% and 98%, with a relative SD of 3.6% to 7.8%.The results obtained show that the proposed method is an accurate, rapid and reliable sample pre-treatment method with respect to giving a good enrichment factor and detection limit for determining quinalphos pesticide residues in different food samples.

Li *et al.* (2019) conducted a field trials where- three different doses of Imidacloprid (IMI) were sprayed on tomato during the fruit setting stage. Degradation of IMI and residue behaviors of its metabolites at different stages were systemically traced and evaluated by ultrahigh-performance liquid chromatography coupled with tandem mass spectrometry (UHPLC/Q-Orbitrap MS). An accurate mass tool was used as the main method to identify the IMI metabolites. The improved method showed high efficiency in detecting IMI and 6-chlorinated nicotinic acid (6-CNA), being able to determine hazardous pesticides at trace levels. The fate of IMI in field tomato was investigated over 28 days. The metabolic mechanism of IMI in tomato is: OH products in the early stage and carbonyl products in the late stage. Under natural conditions, pesticides in tomatoes will gradually decrease with time. In this process, olefin IMI is produced, but it is almost completely metabolized after 28 days. Therefore, even 10 times the recommended dose of IMI pesticide will not endanger human health.

Okediran *et al.* (2019) evaluated pesticide residues in fresh vegetables from three major markets in Lagos and verified compliance of these fresh vegetables with the maximum residue levels (MRLs) as specified by Codex Alimentarius Commission. The residues were extracted by means of multi residue method based on the Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method coupled to Gas Chromatography Mass Spectrometry (GC-MS) to determine two organophosphates (dichlorvos and chlorpyrifos), two organochlorines (endosulfanII and chlorothalonil), two carbamates (carbaryl and carbofuran) and two pyrethroids (alpha-cypermethrin and lambda-cyhalothrin). Fifteen samples of five common vegetables (cabbage, lettuce, fluted pumpkin,bitter leaf and African spinach) were analyzed. The linear ranged used were 0.005, 0.1, 0.25, 0.5 and 1.0mg/l, resulting to r2of ≥0.996. While the mean recoveries obtained for two fortification levels (0.1 and 0.25 ppm) in three replicates for lettuce control sample and spinach control sample were 96.7 to 104.3%, 96.3 to 101.3%, and 92.0 to 114.3%, 92.1 to 102.1% respectively. A satisfactory precision of RSD<20% was recorded. The limit of detection (LOD) and limit of Quantitation (LOQ) were between 0.005-0.050 mg/kg and 0.015-0.150 mg/kg respectively. Pesticide residues detected ranges from 0.025-0.529 mg/kg. endosulfanII, chlorothalonil, carbaryl and carbofuran were not detected during the entire study. However, pesticide residues detected were below the MRLs specified by Codex Alimentarius Commission.

Mohammed *et al.* (2019) conducted a study to analyse 4 organophosphorus pesticide namely chlorpyrifos, diazinon, fenitrothion and quinalphos residues in cabbage. The collected samples were extracted and analyzed by QuEChERS based Gas Chromatography coupled with Flame Thermionic Detector (GC-FTD) method. Total 6 samples (12%) contained pesticide residues and interestingly all of them were above the MRLs set by EC (European Commission). Among the 4 organophosphorus insecticides tested only chlorpyrifos and diazinon were detected above the MRLs. This research represents a snapshot situation of contamination of pesticides in one of the common winter vegetables available in Dhaka City's local markets linked to consumer safety.

Tankiewicz (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. The chosen compounds are commonly detected in fruit and vegetable crops, and some of their metabolites have even been found in human urine. Extraction and clean up parameters were optimized, thus the original QuEChERS method was modified to decrease solvent usage, in accordance with 'green chemistry' principles. The proposed methodology was validated in terms of selectivity, specificity, linearity, precision and accuracy. The obtained limits of detection (LODs) for all investigated pesticides ranged from 5.6 μg kg^{-1} to 15 μg kg^{-1} and limits of quantification (LOQs) from 17 μg kg^{-1} to 45 μg kg^{-1}. The obtained data demonstrated the good reproducibility and stability of the procedure in the tested concentration range up to 10 mg kg^{-1}, with relative standard deviations (RSDs) lower than 10%. Recoveries for spiked pear samples 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. The proposed methodology is applicable for detection and monitoring of selected pesticides not only in fruits and vegetables with high water content, but also in samples containing large amounts of pigments and dyes.

Sapahin *et al.* (2019) described an adequate and simple analytical method based on solid-phase microextraction (SPME) followed by gas chromatography–flame photometric detection (GC–of commercially available fibres FPD) for the determination of eleven organophosphorus pesticide residues (i.e., ethoprophos, sulfotep, diazinon, tolclofos-methyl, fenitrothion, chlorpyrifos, isofenphos, methidathion, ethion, triazophos, leptophos) in vegetables samples (cabbage, kale and mustard) was developed. Important parameters that influence the extraction efficiency (i.e., fibre type, extraction modes, extraction time, salt addition, desorption time and temperature) were systematically investigated. Four types (i.e., 50/30 μm divinylbenzene / carboxen / polydimethylsiloxane (DVB/CAR/PDMS), 65 μm poly dimethylsiloxane/ divinylbenzene (PDMS/DVB), 100 μm polydimethylsiloxane (PDMS), and 85 μm polyacrylate (PA) were evaluated. PA fibre exhibited the best performance and was used for the rest of the studies. The optimised extraction conditions were: extraction time, 30 min at room temperature; stirring speed, 1275 rpm; salt content, 10% NaCl; desorption time and temperature, 11 min at 260 °C; and no pH adjustment of the sample extract. The method was validated over the range 0.1–100 μg/L. Repeatabilities were satisfactory, ranging between 2.44% and 17.9% for all analytes. The limits of detection and quantitation ranged from 0.01 to 0.14 and 0.03 to 0.42 μg/L, respectively. The method was applied to twenty local vegetables (cabbage, kale and mustard) products. Chlorpyrifos (0.22–1.68 μg/kg) was the most detected pesticide in the tested samples. The obtained values are however lower than the Maximum Residue Limits (MRLs) as stipulated in the Food Act & Regulations of Malaysia.

Weijian *et al*. (2019) established a method for the determination of five acylpyrazole pesticide residues in edible vegetable oils using gas chromatography-negative chemical ionization-mass spectrometry (GC-NCI-MS). The pesticides were extracted from a sample with acetonitrile under freezing conditions. A simple cleanup step known as QuEChERS was then conducted. After being identified by GC-NCI-MS, the extracts were quantified using an external standard method that employs a matrix correction standard curve. The linearity of the method was good between 20 and 1000 μg/L, and all limits of quantification were less than 2 μg/kg. Recoveries of all pesticides were in the range of 82.7%-112.4% at the three spiked levels of 0.01, 0.02, and 0.05 mg/kg, and all relative standard deviations were not more than 12.3%.

Concha-meyer *et al.* (2019) determined pesticide residues in frozen fruit and vegetables from Chilean retail stores using UHPLC-Orbitrap MS and QuEChERS™ multiresidue-extraction kit. 237 samples of frozen produce were sampled from different supermarkets and times during the year. Abamectin, Chlorpyrifos, Imidacloprid, Iprodione, λ-cyhalothrin, Spinosad A, and Spinosad D were quantified. Results showed that Iprodione, Spinosad A, and D were the most detected molecules. Pesticides were detected in 96.6% of samples and 21 samples exceeded MRL. Corn and faba beans showed the highest concentration of Iprodione with an average of 6.7 and 5.4 mg/Kg, respectively. Existence of nonconformity in samples highlights the importance to control pesticide residues of Chilean frozen produce, since it represents a latent health threat on consumers.

Hadiana *et al*. (2019) studied forty-eight pesticide residues from different chemical structures including organochlorine, organophosphorus, organonitrogen, dicarboximides, strobilurin, triazine, pyrethroids, and other chemical groups. Pesticide residues in 85 fruits and vegetables were determined and confirmed by GC-MS. The pesticide was extracted with ethyl-acetate, then, the extracts cleaned using high performance gel permeation column chromatography (GPC) and solid phase column (SPE). The mean recoveries of the pesticides were between 81 and 136%. The reproducibility of the relative standard deviation values was 2.1% and 14.8%. Pesticide residues were more frequently found in vegetables (65.5%) than in fruits (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.

Vareli *et al.* (2019) conducted a study on the development of reliable and accurate analytical methods, is a requirement to ensure biobed bioremediation capacity. Two extraction approaches were evaluated for the determination of captan (and its degradation product, tetrahydrophthalimide), chlorothalonil, chlorpyrifos-ethyl, fenitrothion, methidathion, phosmet and tebuconazole in biobeds. These pesticides were selected because of their importance for apple plantations and the biobeds were used for bioremediation of pesticide wastes sprayed on plantations. After some preliminary

experiments, the best extraction approach was selected and subjected to a complete validation study as advised by the SANTE Guidance Document. The validated approach consists of an optimized version of the Dutch Mini-Luke method and is performed in only 4 steps (extraction, phase partitioning, centrifugation and filtration), which makes it very convenient and attractive. Linearity of analytical curves (r^2), residuals, limits of detection (LODs) and quantification (LOQs), matrix effects (%), accuracy (in recovery%) and precision (as repeatability and reproducibility – relative standard deviation, RSD_r and RSD_{wR}, respectively) were assessed. Two internal standards were used for quality control. Validation studies were performed by analyzing blank biobed samples spiked at 50, 100 and 200 μg kg^{-1} (n = 7) which yielded average recoveries from 75 to 117% and $RSD_r \leq$ 14%. The analytical curves obtained from matrix-matched standards were linear ($r^2 \geq$ 0.987) in the concentration range of 10 (or 20) to 300 μg L^{-1} for all compounds, except for captan which was not detected in the validation study. LOQs were equal to 50 μg kg^{-1}. The calculated matrix effects were ≥±20%.

Tripathy *et al.* (2019) developed a simple, rapid and less expensive QuEChERS extraction and cleanup method for simultaneous analysis of 41 multiclass pesticide residue in milk by gas chromatography-electron capture detector (GC-ECD), followed by confirmation of the residues with gas chromatography-mass spectrometer (GC-MS). Effect of sorbent type, temperature, spiking concentration, matrix effect (ME), measurement uncertainty (MU), inter- and intra-assay repeatability, reproducibility of recovery, and trueness of the results were investigated to validate the effectiveness of the method. Limit of determination (LOD) and limit of quantitation (LOQ) for all the analytes ranged within 0.001–0.02 and 0.002–0.05 μg mL^{-1}, respectively. The % recovery of all the pesticides ranged between 91.38 and 117.56% with relative standard deviation (RSD) below 2.79%. The MU for all the analytes was ≤29% of respective LOQs, and except for few pesticides, the ME was largely negative. The method fulfilled all the SANTE guidelines and thus can be extended for routine analysis of multiclass pesticide residue in milk.

Lawal *et al*. (2019) investigated multivariate response surface methodology optimization using Placket–Burman and Box–Behnken designs for the screening and optimization of significant factors for liquid chromatography–tandem mass spectrometry. Consequently, the optimized instrument successfully improved the

sample preparation protocol and the method was validated. However, modified QuEChERS dispersive solid phase extraction coupled with ionic liquid-based dispersive liquid–liquid microextraction were used for the determination of multi-pesticide residues in fruit and vegetable samples. The analysed samples were jackfruit, strawberries, cucumber, pears, and carrots. The resulting linearity range (5–400 μg/kg) and regression coefficient (>0.99) results were satisfactory. The 94.2 and 95.8% accuracy (89–138%) and precision (0–25%) results were satisfactory and within the recommended ranges (≤20%) and (70–120%), respectively. The limits of detection (0.01–0.54 μg/kg) and quantitation (0.03–1.79 μg/kg) were excellent. The matrix effects (≤−87%) for all analysed samples were not significant. The estimated measurement uncertainties (≤27%) were within the acceptable range (≤50%). Justifiably, the response surface methodology optimized instrument and sample treatment techniques were reliable and convenient for multi-pesticide residue determination in various fruits and vegetables.

Konatu and Jardim (2018) developed a new analytical method for multiresidue determination of 16 multiclass pesticides in lettuce using ultra-high performance liquid chromatography with tandem mass spectrometry and positive mode electrospray ionization, using a previously optimized quick, easy, cheap, effective, rugged, and safe method for sample preparation. Validation studies, according to document SANTE/11945/2015, demonstrated that the developed method is selective, accurate, and precise, providing recoveries of 70–120%, relative standard deviations ≤20% and quantification limits from 3 μg/kg. The method was compared with one based on high-performance liquid chromatography with tandem mass spectrometry, in terms of chromatographic performance, detectability and matrix effect for five varieties of lettuce. The new method provided a reduction in the time for the chromatographic analysis of 50%, from 30 to 15 min, using a lower mobile phase flow rate (0.147 mL/min), which reduced the consumption of mobile phase by 25%, and injection of smaller amounts of sample (1.7 μL). Lower limits of quantification were obtained for almost all pesticides studied for green-leaf lettuce. However, in relation to the matrix effect, four of the five types of lettuce studied presented higher matrix effects.

Tomas et al. (2018) conducted a study to investigate the presence of pesticide residues in nationally produced fruits and vegetables for domestic consumption. A total of 135 of the most widely consumed fruits and vegetables were analyzed for 35 pesticides. The analyses utilized a *QuEChERS* multiresidue extraction kit along with tandem gas chromatography–mass spectrometry. The results were evaluated according to maximum residue limits (MRLs) for each commodity and pesticide according to national regulation. Pesticides were detected in 65% of the total samples, in 44% of the positive samples at or below the MRLs, and in 56% above the MRLs. Oranges had the highest pesticide concentration detected, but carrots had the highest frequency of noncompliance among the produce items sampled. Five pesticides were detected at frequencies above 10%, the highest being chlorpyrifos in 25.9% of the total samples.

