RISK ASSESSMENT OF SELECTED PESTICIDE RESIDUES IN TOMATO AND BITTER GOURD COLLECTED FROM KISHOREGANJ DISTRICT OF BANGLADESH

SAMINA JAHAN

DEPARTMENT OF AGRICULTURAL CHEMISTRY
SHER-E-BANGLA AGRICULTURAL UNIVERSITY
DHAKA-1207

JUNE, 2021

RISK ASSESSMENT OF SELECTED PESTICIDE RESIDUES IN TOMATO AND BITTER GOURD COLLECTED FROM KISHOREGANJ DISTRICT OF BANGLADESH

BY

SAMINA JAHAN

REGISTRATION NO. 13-05404

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

MASTER OF SCIENCE
IN
AGRICULTURAL CHEMISTRY

SEMESTER: JANUARY- JUNE, 2021

Approved by:

Supervisor   **Co-Supervisor**

Dr. Md. Tazul Islam Chowdhury
Professor
Department of Agricultural Chemistry
Sher-e-Bangla Agricultural University
Dhaka-1207

Dr. Mohammad Dalower Hossain Prodhan
Senior Scientific Officer
Pesticide Research & Environmental Toxicology Section
Entomology Division
Bangladesh Agricultural Research Institute
Gazipur-1701

Prof. Dr. Sheikh Shawkat Zamil
Chairman
Examination Committee

CERTIFICATE

This is to certify that thesis entitled **"RISK ASSESSMENT OF SELECTED PESTICIDE RESIDUES IN TOMATO AND BITTER GOURD COLLECTED FROM KISHOREGANJ DISTRICT OF BANGLADESH"** submitted to the Faculty of Agriculture, 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 *SAMINA JAHAN, Registration No. 13-05404* under my supervision and guidance. No part of the thesis has been submitted for any other degree or diploma.

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

Dated: 20.02.2022
Dhaka, Bangladesh

_____
Dr. Md. Tazul Islam Chowdhury
Professor
Department of Agricultural Chemistry
Sher-e-Bangla Agricultural University
Supervisor

DEDICATED TO
MY
BELOVED FAMILY

ACKNOWLEDGEMENT

RISK ASSESSMENT OF SELECTED PESTICIDE RESIDUES IN TOMATO AND BITTER GOURD COLLECTED FROM KISHOREGANJ DISTRICT OF BANGLADESH

ABSTRACT

An experiment was performed to analyze selected pesticide residues in tomato and bitter gourd and to assess the chronic health risk indices associated with the residues. The samples were procured from five vital markets of five upazilas namely Kishoreganj Sadar, Katiadi. Bajitpur, Kuliarchar and Bhairab of Kishoreganj district and transported to the Pesticide Analytical Laboratory, Pesticide Research and Environmental Toxicology Section, Entomology Division of Bangladesh Agricultural Research Institute (BARI), Gazipur. Total 70 samples of two vegetables were analyzed using modified Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) extraction method and Gas Chromatography (GC) coupled with Electron Capture Detector (ECD) for the determination of residues of three pesticides namely acetamiprid, cypermethrin, and lambda-cyhalothrin. The chronic health risk indices of the detected pesticide residues were calculated based on the estimated daily intake (EDI) and acceptable daily intake (ADI) for both adult and children population. Out of 35 analyzed samples of tomato, only 3 samples contained residues of cypermethrin and acetamiprid which were below the maximum residue limits set by European Union (EU-MRL) and the rest 32 samples contained no detectable residues. In case of 35 samples of bitter gourd, 4 samples contained residues of acetamiprid and lambda-cyhalothrin and 31 samples were free from detectable residues. Out of those 4 contaminated samples, 2 samples contained lambda-cyhalothrin exhibited residue level above the maximum residue limits (EU-MRLs) and the other 2 samples contained acetamiprid showed the residue level below the maximum residue limits (EU-MRLs). All the contaminated samples posed no risk for adult as the risk index values were below one but two samples with lambda-cyhalothrin indicate associated risk for children. This study revealed an overall scenario of selected pesticide residues in tomato and bitter gourd collected from different markets of Kishoreganj district and also reflected the chronic health effects of these residues on the population.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

Full Word(s)	Abbreviations
Acceptable Daily Intake	ADI
Association of Analytical Communities	AOAC
Acute Reference Dose	ARfD
Bangladesh Agricultural Research Institute	BARI
Days After Application	DAA
Days After Spraying	DAS
Dispersive Liquid–Liquid Micro-Extraction	DLLME
Dispersive-Solid Phase Extraction	d-SPE
Estimated Average Daily Intake	EADI
Electron Capture Detector	ECD
Estimated Daily Intake	EDI
et alii, et aliae (and others)	*et al*
et cetra (and so on)	etc
European Union	EU
Food and Agricultural Organization	FAO
Flame Thermionic Detector	FTD
Gram	g
Gas Chromatography-Mass Spectrometry	GC-MS
High Performance Liquid Chromatography	HPLC
Hazard Quotient	HQ
Hazard Risk Index, Health Risk Index	HRI
Integrated Pest Management	IPM
Kilogram	kg
Liquid Chromatography-Mass Spectrometry	LC-MS
Limit Of Detection	LOD
Limit Of Quantification	LOQ
Milligram	mg
Maximum Residue Limit	MRL
Not Detected	ND
Nitrogen