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. Thirteen 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 (shehuigongzhi) 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 ($X2=9.69$, $0.005<P<0.010$). This indicate 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.

Stachniuk *et al*. (2018) carried out a study to evaluate pesticide residues contamination in fresh and frozen fruits and vegetables, agricultural raw material, and the estimation of the multi-residue method effectiveness expressed as the proportion of pesticides detected in food samples to the total number of pesticides analyzed by multiresidue methods. A total of 144 samples (of black currants, red currants, raspberries, cherries, strawberries, blackberries, cauliflowers and broccoli) were analyzed using LC-MS/MS method for the determination of 60 pesticides. QuEChERS extraction, matrix-matched calibration and dynamic multiple reaction monitoring method were used. Residues of 15 compounds, mainly fungicides and insecticides, were detected in 46 samples. The percentage of samples with residues above the maximum residue levels (MRL) was 15%, whereas samples with residues below MRL were 17%. A total of 13 samples contained more than one pesticide residue. Pesticide residues were detected most often in samples of black currants (50%), broccoli (36.4%), raspberries (29%) and red currants (21.8%). The most frequently detected pesticides were carbendazim and acetamiprid. The proportion of pesticides detected during study to the total number of analyzed pesticides amounted to 25%.

Galani *et al*. (2018) evaluated the residues of 99 pesticides in 72 samples of 12 agricultural products using QuEChERS 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 residues of 62 pesticides, including 12 banned compounds, were found in the samples. Insecticides (39.7%) were the most prevalent group, with all the samples containing at least one pesticide. Twenty-one pesticides (34.4%) exceeded their European Union maximum residue limits (MRLs) and 22 pesticides (34.4%) were found in all 6 sampling locations. Malathion and p,p'-DDT were the most distributed pesticides, found in almost all the samples and sampling sites. Food items with the highest rates of positive results were chili pepper (23.2%), white pepper (20.2%), kidney beans (17.3%), and soybeans (17.2%). Samples with residues above their MRLs represented 38% of all the positive analyses; chili pepper (6.4%) and kidney beans (5.5%) were found to have the most residues above their MRLs.

Ibrahim *et al*. (2018) experimented the persistence patterns of malathion, fenitrothion and deltamethrin in tomato and cucumber. Residues were determined by gas liquid chromatography. Results confirmed that the initial deposit of malathion and fenitrothion on and in the cucumber fruits (7.603 and 9.043 μg/g) were higher than on and in tomato fruits (5.390 and7.110) respectively. Data also indicated that the initial residue of deltamethrin on and the tomato fruits (3.660) was higher than the initial deposit of deltamethrin on and in the cucumber fruits (3.643). Results showed that, the consumable safety time was found to be 10 and 14 days after application on tomato and cucumber. This was found to be enough to reduce the residue to below the maximum residue limits (MRL).

Kiwango *et al*. (2018) reported malpractices in the use of pesticides in vegetable production in the horticultural sector in developing countries. This can result in excessive use of pesticides and, subsequently, in unacceptable levels of pesticide residues in foods of horticultural origin. Consumption of vegetables containing unacceptable levels of pesticide residues is of public concern due to its potentially harmful effects on human health. In this work, it was reviewed that pesticides are rarely applied to vegetables following good agricultural practices. Results from this

research will allow for the allocation of resources for improvement, monitoring and control practices to minimize the risk of unwanted pesticide residues in vegetables.

Kumari *et al.* (2018) conducted a study to determine pesticide residues in fruits and vegetables samples collected from K.R market 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.

Huifen *et al*. (2018) established a multi-residue determination method after optimization of the QuEChERS pretreatment method, combined with liquid chromatography-tandem mass spectrometry (LC-MS/MS) technology, for 105 typical insecticides, bactericides, herbicides, and plant growth regulators in vegetables. The target compounds were extracted by acetonitrile, purified with 150 mg primary secondary amine (PSA), 150 mg EC-C18, and 30 mg graphitized carbon black (GCB) adsorbents. The standard curves of 105 target compounds were linear in the concentration range of 0.010-0.200 mg/L, with correlation coefficients (r)>0.99. The limit of quantification was 0.010 mg/kg, the recoveries were between 68.2% and 108% at three spiked levels, and the RSDs of the method were between 1.02% and 11.8%. The method is suitable for the rapid determination of the common pesticides in vegetables owing to its advantages of rapidity, simplicity, and better purification.

Chen *et al*. (2018) developed a very quick, easy, cheap, effective, rugged and safe (QuEChERS) procedure by using ultra-high performance liquid chromatography

coupled with tandem mass spectrometry for simultaneous determination of afidopyropen and its metabolite M440I007 residues in tomato, watermelon, pepper, cucumber, pear, grape, cabbage etc. The target compound was determined in less than 5.0 min using an electrospray ionisation source in positive mode (ESI^+). The limit of quantification was 1 μg kg^{-1} in different matrices. Two sorbents primary secondary amine and graphitised carbon black were used in the QuEChERS procedure, and matrix-matched standards gave satisfactory recoveries and relative standard deviation (RSD) values in different matrices at three spiked levels (1, 10 and 500 μg kg^{-1}).

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.

Liang *et al*. (2018) analyzed 420 samples of 10 different types of fresh vegetables for pesticide multi-residue contents using gas chromatograph and NY/T 761-2008 pesticide multi-residue screen methods. The residues exceeded MRLs of forbidden pesticides found were: carbofuran 0.110 mg/kg (kidney bean) and methamidophos 0.037 mg/kg (celery), methamidophos 0.037 mg/kg (tomato), aldicarb 0.013 mg/kg (kidney bean), omethoate 2.200 mg/kg (celery), carbofuran 0.052 mg/kg (green pepper), parathion 0.056 mg/kg (celery) and carbofuran 0.030 mg/kg (celery). Also, chlorpyrifos used as unforbidden pesticide was most frequently found above MRL, rape (0.820 mg/ kg) and celery (0.365 mg/kg), celery (0.330 mg/kg), lettuce (0.298 mg/kg), rape (0.910 mg/kg) and lettuce (0.230 mg/kg). In addition, cypermethrin used as unforbidden pesticide was found above MRL only once in rape (1.270 mg/kg) and

none of unforbidden pesticides above MRL was found. Most of the samples (96%) were up to the national standard.

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.

Li *et al*. (2018) conducted an experiment with 439 pesticides in fruits and vegetables using GC-quadrupole-time-of-flight MS (GC-Q-TOF/MS) technique through solid-phase extraction (SPE), whereby pesticides are extracted from fruit and vegetable substrates by using 40 mL 1% acetic acid in acetonitrile (v/v), purified by the Carbon/NH_2 SPE cartridge, and finally detected by GC-Q-TOF/MS, the rapid analysis of 439 pesticides in fruits and vegetables can be achieved. The methodology verification results show that more than 70 and 91% of pesticides, spiked in fruits and vegetables with concentrations of 10 and 100 μg/kg, respectively, saw recoveries that conform to the European Commission's criterion of between 70 and 120% with RSD ≤20%. Eighty-one percent of pesticides have screening detection limits lower than 10 μg/kg, which makes this a reliable analysis technology for the monitoring of pesticide residues in fruits and vegetables.

Prodhan *et al.* (2018) conducted a research work 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.

Hasan *et al*. (2017) initiated a study to quantify pesticide residues in country bean collected from different markets of Dhaka city. The collected samples were analyzed using modified QuEChERS Extraction and Gas Chromatography. They have been detected two organophosphorus insecticides (Dimethoate and Quinalphos) in the analyzed country bean samples. Among the 50 analyzed samples of country bean, 10 samples (20%) contained residues of Dimethoate and Quinalphos, of which 5 samples were above the maximum residue limits (MRLs). Most of the contaminated samples (8 samples) contained residue of Dimethoate.

Akter *et al.* (2017) conducted a study for the determination of pesticide residues in eggplant collected from different local markets of Mymensingh Sadar, Mymensingh. The collected samples were extracted using modified QuEChERS Extraction and analyzed with Gas chromatography. This study reflects the overall scenario of pesticide residue contamination in eggplant available in the local markets of Mymensingh Sadar, Mymensingh. In this study, a simple and efficient multiple

pesticide residue analytical method based on QuEChERS extraction and gas chromatography-flame thermionic detector (GC-FTD) was used for the determination of pesticide residues. Among the 50 analyzed samples, 11 (22% of the total number of the samples) contained 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.

Elguetaa *et al*. (2017) conducted a study to investigate pesticide residue concentrations and potential human health risk with 118 vegetable samples. The pesticide residues were determined using the multiresidue QuEChERS method by gas chromatography as well as high-performance liquid chromatography. The results indicated that 27% of the total samples contained pesticide residues above the maximum residue limits of each active ingredient. The maximum estimated daily intake obtained for carbon disulphide (CS_2), methamidophos, azoxystrobin and cypermethrin were 0.57, 0.07, 0.06 and 0.05 mg kg-1, respectively, which was higher than their acceptable daily intake.

Sebastian *et al*. (2017) developed a multiresidue QuEChERS method by gas chromatography as well as high-performance liquid chromatography for the determination of pesticide residues. The results indicated that 27% of the total samples contained pesticide residues above the maximum residue limits of each active ingredient. The maximum estimated daily intake obtained for carbon disulphide (CS2), methamidophos, azoxystrobin and cypermethrin were 0.57, 0.07, 0.06 and 0.05 mg kg−1, respectively, which was higher than their acceptable daily intake. It is concluded that inhabitants of the North Central agricultural area of Chile are not exposed to health risks through the consumption of leafy vegetables with the exception of methamidophos

Jian *et al*. (2017) established a LC-MS/MS method for the determination of eight pesticides (triadimefon, sulfoxaflor, flusilazole, tebuconazole, difenoconazole, amitraz, azoxystrobin, and thiophanate-methyl) in Lyciumbarbarum. The samples were extracted with acetonitrile, and then cleaned up by primary secondary amine. The extracts were diluted with 0.1% formic acid in water. The results showed that at the fortified levels of 0.01–10 mg/kg, the average recoveries of these pesticides

ranged from 82.1% to 96.2% with the relative standard deviations lower than 7%. The half-lives of eight pesticides were 1.3–5.0 days in fruits. The pre-harvest interval of all pesticides mentioned above Lyciumbarbarum were investigated. Tebuconazole (14 days), sulfoxaflor (14 days) and flusilazole (28 days) have longer pre-harvest interval than the others which have 7 days. The dietary risks, assessed as hazard quotients, were far below 100%. The results showed that the eight pesticides applied to Lyciumbarbarum were comparably safe for the consumer.

Peng *et al*. (2017) developed a novel carboxylated multi-walled carbon nano tubes (MWCNTs-COOH) dispersive solid phase extraction (d-SPE) method combined with gas chromatography (GC) with an electron capture detector (ECD) for the determination of seven pyrethroid pesticides in cucumber, spinach, eggplant, tomato and carrot. We optimised d-SPE conditions including the type and volume of the extractant, the type and amount of the sorbent, and shaking time. Under the optimal conditions, the linear range was from 2.0 to 2000 μg kg^{-1}. The recoveries were from 88.5% to 108.2%, with the corresponding RSDs <6%, correlation coefficients 0.9987–0.9998, LOD 0.5–2.9 μg kg^{-1} and LOQ 1.5–9.7 μg kg^{-1}.

Mbulaheni *et al.* (2016) conducted a study to determine pesticide residue levels in fruits and vegetables sold from two of the biggest fresh produce markets. They observed that in most countries, fresh produce sold at local markets is usually not analyzed for agricultural chemical residues as export products are, which raises concerns about the perceived safety levels of local food supplies in contrast with exported products. A total of 199 fruit and vegetable samples were collected and analyzed for 74 pesticides commonly used in the horticultural sector. Of the samples analyzed, 91% were compliant with set maximum residue levels (MRLs). The remaining samples either contained unregistered chemicals (8%) or exceeded set MRL values (1%). Products containing more than one pesticide residue constituted 4.02% of all samples tested. Imazalil and iprodione were found to be the most frequently detected pesticides (12 samples each). Boscalid, endosulfan, profenofos, and procymidone were associated with the most noncompliance, including exceeding MRL values or being unregistered for the specific crop.

Amelina and Andoralovb (2016) has been proposed a method for the simultaneous identification and determination of 111 pesticides from various classes in food by

high performance liquid chromatography–high resolution time of flight mass spectrometry combined with simple and fast sample preparation technique. Possibility of the identification and determination of pesticides in drinking, natural, and ground waters without sample preparation has been demonstrated. A scheme of the identification and determination of the detected analytes using the standard addition method has been suggested. The limit of detection is 0.05 (0.1) μg/(L)kg. The relative standard deviation of the results of analysis does not exceed 0.1. The time of identification is 30–40 min

Zhang *et al*. (2016) developed a rapid, efficient, and environmentally friendly method using quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction method combined with ionic liquid-based dispersive liquid-liquid micro extraction (QuEChERS-IL-DLLME) prior to high-performance liquid chromatography coupled with photodiode array detection (HPLC-PDA) has been developed for the determination of six triazole fungicides (triazolone, triadimenol, epoxiconazole, flusilazole, tebuconazole, and diniconazole) in various fruits (pear, apple, and grapefruit). And the proposed method was successfully applied for the determination of trace amounts of triazole fungicides in various fruits including pear, apple, and grapefruit.

Prodhan *et al.* (2016) has been developed and validated a multiresidue analytical method for the determination of pesticide residues in cauliflower collected from different market places in Thessaloniki, Greece. In this study, the liquid chromatography tandem mass spectrometry (LC-MS/MS) was used for the quantification of pesticide residues at trace levels. Among the 120 analyzed samples, 48 (40% of the total no. of samples) were found to have pesticide residues. The detected pesticides were chlorpyrifos, cypermethrin, deltamethrin and indoxacarb.

Prodhan *et al.* (2016a) has been developed and validated a multiresidue analytical method to determine pesticide residues in cabbage collected from different market places in Thessaloniki, Greece. In this study, the modified QuEChERS extraction in combination to liquid chromatography tandem mass spectrometry (LC-MS/MS) was used for the quantification of pesticide residues at trace levels. 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. Of the

detected pesticides, three were insecticides (chlorpyrifos, cypermethrin and deltamethrin) and two were fungicides (fluopicolide and propamocarb hydrochloride).

Andrascikova and Hrouzkova (2016) developed a fast, efficient, and simple method for determination of pesticide residues in pumpkin seeds by combining QuEChERS and dispersive liquid–liquid micro extraction (DLLME) followed by gas chromatography and mass spectrometry (GC-MS). The developed and validated method was successfully applied for the extraction and determination of pesticide residues in 16 real samples with 2 positive findings below maximum residue limits (MRL). Limits of detection (LODs) of the proposed method are below the MRLs established by the European Union.

Rai *et al*. (2016) conducted a research using quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction method combined with dispersive liquid-liquid micro extraction (DLLME) for the quantitative determination of 36 multiclass, multiresidue pesticides (13 organochlorines, 11 organophosphates, and 12 synthetic pyrethroids) in different vegetables and fruits without primary and secondary amine (PSA) cleanup step followed by gas chromatography-mass spectrometry (GC-MS) analysis. The samples collected from Lucknow City, India, were analyzed for the presence of pesticides and only three pesticides β-cypermethrin, λ-cyhalothrin, and chlorpyrifos were found to have value above PFA-1954/CODEX-MRL values.

Zanella *et al*. (2016) conducted a research on different extraction procedures based on the QuEChERS method for multi-residue determination of pesticides in orange juice by ultra-high performance liquid chromatography coupled to tandem mass spectrometry (UHPLC–MS/MS). After choosing preliminary conditions, an experimental design was carried out with the variables of C18, PSA, NaOH and CH_3COONa to optimize the sample preparation step. The validation results of the method were satisfactory, since the method presented recoveries between 70% and 118%, with RSD lower than 19% for spike levels between 10 and 100 µg/L. The method limit of detection (LOD) and limit of quantification (LOQ) ranged from 3.0 to 7.6 µg/L and from 4.9 to 26 µg/L respectively. The method developed was adequate for the determination of 74 pesticide residues in orange juice.

Stocka *et al*. (2016) used QuEChERS sample preparation method for the determination of ten pesticides and their metabolites in fruits (apples, grapes) and

vegetables (tomatoes, peppers), coupled to gas chromatography with an electron capture detector (GC-ECD). The GC-ECD method was validated in terms of its linearity, selectivity and recovery. The limits of detection for all investigated analytes ranged from 0.003 to 0.011 mg kg^{-1} and limits of quantification ranged from 0.009 to 0.03 mg kg^{-1}. The mean recoveries from four matrices for development method ranged from 70 to 120%, with relative standard deviations in the range of 3.9 to 7.2% for all ten test compounds. The QuEChERS approach takes advantages of the wide analytical scope and high degree of selectivity and sensitivity, it is simple, rapid and requires low solvent consumption, which, in the era of green chemistry, represents a significant advantage.

Park *et al*. (2016) investigated a total of 230 pesticide residues in 8496 samples of leafy vegetables (e.g. *Brassica* sp. namai, leafy lettuce, spinach, perilla leaves, crown daisy, marshmallow, aster scaber, pimpinellabrachycarpa and chinese chive). The result showed that among 8496 samples, 61 different pesticides were detected in 890 samples, of which 118 samples exceeded the Korean maximum residue limits (KMRLs).

Mukherjee *et al*. (2015) carried out a research on "analytical method validation and comparison of two extraction techniques for screening of azoxystrobin using LC–MS/MS" where a simple analytical method was developed and validated in chilli, tomato, grape and mango fruits using liquid chromatography tandem mass spectrometry. The method comprised of extraction with ethyl acetate and cyclohexane mixture followed by d-SPE cleanup employing modified quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction method and quantified in LC–MS/MS using gradient elution. The method was validated in concentration ranging from 0.01 to 0.1l µg g^{-1}. The recovery of azoxystrobin in different crops was ranging from 84.36 to 95.64 % at three different concentration levels of analytes with relative standard deviation of 4–14 %. The global uncertainty was calculated at limit of quantification level i.e. 0.011 µg g^{-1}. The PHI values of azoxystrobin in chilli, tomato, grape and mango fruits were determined as 4.76, 3.90, 4.06 and 10.74 days respectively.

Abdulhamid *et al.* (2015) conducted a study for the determination of organochlorine and pyrethroid pesticide residues in *Amaranthushybridus* (spinach), *Hibiscus esculentus* (okra) and *Telfairiaoccidentalis* (fluted pumpkin leaves) by QuEChERS

Method and Gas Chromatography Triple Quadrupole Mass Spectrometry. The concentration of organochlorine and pyrethroid pesticide residues in *Amaranthushybridus* (spinach), hibiscus esculentus (okra) and telfairiaoccidentalis (fluted pumpkin) sampled from seven farms in Minna, Nigeria were investigated using gas chromatography triplequadrupole mass spectrometry. The analysis showed 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 however not confirmed in these samples.

Biziuk *et al*. (2015) applied multiresidue methods for the determination of currently used pesticides in fruits and vegetables using QuEChERS technique. They stated that all over the world, applied pesticides are some of the most common pollutants of the environment because of their stability, mobility, their consequent long-term adverse effects on living organisms in general and human health in particular. The analysis of food samples for the presence of pesticides causes a lot of difficulties in consideration of specificity of sample preparation based on multistage operations of purification of sample containing vestigial amount of analyte with simultaneous large amount of interferents.

Prodhan *et al.* (2015) undertook an experiment to determine pesticide residues in 72 fresh eggplant samples collected from different market in Thessaloniki, Greece with Liquid Chromatography-Mass Spectrometry by adopting QuEChERS extraction method. Among the 72 analyzed samples, 34 (47 % of the total number 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 (European Union- Maximum Residue Limits).

Prodhan *et al.* (2015a) has been developed and validated a precise and an effective analytical method to determine pesticide residues in melon collected from different market places in Thessaloniki, Greece. In this study, the modified QuEChERS extraction in combination to liquid chromatography tandem mass spectrometry (LC-MS/MS) was used for the quantification of pesticide residues at trace levels. In this study, both insecticides and fungicides have been detected in melon samples. Among the 122 analyzed samples, 32 (26% of the total number of samples) were found to have pesticide residues.

Islam *et al.* (2014) 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. On the basis of questionnaires, 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. In two selected locations of Narsinghdi, 8.33 to 45.00 percent farmers were recorded to apply different pesticides every day and in some cases even twice in a day on vegetables. A total of 42 samples were collected from fields and markets and multiple pesticide residue analysis was done by Gas Chromatography (GC) with Flame Thermionized Detector (FTD) and Electron Capture Detector (ECD). Out of 42 samples, 27 had pesticide residue. Among these 27 samples, 14 samples had pesticide residues above the Maximum Residue Limit (MRL). The detected pesticides were diazinon, malathion, quinalphos, fenitrothion, cypermethrin, fenvalerate and propiconazole.

Hossain *et al.* (2014) conducted a study to determine the pre harvest interval (PHI) for cypermethrin and acephate in Yard long bean depending on Maximum Residue Limit (MRL) set by FAO/ WHO. Two supervised field trials were conducted and sprayed with the field dose (2 ml/L of water for acephate) and for cypermethrin, it was1 ml/L of water. Samples were collected at 0, 1, 3, 5, 7, 10, 12, and 15 days after spray. The collected samples were analyzed using Gas Chromatography (GC) coupled with Flame Thermionic Detector (FTD) and Electron Capture Detector (ECD). The level of residues were detected up to 10 DAS for cypermethrin (0.096 mg/kg), and 7 DAS for acephate (0.435 mg/kg), however, the level of detected residues for both of the pesticides were above MRLs up to 5 DAS. Therefore, The PHI was determined for both of the pesticides were 7 DAS.

Satpathy *et al*. (2014) conducted a research on ‘‘Development and validation of multi-Residue analysis of 82 pesticides in grapes and pomegranate as per the requirements of the European Union (EU) and codex alimentarius using GC-MS/MS with Compound Based Screening’’. They validated the (QuEChERS) multi-residue method for the extraction of 82 pesticides belonging to various chemical classes from grapes and pomegranate (commodities with high sugar and low lipid contents). They found that matrix-matched calibration results have demonstrated good reproducibility, robustness and linearity and spiking levels for the recovery experiments as 0.005, 0.01

and 0.1 mg/kg for GC-MS/MS analyses. They also found the mean recoveries mostly ranged between 70 and 110 % (91% on average), and RSD were generally below 12% (7.3% on average). For all compounds LODs were 0.001 to 0.005 mg/kg and LOQs were 0.005 to 0.020 mg/kg.

Hossain *et al*. (2013) carried out a research on "Health Risk Assessment of Pesticide Residues via Dietary Intake of Market Vegetables from Dhaka, Bangladesh" where they used gas chromatography with a photo diode array detector (HPLC-PDA) to determine six organophosphorus (chlorpyrifos, fenitrothion, parathion, ethion, acephate, fenthion), two carbamate (carbaryl and carbofuran) and one pyrethroid (cypermethrin) pesticide residues in twelve samples of three common vegetables (tomato, lady's finger and brinjal). Pesticide residues ranged from below detectable limit (<0.01) to 0.36 mg/kg. Acephate, chlorpyrifos, ethion, carbaryl and cypermethrin were detected in only one sample, while co-occurrence occurred twice for fenitrothion and parathion. Apart from chlorpyrifos in tomato and cypermethrin in brinjal, all pesticide residues exceeded the maximum residue limit (MRL). Hazard risk index (HRI) for ethion (10.12) and carbaryl (1.09) was found in lady's finger and tomato, respectively.

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

Panhwar and Sheikh (2013) carried out a research to analyze the effect of traditional food processing on the reduction of pesticide residues in cauliflower through GC-μECD and HPLC. The results revealed that the residual level of pesticides in unwashed unprocessed cauliflower samples are beyond their recommended MRLs i.e Bifenthrin, endosulfan, profenofos, emamectin benzoate, imidacloprid and diafenthiuron and the respective values were 0.151, 0.671, 0.172, 1.04, 1.011 and

0.052mg/kg, respectively which is far above their respective MRLS set by FAO i.e. 0.05, 0.5, 0.05, 0.5, 0.4 and 0.02mg/kg. The results of the present study showed that, the plain washing and detergent washing reduced the fat soluble pesticides in the average of 28% and 48%, respectively whereas average of water soluble pesticides was found 40% and 55%, respectively. Plain washing followed by frying reduced the fat soluble residues more (up to 98%) as compared to water soluble pesticides (91%). Sun drying (up to 93% for fat soluble and 96% for water soluble pesticide), dehydration (up to 84% for fat soluble and 87% for water soluble pesticide) and blanching (up to 72% for fat soluble and 79% for water soluble pesticide).

Cho *et al*. (2013) conducted a research on the "Evaluation of QuEChERS Method for the Determination of Pesticide Residues Using GC/NPD and GC/ECD" where the modified QuEChERS method was evaluated for rapid determination of pesticide residue in spinach by gas chromatography-nitrogen phosphorus detector and electron capture detector. They selected fifty GC amenable pesticide and found that the detector response linear with determination coefficient higher than 0. 995.They also found that the LODs for most compound ranged between 0.001 and 0.1µg/g and about 90% of the compound had LODs of less than 0.05 µg/g. The recoveries 80-120% and relative standard deviation (less than 20%) were within acceptable level except for dichlorvos, propamocarb, chlorothalonil, dichlofluanid, cyhalothrin and fenvalerate.

Milhome *et al*. (2013) carried out a research on the "Validation and Uncertainty of the method for multiresidue analysis of 35 pesticides in melon using Gas Chromatography Coupled to Quadropole Mass Spectrometry (GC-QP/MS)" and determined various validation parameters such as (selectivity, linearity, LOD, LOQ, accuracy and precision) according ABNT NBR 14029:2005. The recoveries rate for all the pesticide they studied was from 63-117% with RSD lower than 15% in the concentration range of 0.05-0.20mg/kg. They also found the LOQ for most compounds were below the MRLs established in Brazil.

Chauhan (2012) found five commonly used pesticides in vegetables, namely endosulfan, carbendazim, chlorpyrifos, cypermethrin and imidacloprid using GC-ECD and HPLC-UV-VIS type analytical techniques. Out of the five pesticides monitored, four of them were insecticides belonging to organochlorine,

organophosphate, pyrethroidand nicotine based groups respectively and one was fungicide belonging to the benzimidazole group. The analysis revealed that most of the vegetables have endosulfan residues above MRL (maximum residue limit) values followed by carbendazim, chlorpyrifos, imidachloprid and cypermthrin respectively. Amongst the different vegetable samples cauliflower and tomato had carbendazim residues higher than the recommended MRL's whereas cabbage had endosulfan contamination higher than the recommended MRL values.

Dasika *et al*. (2012) carried out a research on "Pesticide residue analysis of fruits and vegetables" where they described an efficient and effective analytical method to screen pesticides in fruits and vegetable samples using liquid chromatography tandem mass spectrometry (LC-MS/MS). They used QuEChERS method with acetate buffering (AOAC Official Method 2007.01) for sample preparation, which has been previously shown to yield high-quality results for hundreds of pesticide residues in foods.

Kanda *et al*. (2012) conducted a research using Gas Chromatography on the extracts from soil, water and vegetable samples. In soil samples, the concentrations of pesticide residues are lower than 20 μg/kg of dry material. For water samples, contamination levels vary from 0.02 to 1.1 μg/L of dry material with the highest levels for metalaxyl M (1.1 μg/L) and for dimethoate (1 μg/L). In vegetables, the concentrations measured are between 0.01 and 0.1 mg/kg of dry material. All these concentrations are affected by a positive factor of the maximum limits of residues.

Parveen *et al*. (2011) conducted a research on the "Monitoring of Multi-Residue Pesticide Residues in some fruits in Karachi, Pakistan" where they tested 120 sample of different fruits including apple, apricot, persimmon, chiku, citrus, grapes, guava, mango, papaya, peach, pulm and pomegranate procured from different selling point of Karachi. They analyzed the samples for multiple pesticide residue using GC/FID and HPLC/UV. They found and exceeding level of contamination that is 62.5% of samples contained residues of pesticide while 22% exceeded the maximum residue limit (MRL) according to FAO/WHO.

Farag *et al*. (2011) carried out a research on the ‘‘monitoring of pesticide residues in some Egyptian herbs, fruits and vegetables’’. He collects One hundred thirty-two samples of fruits, vegetables, herbs and spices from Egyptian local markets and analyzed for pesticide residues. He found that contamination with pesticide residues reached 54.55% while samples free from contamination reached 45.45%. He observed only one sample from 132 analyzed samples violated the Maximum Residue Limits (MRLs) of the Codex Committee. From the 132 analyzed samples, 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.

Sahoo *et al*. (2011) conducted a research work on the ‘‘development and validation of QuEChERS Method for the estimation of Propamocarb Residues in Tomato *(Lycopersicon esculentum)* Mill and Soil’’. In his study an easy, simple and efficient analytical method was standardized and validated for the estimation of residues of propamocarb in tomato and soil. QuEChERS method included extraction of the sample with ethyl acetate and cleanup by treatment with PSA and graphitized carbon. Final clear extracts of ethyl acetate were concentrated under vacuum to almost dryness and reconstituted into hexane. The residues of propamocarb were estimated using gas chromatograph-mass spectrometry (GC-MS). They found that propamocarb presented a distinct peak at retention time of 8.962 min. and the consistent recoveries of propamocarb ranging from 87 to 92 percent were observed when they spiked the sample at 0.10, 0.50 and 1.00 mg·kg–1 levels. They also determined the limit of quantification (LOQ) of their method was 0.10 mg/kg.

Prodhan *et al*. (2010) has been developed an analytical method for the determination of pesticide residues in fish using Gas Chromatogarphy-Mass Spectrometry (GC-MS). A total of 125 samples of fish covering Rui, Carp, Shrimp, White fish, and Fin fish were collected from Dhaka, Khulna and Chittagong region of Bangladesh and carried to the Pesticide Analytical Laboratory (PAL), Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipur. All samples were extracted and prepared for injection using the standard protocols for multi-residue analyses during September, 2007 to April, 2008. The elutes were injected into either GCMS-EI or GCMS-NCI depending on the nature of target insecticides. Results revealed that among 125 samples, 49 had insecticide residues. Out of seven samples from Dhaka, 2

had multiple insecticide residues and 1 had single insecticide residue. The detected carbofuran residues ranged from 0.29 to 1.13 ppm, the residues of diazinon, carbaryl and fenvalerate were 1.38, 0.35 and 0.009 ppm, repectively. Out of 60 samples from Chittagong, 8 had multiple insecticide residues and 15 had single insecticide residue. The detected residues of carbofuran, diazinon, fenvalerate, chlorpyrifos, heptachlor and DDT ranged from 0.17-0.89 ppm, 0.03-2.75 ppm, 0.01-0.03 ppm, 0.005 ppm, 0.19-1.15 ppm and 0.06-0.52 ppm, repectively. Out of 58 samples from Khulna, 9 had multiple insecticide residues and 14 had single insecticide residue. The detected residues of carbofuran, diazinon and DDT ranged from 0.03-1.25 ppm, 0.02-1.03 ppm and 0.04-0.12 ppm respectively. Thus 22 samples contained insecticide residue above ADI (Acceptable Daily Intake) referring to average body weight of 50 kg/person, of which 02 samples collected from Dhaka, 10 from Chittagong and 10 from Khulna region.

Charan and Sharma (2010) monitored pesticide residues in vegetables to find out the severity of such synthetic agrochemicals on human being. A total of 182 samples of six vegetables were collected for pesticide residue analysis from different agricultural fields of central Aravalli region, when they were ready for transportation to market. The analysis of samples for different pesticide residues were carried out on GC-ECD and GC-NPD systems equipped with capillary columns by using a multiple residue method. About 40.11% of total analyzed samples were contaminated with different pesticide residues, among which 35.62% of total contaminated samples were exceeded the maximum residual limit (MRL) values.

Schreiber and Wittrig (2010) carried out a research on “enhanced LC/MS for the quantitation and identification of pesticide in food sample” where he collected a variety of fruit and vegetable samples including apple, banana, carrot, cucumber, curry powder grapes, grapefruit, hazelnut, lemon, nectarine, orange, pear, raspberry, red pepper, raisin, salad, spinach and tomato from a supermarket and extracted using QuEChERs procedure. They injected the extracted sample into a liquid chromatography tandem mass spectrometry system where a total number of 12 pesticides were detected. They found 70-120% recovery for most of the pesticide with %CV<15%. They also found methamidophos 130 µg/kg, omithoate 42 µg/kg, thiamethoxam 48 µg/kg, dimethoate 54 µg/kg, clothianidin 14µg/kg, imadacloprid 2.4

µg/kg, promamocarb 98 µg/kg, carbyl 499 µg/kg, metalaxyl 5.1 µg/kg, myclobutanil 3.4 µg/kg, spinosyn A 6.1 µg/kg, spinosyn D 6.8 µg/kg.

Prodhan *et al*. (2009) undertook a research on the "Quantification of Organophosphorus and Organochlorine insecticide residues from fish sample using simple GC technique" to develop a simple technique for the quantification of organophosphorus and organochlorine insecticide residues from fish samples using Gas Chromatograph (GC) couple to Electron Capture Detector (ECD) and Flame Thermionic Detector (FTD). They collected sixty eight samples of fish (Rui, Shrimp & Others) from Dhaka, Khulna and Chittagong and carried to the Pesticide Analytical Laboratory, Entomology Division, Bangladesh Agricultural Research Institute, Gazipur. They extracted and prepared all samples for injection using the standard protocols for residue analyses during August, 2008 to July, 2009. They also injected all samples in GC-ECD for the determination of organochlorine insecticides and in GC-FTD for the determination of organophosphorus insecticides. Their results revealed that among 68 samples, 13 had insecticide residues. For Dhaka, of six samples 1 had DDT residue. The level of detected residue was 0.28 ppm. For Chittagong, out of 23 samples 3 had diazinon residue. The range of detected residue was 0.03-0.120 ppm. For Khulna, of 39 samples 9 had diazinon residue. They found the range of detected residue was 0.04-0.205 ppm. Considering the average body weight (50 kg/person), 4 samples contained residues above MRL.

Kabir *et al*. (2008) developed an analytical method for the determination of residue of diazinon and carbosulfan in brinjal and quinalphos in yard long bean under supervised field trial. The present study was undertaken to detect and quantify the left over residue of diazinon and carbosulfan in brinjal and Quinalphos in yard long bean and comparison between the detected residue level with maximum residue level (MRL) set by FAO (1970). Three supervised field trials (two for brinjal and one for yard long bean) were carried out sprayed with the field dose (1.5 ml/L of water) of diazinon, carbosulfan, and quinaiphos. Samples were collected daily after spraying till residue were found. In case of diazinon, left over residue was found upto 6 days after spray (DAS), and upto 3 DAS, the level of residue was above the MRL. Carbosulfan residue was detected till 7 DAS and the detected quantity of residue was above MRL

upto 3 DAS. Left over residue of quinalphos in yard long bean sample was detected upto 6 DAS and upto 4 DAS the level of residue was above the MRL.

Kabir *et al.* (2008a) conducted an experiment to quantify the purity in respect of active ingredient (AI) of some common insecticides used against vegetable insect pests. A series of analyses were made at Pesticide Research Laboratory, Pesticide Research & Environmental Toxicology Section, Entomology Division, BARI, Gazipur using GC-2010 (with FID and ECD detectors) and HPLC- 20A Prominence (with PDA detector). Tested insecticides were 9 brands of carbofuran 5G and 3G, 2 brands of carbaryl 85SP, 3 brands of carbosulfan 20EC, 8 brands of malathion 57EC, 9 brands of diazinon 10G and 60EC, 3 brands of quinalphos 25EC, 3 brands of dimethoate 40EC, 4 brands of cypermethrin 10EC and 7 brands of chloropyrifos 20EC). These collected insecticides were collected from pesticide traders of Jessore and Tongi region of Bangladesh. Results of the present investigation clearly indicated that most of the marketed insecticides were found to have lower AI (≤60%) than that stated on the label. In some cases AI of unknown chemical was being used. Of 9 tested brands of carbofuran, 3 were found to have 100% purity, 5 had 75-78% AI and 1 had nothing except carrier. Among 2 tested brands of carbaryl none had >50% purity while all brands of carbosulfan were found to have 78-98% purity. Eight brands of malathion were tested, of which only 2 were found as pure, 5 had 80-90% AI and 1 had 60% AI. Of 9 tested brands of diazinon, only 1 had >90 AI, while 3 had 80%, 4 had 40% and the other 1 had 10%. All 3 tested brands of quinalphos provided 68-76% AI, while all dimethoate had only 15-20% AI. Among 4 brands of cypermethrin, 3 consisted of 100% AI, only 1 had 65%. Seven brands of chloropyrifos were analyzed, 2 were found to have 100% purity, 3 had 91-97% and 2 had 85-87% AI.

Kabir *et al.* (2007) conducted an experiment at the Regional Sugarcane Research Station, Gazipur in which carbofuran (2 kg AI/ha) was applied in sugarcane field to document the level of carbofuran residue left in soil and plant samples after different days of application (DAA). Plant and soil samples were analyzed by using GCMS-EI. Carbofuran residues were found even at 90 DAA both in soil and plant. In case of soil, the amount of carbofuran residues were 24.84, 3.32, 2.12, 0.59, 0.035, 0.02 and 0.005 ppm at 0, 3, 7, 15, 30, 60 and 90 DAA, respectively. In case of plant samples, the lower residue (0.0035 ppm) was observed at 0 DAA compared to those at 3 DAA (0.075 ppm), 7 DAA (0.035 ppm) and 15 DAA (0.015 ppm). At 60 and 90 DAA,

residues were the same (0.002 ppm) while at 30 DAA it was 0.0025 ppm. The highest level of carbofuran residue (0.075 ppm) in plant samples was found at 3 DAA which is lower than FAO/WHO recommended MRL (0.1mg/kg crop).

CHAPTER III

MATERIALS AND METHODS

The vegetable (eggplant and country bean) samples were collected from 5 different markets of Barishal district and carried to the Pesticide Analytical Laboratory, Entomology Division, BARI, Joydebpur, Gazipur for pesticide residue analysis during November 2019 to February 2020. 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 Barishal district. The area of Barishal district is about 13644.85 km^2, located at 22.30° North latitude and 90.20° East longitude with an elevation of 1.2 meter from the sea level. In this study, vegetables were collected from Rupatoli Bazar, Sagardi Bazar, Chowmatha Bazar, Notun Bazar and Nothullabad Bazar in Barishal city. These markets are famous for vegetables. The vegetables of these markets come from different places of Barishal like Lakutia, Shawarupkathi, Rajapur, Patuakhali, Bhola, Agailjhara, Bhandaria, Barguna, Pirojpur, Charfashion, Jhalokati and also from some nearby places.

3.2 Sample collection

A total of 60 samples (30 country bean and 30 eggplant) were collected for this study. Six samples of country bean and six samples of eggplant were collected from each market (Rupatoli, Sagardi, Chowmatha, Notullabad and Notun Bazar) presented in Table 1 and Table 2. The quantity of each sample was 1 Kg for the selected vegetables. The samples were collected in clean transparent air tight polyethylene bags and each bag was properly labeled with sample number and sources. Samples were collected in individual polyethylene bag to avoid cross contamination.

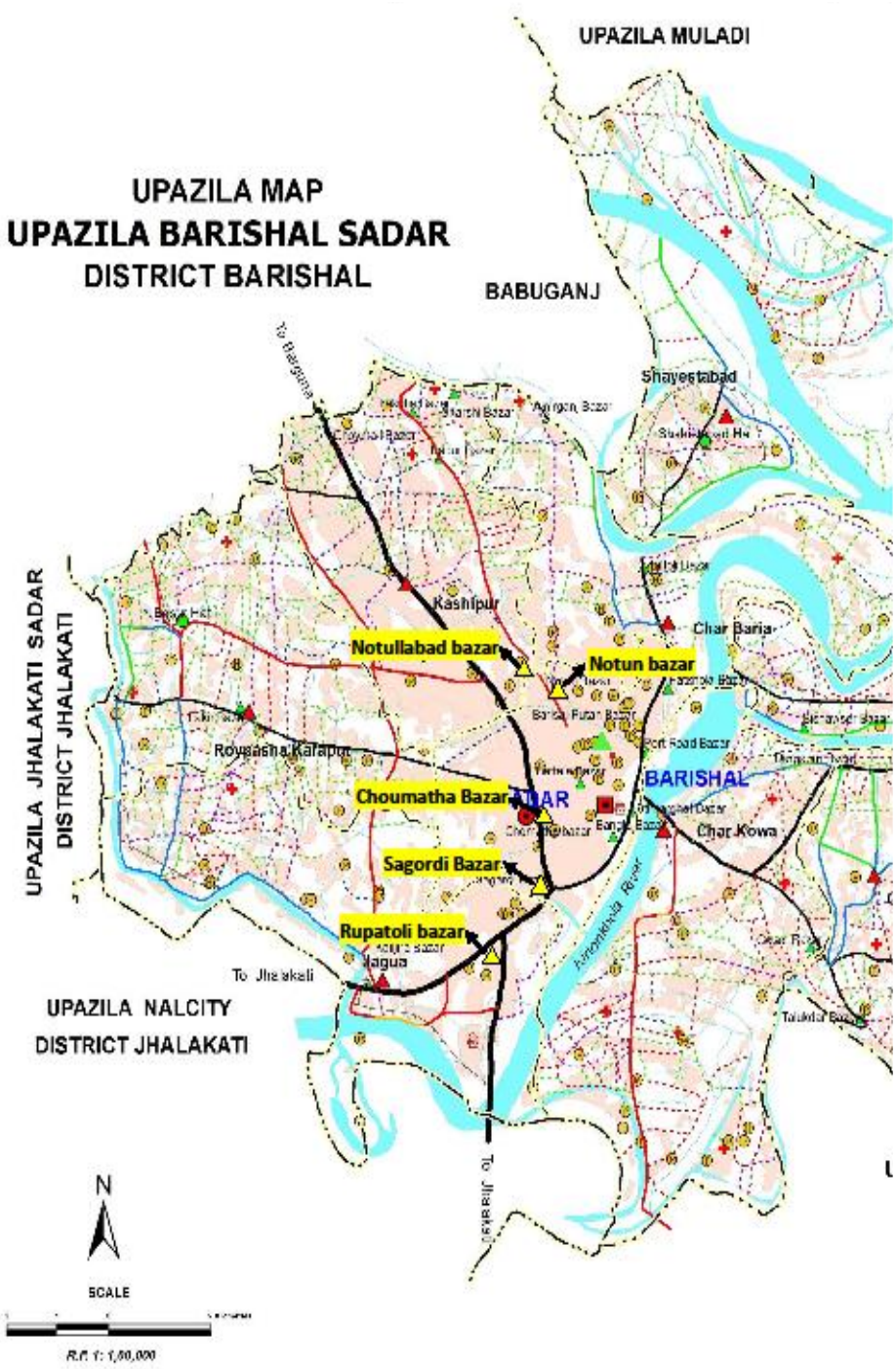


Figure 1. Map showing the places of sample collection in Barishal district.

Table 1: Sources and places of collection of country bean samples

Area of Collection	Sample ID	Source*
Rupatoli Bazar	BaBe-1	Agailjhara
	BaBe-2	Bhola
	BaBe-3	Pirojpur
	BaBe-4	Lakutia
	BaBe-5	Charfashion
	BaBe-6	Bhandaria
Sagardi Bazar	BaBe-7	Pirojpur
	BaBe-8	Jhalokati
	BaBe-9	Lakutia
	BaBe-10	Rajapur
	BaBe-11	Patuakhali
	BaBe-12	Bhola
Chowmatha Bazar	BaBe-13	Swarupkati
	BaBe-14	Lakutia
	BaBe-15	Jhalokati
	BaBe-16	Charfashion
	BaBe-17	Agailjhara
	BaBe-18	Barguna
Notun Bazar	BaBe-19	Patuakhali
	BaBe-20	Rajapur
	BaBe-21	Pirojpur
	BaBe-22	Swarupkati
	BaBe-23	Lakutia
	BaBe-24	Bhola
Nothullabad Bazar	BaBe-25	Patuakhali
	BaBe-26	Charfashion
	BaBe-27	Agailjhara
	BaBe-28	Swarupkathi
	BaBe-29	Bhandaria
	BaBe-30	Barguna

* According to the retailer's opinion

Table 2: Sources and places of collection of eggplant samples

Area of Collection	Sample ID	Source*
Rupatoli Bazar	BaBj-1	Patuakhali
	BaBj-2	Rajapur
	BaBj-3	Pirojpur
	BaBj-4	Swarupkati
	BaBj-5	Lakutia
	BaBj-6	Bhola
Sagardi Bazar	BaBj-7	Patuakhali
	BaBj-8	Charfashion
	BaBj-9	Agailjhara
	BaBj-10	Swarupkathi
	BaBj-11	Bhandaria
	BaBj-12	Barguna
Chowmatha Bazar	BaBj-13	Pirojpur
	BaBj-14	Jhalokati
	BaBj-15	Lakutia
	BaBj-16	Rajapur
	BaBj-17	Patuakhali
	BaBj-18	Bhola
Notun Bazar	BaBj-19	Agailjhara
	BaBj-20	Bhola
	BaBj-21	Pirojpur
	BaBj-22	Lakutia
	BaBj-23	Charfashion
	BaBj-24	Bhandaria
Nothullabad Bazar	BaBj-25	Swarupkati
	BaBj-26	Lakutia
	BaBj-27	Jhalokati
	BaBj-28	Charfashion
	BaBj-29	Agailjhara
	BaBj-30	Barguna

* According to the retailer's opinion

The quantity of each sample was 1 Kg for all the vegetables. The samples were collected in clean transparent air tight polyethylene bag and each bag was properly labeled with sample number and sources. Sample was collected in individual polyethylene bag to avoid cross contamination.

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 acetamiprid, cypermethrin, lambda-cyhalothrin, and thiram 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

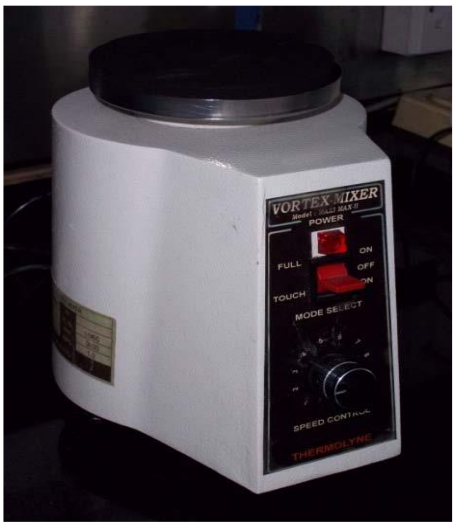


Plate 2. Vortex Mixer

Plate 3. Centrifuge Machine

Plate 4. Gas Chromatogram(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

3.5.1 Some pictorial view related to sample preparation:

Plate 5: Chopping of collected Sample

Plate 6: Homogenization of collected Sample

Plate 7: Adding Acetonitrile

Plate 8: Adding of salt (NaCl and MgSO4)

Plate 09: Shaking of sample

Plate 10: Centrifuging the sample

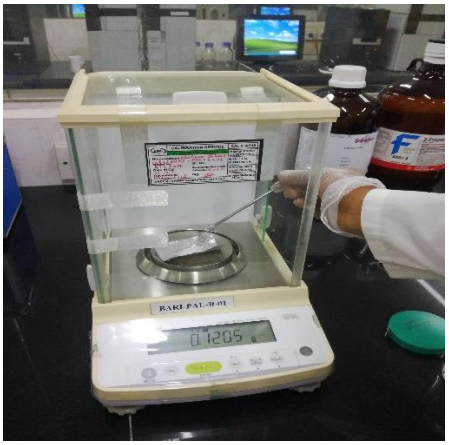


Plate 11: Weighing of PSA

Plate 12: Taking supernatant to the test tube

Plate 13: Filtration through PTFE filter

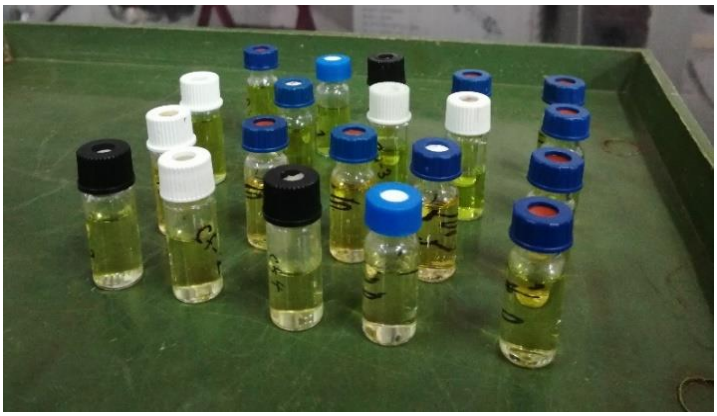


Plate 14. Sample extract ready for injection

3.6 Preparation of pesticide standard solution

Pesticide standard stock solutions of acetamiprid, cypermethrin, lambda-cyhalothrin and thiram were prepared separately in acetonitrile (ACN) at a concentration of 1000 mg/L and stored at -20°C until use. A mixed standard solution of 50 mg/L in ACN 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 ACN 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 ACN were prepared by transferring the appropriate amount from 10 mg/L intermediate mixed standard solution into ten separate 10-mL volumetric flasks. All the standard solutions were kept in a refrigerator 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 technique 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 the extraction of both polar and non-polar pesticide. This sample initial step simultaneously extracts 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.

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 ground 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 $MgSO_4$ and 1g 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 $MgSO_4$ 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 Electron Capture Detector (ECD) for the detection of three insecticides (acetamiprid, cypermethrin, and lambda-cyhalothrin) and 1 fungicide (thiram). The capillary column was AT-1, length was 30m, ID was 0.25mm and film thickness was 0.25µm. Nitrogen was used as carrier and make up gas for GC-ECD. The identification of suspected pesticide was performed by peak retention times in samples to those of peaks in the pure analytical standards (Figure 2-9). The instrument conditions are described in Table 3-7.

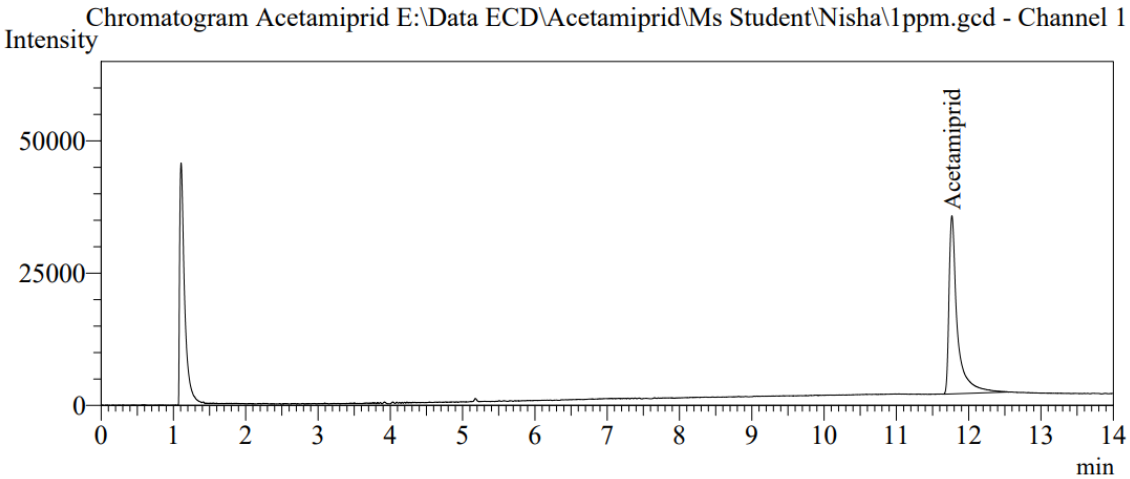


Figure 2. Typical Chromatograms of acetamiprid standards run by GC-ECD

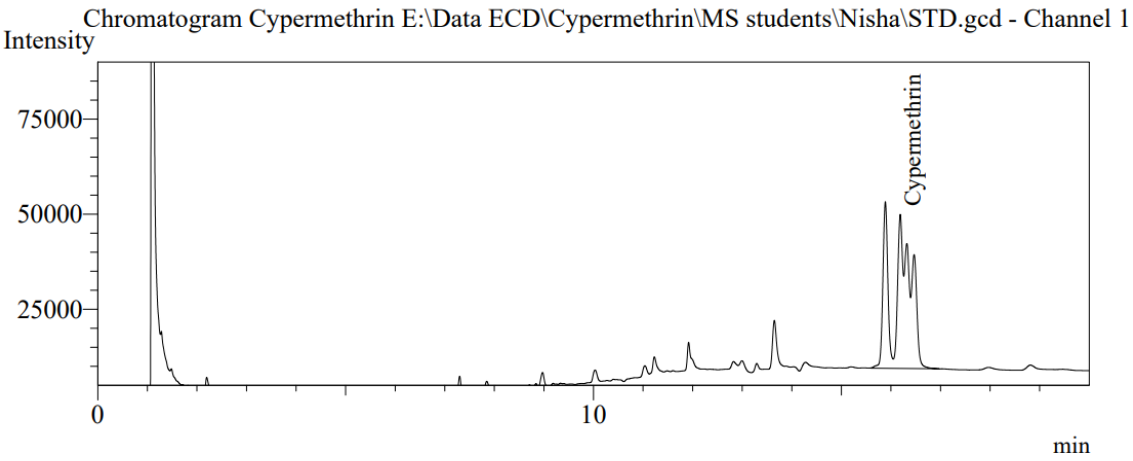


Figure 3. Typical Chromatogram of cypermethrin standard run by GC-ECD

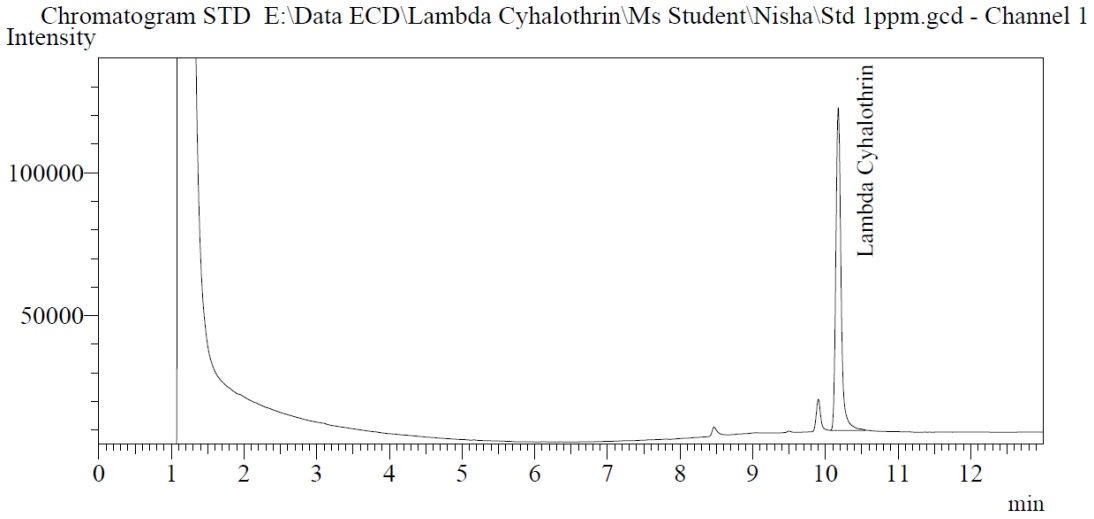


Figure 4. Typical Chromatogram of lambda-cyhalothrin standard run by GC-ECD

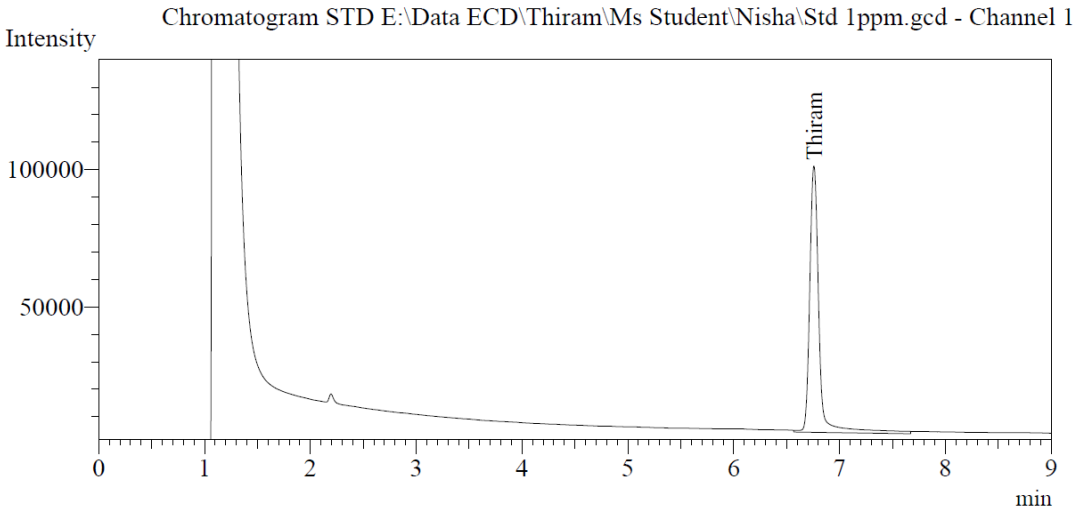


Figure 5. Typical Chromatograms of thiram standard run by GC-ECD

Table 3. The instrument parameters for GC-ECD

Instruments	**Conditions**
Injection port SPL	Injection mode: split; temperature:280°C; flow control mode: linear velocity; split ratio: 10:0
Detector channel 1 ECD	Temperature:300°C; current: 0.50 Pa; make up flow: 30 mL/min;

Table 4. Conditions for column oven temperature for acetamiprid determination

Column oven	Rate	Temperature (°C)	Hold time (min)
Initial temperature: 160°C	-	160	0
	15.0	220	0
	10.0	250	0
	5.0	270	3

Table 5. Conditions for column oven temperature for cypermethrin determination

Column oven	Rate	Temperature (°C)	Hold time (min)
Initial temperature: 160°C	-	160	1
	10	270	8

Table 6. Conditions for column oven temperature for thiram determination

Column oven	Rate	Temperature (°C)	Hold time (min)
Initial temperature: 220°C	-	220	0
	5.0	250	3

Table 7. Conditions for column oven temperature for lambda-cyhalothrin Determination

Column oven	Rate	Temperature (°C)	Hold time (min)
Initial temperature: 160°C	-	160	0
	15	220	0
	10.0	270	4

3.9 Calibration curve preparation

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 6-9). Each peak was characterized by its retention time. Sample results were expressed in mg/kg automatically by the GC software.

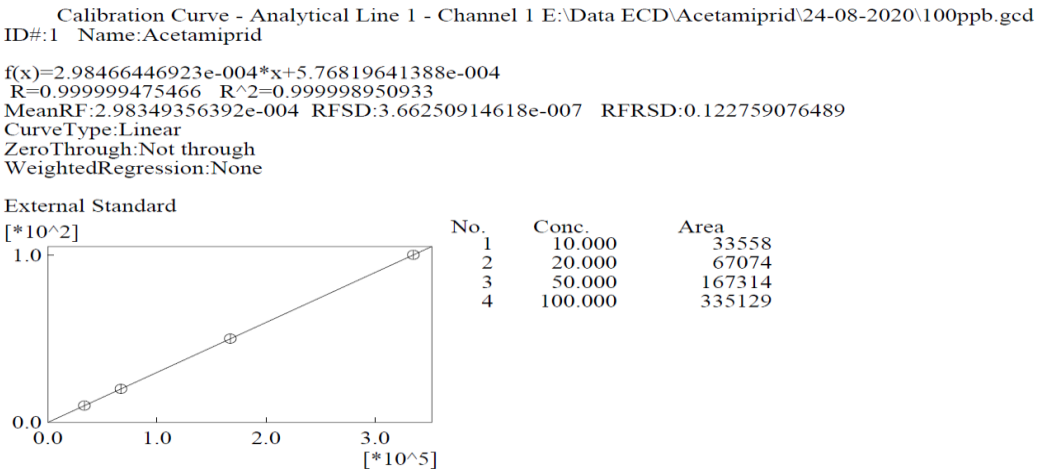


Figure 6. Calibration curve prepared for acetamiprid made with different concentrations ranging from 10 µg/L to 100 µg/L.

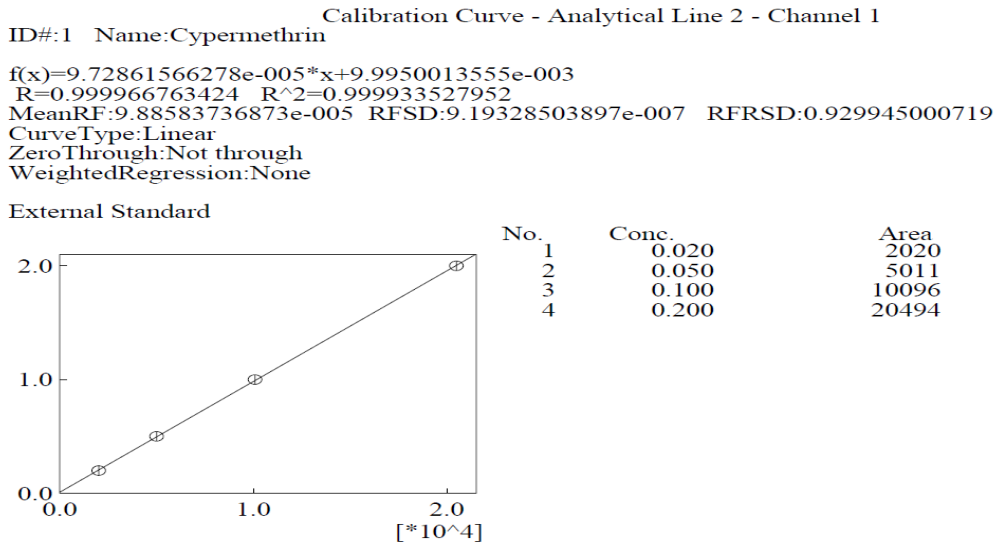
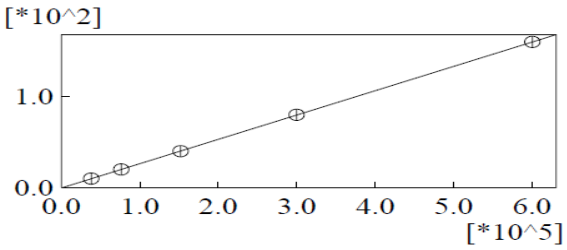


Figure 7. Calibration curve prepared for cypermethrin made with different concentrations ranging from 20 µg/L to 200 µg/L.

Calibration Curve - Analytical Line 1 - Channel 1
ID#:1 Name:Thiram

f(x)=2.67125267516e-004*x-0.358918911314
R=0.999994312816 R^2=0.999988625665
MeanRF:2.63979444472e-004 RFSD:2.38482372024e-006 RFRSD:0.903412659654
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard



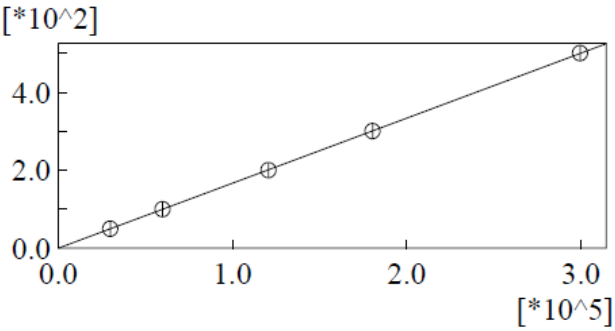
No.	Conc.	Area
1	10.000	38131
2	20.000	76418
3	40.000	152201
4	80.000	300024
5	160.000	600448

Figure 8. Calibration curve prepared for thiram made with different concentrations ranging from 10 µg/L to 160 µg/L.

Calibration Curve - Analytical Line 1 - Channel 1
ID#:1 Name:Lambda Cyhalothrin

f(x)=1.66809373616e-003*x-0.347455682203
R=0.999991464358 R^2=0.999982928789
MeanRF:1.66651033293e-003 RFSD:6.5983219302e-006 RFRSD:0.395936454746
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard



No.	Conc.	Area
1	50.000	29871
2	100.000	59888
3	200.000	120696
4	300.000	180415
5	500.000	299581

Figure 9. Calibration curve prepared for lambda-cyhalothrin made with different concentrations ranging from 50 µg/L to 500 µg/L.

CHAPTER IV

RESULTS AND DISCUSSION

60 samples of vegetable (country bean and eggplant) were collected from 5 different markets (Rupatoli Bazar, Sagardi Bazar, Chowmatha Bazar, Notun Bazar and Nothullabad Bazar) of Barishal 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 Bean

The concentrated extracts of bean samples collected from different markets of Barishal city were analyzed by GC-2010 (Shimadzu) with Electron Capture Detector (ECD) with the pre-set parameters. Figure 10-14 shows the chromatograms of the injected extracts of bean sample containing detected pesticides.

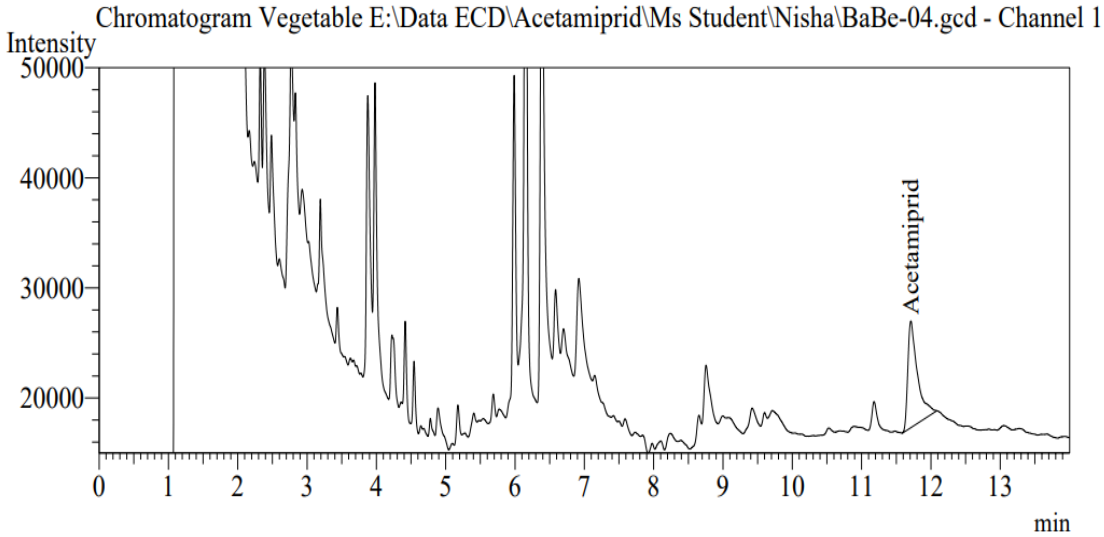


Figure 10. Chromatogram of acetamiprid found in one of the bean sample (BaBe-04) collected from Rupatoli bazar.

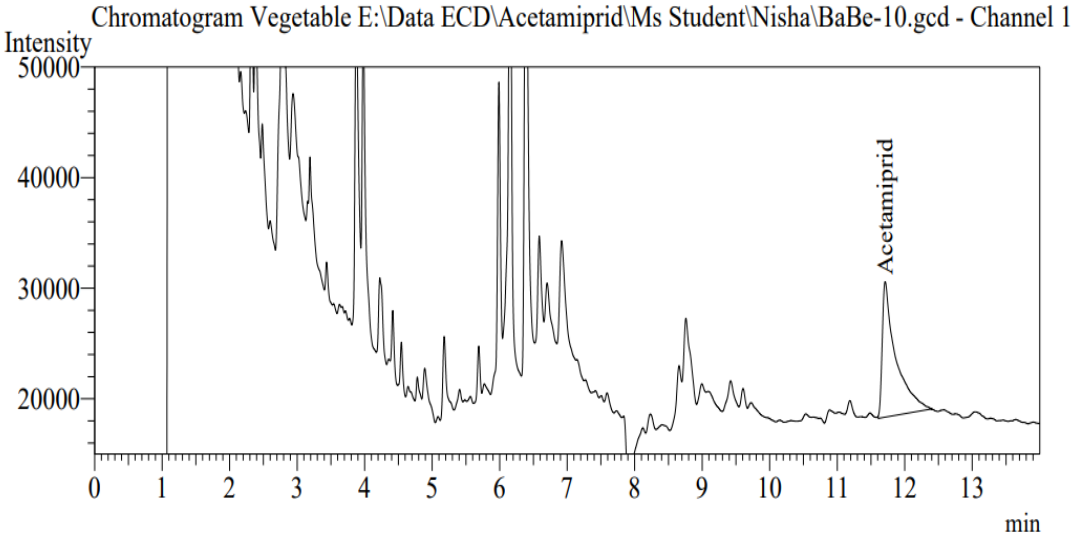


Figure 11. Chromatogram of acetamiprid found in one of the bean sample (BaBe-10) collected from Sagardi bazar.

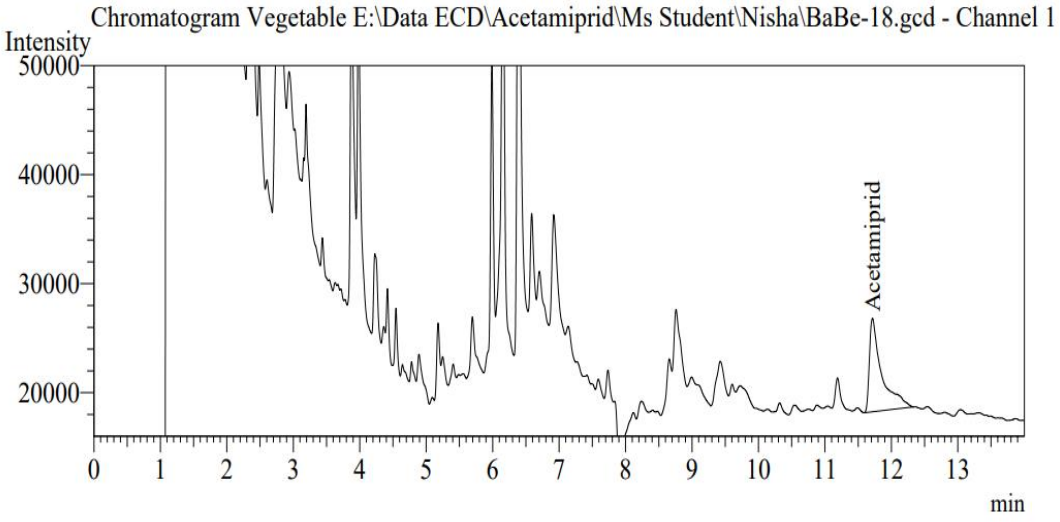


Figure 12. Chromatogram of acetamiprid found in one of the bean sample (BaBe-18) collected from Chowmatha bazar.

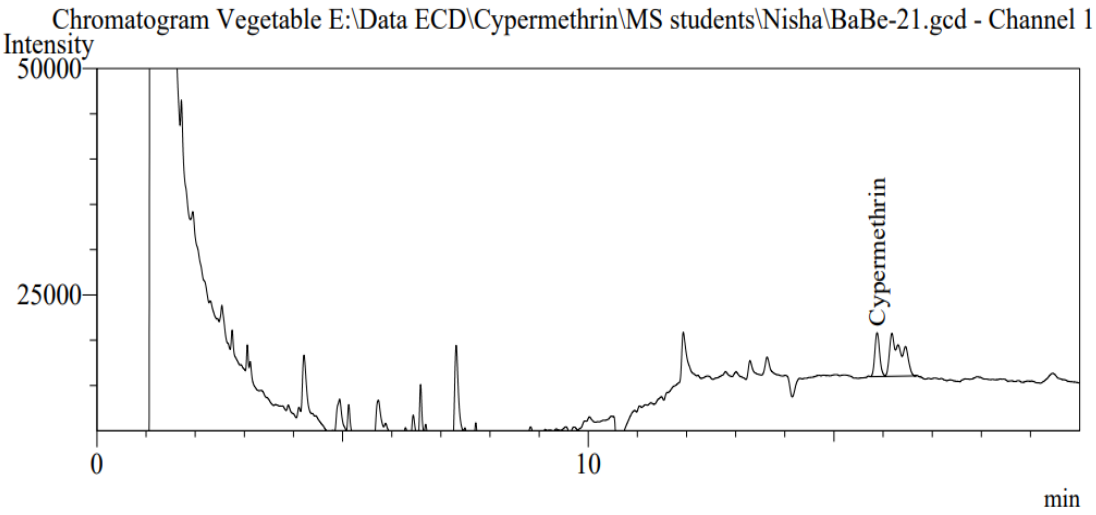


Figure 13. Chromatogram of cypermethrin found in one of the bean sample (BaBe-21) collected from Notun bazar.

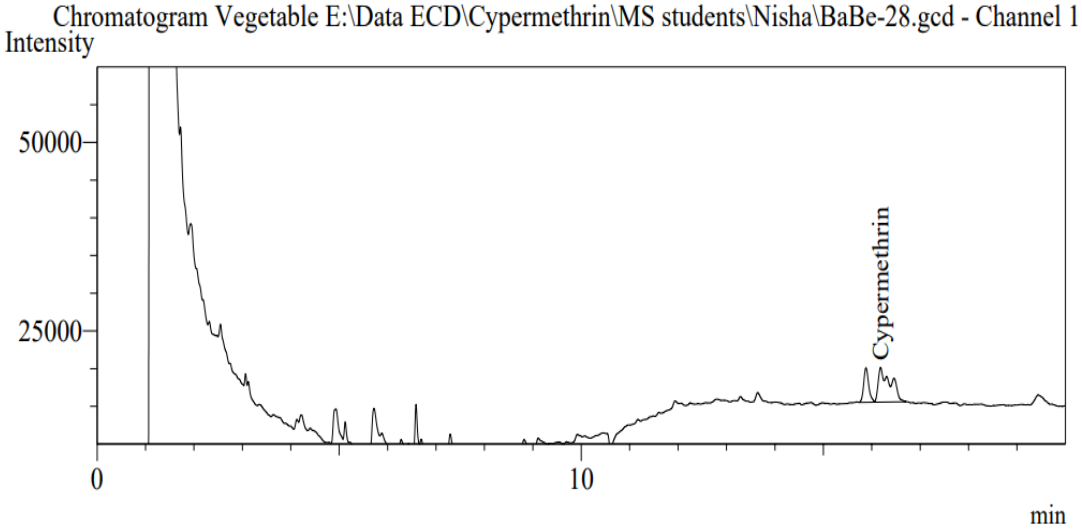


Figure 14. Chromatogram of cypermethrin found in one of the bean sample (BaBe-28) collected from Nothullabad bazar.

The level of pesticide residues found in the analyzed bean samples and their maximum residue levels are outlined in Table 8.

Table 8. The level of residues (mg/kg) of different pesticides found in the analyzed country bean samples

Area of Collection	Sample ID	Name of detected pesticide	Level of residue (mg/kg)	MRLs (mg/kg)
Rupatoli Bazar	BaBe-1	ND	-	-
	BaBe -2	ND	-	-
	BaBe -3	ND	-	-
	BaBe -4	Acetamiprid	0.341	0.6*
	BaBe -5	ND	-	-
	BaBe -6	ND	-	
Sagardi Bazar	BaBe -7	ND	-	-
	BaBe -8	ND	-	-
	BaBe -9	ND	-	-
	BaBe -10	Acetamiprid	0.672	0.6*
	BaBe -11	ND	-	-
	BaBe -12	ND	-	-
Chowmatha Bazar	BaBe -13	ND	-	-
	BaBe -14	ND	-	-
	BaBe -15	ND	-	-
	BaBe -16	ND	-	-
	BaBe -17	ND	-	-
	BaBe -18	Acetamiprid	0.278	0.6*
Notun Bazar	BaBe -19	ND	-	-
	BaBe -20	ND	-	-
	BaBe -21	Cypermethrin	0.116	0.7*
	BaBe -22	ND	-	-
	BaBe -23	ND	-	-
	BaBe -24	ND	-	-
Nothullabad Bazar	BaBe -25	ND	-	-
	BaBe -26	ND	-	-
	BaBe -27	ND	-	-
	BaBe -28	Cypermethrin	0.081	0.7*
	BaBe -29	ND	-	-
	BaBe -30	ND	-	-

*According to the EU Pesticide Database (European Commission 2019)

Thirty samples of country bean collected from 5 different markets of Barishal city (Rupatoli, Sagardi, Chowmatha, Notun, Nothullabad Bazar) and were analyzed to find out the presence of left over residue of four pesticides (acetamiprid, cypermethrin, lambda-cyhalothrin and thiram). Out of 30 samples, 5 samples (17% of the total

number of samples) contained acetamiprid and cypermethrin residues and 25 samples (83% of the total number of samples) contained no detectable residues of the sought pesticides. Acetamiprid was the most frequently used pesticide which was identified in the country bean samples. In case of 30 samples of country beans collected from those bazars contained no residues of thiram and lambda-cyhalothrin. The findings of the present investigation agree with the findings of Islam *et al*. (2019), they found that among the 65 analyzed eggplant samples, 8 (12.3% of the total number of samples) were contaminated with pesticide residues and all of the contaminated samples contained residues above Maximum Residue Limit (MRL) set by European Commission (EC) collected from different markets of Savar, Dhaka of Bangladesh. The results of the present study are also supported by the findings of Islam et al. (2014), who reported 15 out of total 42 samples (about 35.71%) of eggplant, cauliflower and country bean contained no residues of the sought pesticides collected from fields and markets in Narsingdi district of Bangladesh.

Pesticide residue status in the samples of country bean collected from Rupatoli area:

Six country bean samples were collected from Rupatoli area, where one sample (BaBe-04) contained pesticide residues. This sample (BaBe-04) contained acetamiprid at a level of 0.341 mg/kg, which was below the EU-MRL (0.6 mg/kg). The other 5 samples contain no detectable pesticide residues. According to retailer's opinion, this residue detected sample (BaBe-04) was collected from Lakutia area.

Pesticide residue status in the samples of country bean collected from Sagardi Bazar area:

Only one sample (BaBe-10) contained residue of acetamiprid (0.672 mg/kg) and the other five samples contained no detectable pesticide residues among the six samples collected from Sagardi Bazar area. The level of detected residue was 0.672 mg/kg, which was above EU-MRL (0.6 mg/kg). According to retailer's opinion, this contaminated sample (BaBe-10) originated from Rajapur area.

Pesticide residue status in the samples of country bean collected from Chowmatha Bazar area:

Among the six samples of country bean from Chowmatha Bazar, one sample (BaBe-18) contained acetamiprid residue. The residue level was 0.278 mg/kg, which was

below the EU-MRL (0.6 mg/kg). This contaminated sample (BaBe-18) was collected from Barguna area. The other 5 samples contain no detectable pesticide residues.

Pesticide residue status in the samples of country bean collected from Notun Bazar area:

0ne sample (BaBe-21) of country bean contained residue of cypermethrin among the six samples collected from Notun bazar area. The sample ID of BaBe-21 contained 0.116 mg/kg of cypermethrin residue, which was below the Maximum Residue Level (0.7 mg/kg). This residue contaminated sample belonged to Pirojpur area. The other 5 samples contain no detectable pesticide residues.

Pesticide residue status in the samples of country bean collected from Nothullabad area:

Only one sample (BaBe-28) contained residue of cypermethrin and the other five samples contained no detectable pesticide residues among the six samples collected from Nothullabad Market area. The level of detected residue was 0.081 mg/kg, which was lower than the EU-MRL (0.7 mg/kg). This contaminated sample (BaBe-28) was originated from Swarupkathi area.

4.2 Pesticide residues in eggplant

The concentrated extracts of eggplant samples collected from different markets of Barishal city and were analyzed by GC-2010 (Shimadzu) with Electron Capture Detector (ECD) with the pre-set parameters. Figure 15-18 shows the chromatograms of the injected extracts of eggplant sample containing detected pesticides.

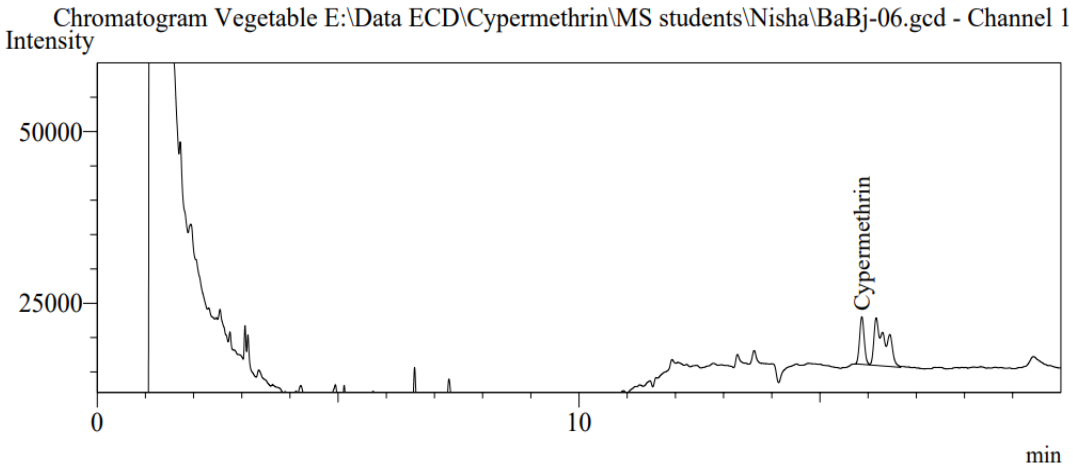


Figure 15: Chromatogram of cypermethrin found in one of the eggplant sample (BaBj-06) collected from Rupatoli bazar.

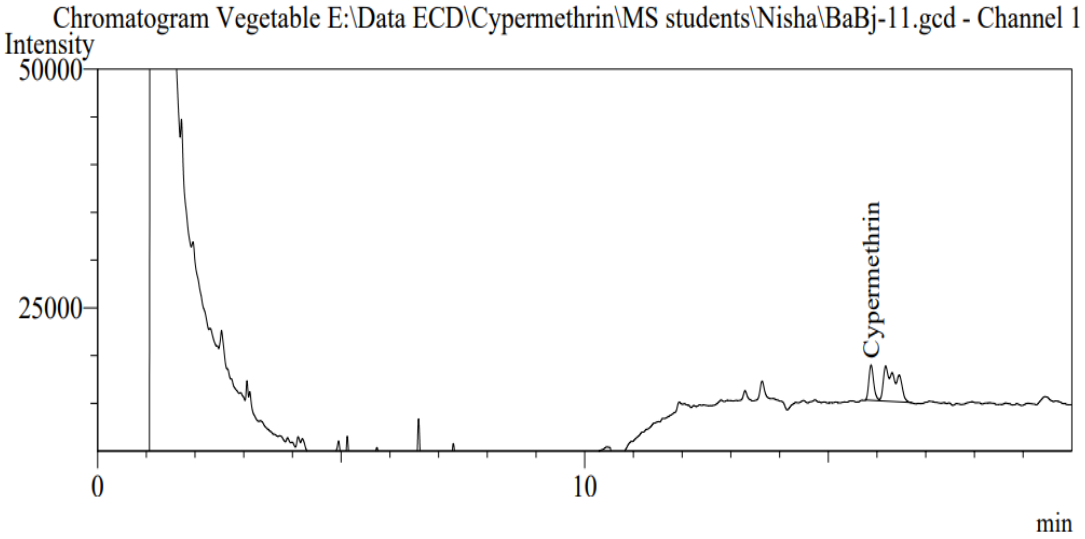


Figure 16: Chromatogram of cypermethrin found in one of the eggplant sample (BaBj-11) collected from Sagardi bazar.

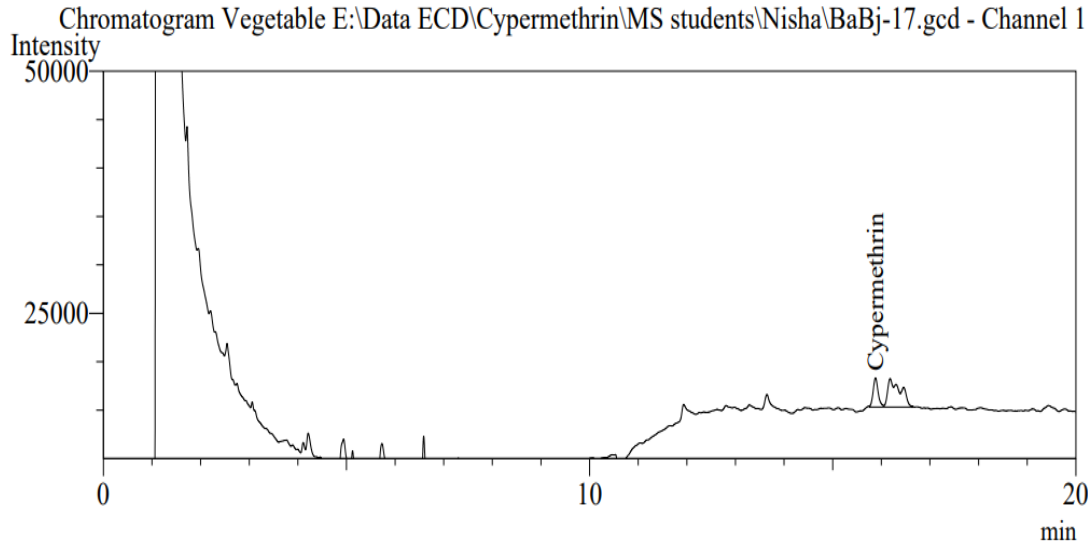


Figure 17: Chromatogram of cypermethrin found in one of the eggplant sample (BaBj-17) collected from Chowmatha bazar.

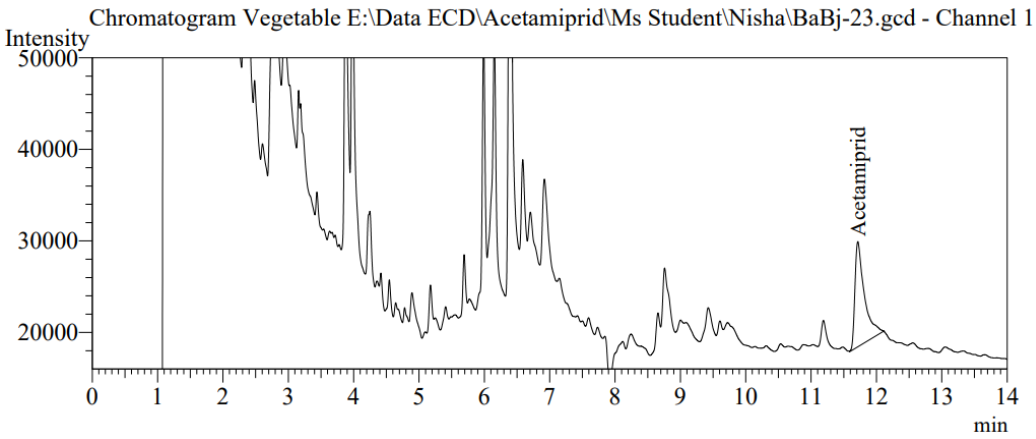


Figure 18: Chromatogram of acetamiprid found in one of the eggplant sample (BaBj-23) collected from Notun bazar.

The level of pesticide residues found in the analyzed eggplant samples and their maximum residue levels are presented in Table 9.

Table 9. The level of residues (mg/kg) of different pesticides found in the eggplant samples

Area of Collection	**Sample ID**	**Name of detected pesticide**	**Level of residue (mg/kg)**	**MRLs (mg/kg)**
Rupatoli Bazar	BaBj-1	ND	-	-
	BaBj-2	ND	-	-
	BaBj-3	ND	-	-
	BaBj-4	ND	-	-
	BaBj-5	ND	-	-
	BaBj-6	Cypermethrin	0.156	0.5*
Sagardi Bazar	BaBj-7	ND	-	-
	BaBj-8	ND	-	-
	BaBj-9	ND	-	-
	BaBj-10	ND	-	-
	BaBj-11	Cypermethrin	0.090	0.5*
	BaBj-12	ND	-	-
Chowmatha Bazar	BaBj-13	ND	-	-
	BaBj-14	ND	-	-
	BaBj-15	ND	-	-
	BaBj-16	ND	-	-
	BaBj-17	Cypermethrin	0.071	0.5*
	BaBj-18	ND	-	-

Notun Bazar	BaBj-19	ND	-	-
	BaBj-20	ND	-	-
	BaBj-21	ND	-	-
	BaBj-22	ND	-	-
	BaBj-23	Acetamiprid	0.389	0.2*
	BaBj-24	ND	-	-
Nothullabad Bazar	BaBj-25	ND	-	-
	BaBj-26	ND	-	-
	BaBj-27	ND	-	-
	BaBj-28	ND	-	-
	BaBj-29	ND	-	-
	BaBj-30	ND	-	-

*According to the EU Pesticide Database (European Commission 2017)

Thirty samples of eggplant collected from 5 different markets of Barishal city (Rupatoli, Sagardi, Chowmatha, Notun and Nothullabad Market) and were analyzed to find out the presence of left over residues of four pesticides (acetamiprid, cypermethrin, lambda-cyhalothrin and thiram). Out of 30 samples, 4 samples (13% of the total number of samples) contained pesticide residues and 26 samples (87% of the total number of samples) contained no detectable residues of the sought pesticides. Cypermethrin was the most used pesticide which was identified in eggplant in the studied area. The presence of left over residues of thiram and lambda-cyhalothrin did not found in those five market samples.

The outcome of the present study is in a good agreement with the outcome of Akter *et al.* (2017), they found that among the 50 analyzed samples of the eggplants, 11 (22% of the total number of the samples) contained residues of diazinon, dimethoate, quinalfos, and chlorpyrifos in eggplant collected from Mymensingh district of Bangladesh, of which, 2 had multiple pesticide residues and 5 contained residues above the EU-MRLs. The results of this study also supported by the findings of Hasan et al. (2017), they found that out of 50 analyzed samples, 10 samples (20%) contained residues of dimethoate and quinalphos in eggplant collected from different markets of Dhaka district of Bangladesh.

Pesticide residue status in the samples of eggplant collected from Rupatoli Bazar area:

Six samples of eggplant were collected from Rupatoli area, among them one sample (BaBj-06) contained residue of cypermethrin. The level of detected pesticide residues was 0.156 mg/kg, which was lower than the Maximum Residue level (0.5 mg/kg). This residue contained sample (BaBj-06) come from Bhola area. The other 5 samples contain no detectable pesticide residues.

Pesticide residue status in the samples of eggplant collected from Sagordi Bazar area:

Among the six samples of eggplant collected from Sagordi Bazar, one sample (BaBj-11) contained residues of pesticide. Sample ID of BaBj-11 contained residues of cypermethrin, where the level of this residue was 0.090 mg/kg and the level was below EU-MRL (0.5 mg/kg). According to retailer opinion, this sample (BaBj-11) came to this market from Bhandaria area of Pirojpur district. The other 5 samples contain no detectable pesticide residues.

Pesticide residue status in the samples of eggplant collected from Chowmatha Bazar area:

Among the six samples of eggplant collected from Chowmatha bazar, one sample (BaBj-17) contained residue of pesticides. This sample contained residue of cypermethrin, where the level of residues was 0.071 mg/kg. The level of residue of this sample was lower than the EU-MRL (0.5 mg/kg). Patuakhali area was the source of this contaminated sample (BaBj-17). The other 5 samples contain no detectable pesticide residues.

Pesticide residue status in the samples of eggplant collected from Notun Bazar area:

Six samples of eggplant were collected from Notun bazar area, among them, one sample (BaBj-23) contained residue of acetamiprid. The level of detected pesticide residue was 0.389 mg/kg, which was higher than the Maximum Residue level (0.2 mg/kg). According to retailer opinion, the contained sample (BaBj-23) came from Charfashion area of Bhola district. The other 5 samples contain no detectable pesticide residues.

Pesticide residue status in the samples of eggplant collected from Nothullabad Bazar area:

In case of six samples of eggplant collected from Nothullabad Bazar contained no residues of the sought pesticides.

CHAPTER V

SUMMARY AND CONCLUSION

Vegetables are most important sources of vitamin and nutrition in our country, but it contributes a very poor portion in our daily intake because of its low production. The main obstacle of vegetable production in our country is infestation of insect pests and diseases. To increase the vegetable production, use of different pesticides and other chemicals have become a common agricultural practice by the farmers, and a major portion of these pesticides are intercepted by the plant leaves during application.

The purpose of this study was intended to identify and quantify the pesticide residue level present in the vegetable available in various local markets of Barishal City. Thirty samples of country bean and thirty samples of eggplant were collected from five different locations (Rupatoli, Sagardi, Chowmatha, Notun and Nothullabad bazar) of Barishal City and carried to the Pesticide Analytical Laboratory, Pesticide Research & Environmental Toxicology Section, Division of Entomology, Bangladesh Agricultural Research Institute (BARI), Gazipur, Bangladesh. The QuEChERS extraction technique was applied for the extraction and cleanup of the collected samples. Gas chromatography associated with Electron Capture Detector (ECD) was used to identify and quantify the level of pesticide residues present in the extracted samples. Four most commonly used pesticides i.e. acetamiprid, cypermethrin, lambda-cyhalothrin and thiram were selected for this study.

Among the 30 samples of country bean, 5 samples (17% of the total number of samples) contained residues of acetamiprid and cypermethrin, and among them, 4 samples contained residues below the EU-MRL and 1 sample had residue above the EU-MRL. On the other hand, 25 samples (83% of the total number of samples) contained no detectable residues of the sought pesticides.

Out of 30 samples of eggplant, 4 samples (13%) contained residues of acetamiprid and cypermethrin and among them, 3 samples contained residues below the EU-MRL and 1 sample had residue above the EU-MRL. Other 26 samples (87% of the total number of samples) contained no detectable residues of the sought pesticide. According to retailer's opinion, Lakutia, Rajapur, Barguna, Pirojpur and Swarupkathi areas were identified pesticide contamination area for country bean. In case of

eggplant, Bhola, Bhandaria, Patuakhali and Charfashion areas were identified pesticide contamination area. Acetamiprid and cypermethrin were the most commonly used pesticides in this area. The presence of thiram and lambda-cyhalothrin residue did not found in any of the analyzed samples.

Now day's pesticide residues in vegetables and other foods have become a most important concern and a safety issue for the consumers. This study will help to understand the residual contamination of studied vegetables in the study area and will help to increase public awareness as well.

Recommendations for further research:

The research has done only five market places of Barishal district of Bangladesh. More research work should be done in other areas of Barishal district of Bangladesh in order to find out the actual scenario of pesticide residue load in different vegetables grown in this district. This research work was carried out only for two vegetables (country bean and eggplant), more research work containing different vegetables should be done to find out the harmful effect of pesticide residues in order to save the peoples of Bangladesh.

CHAPTER VI

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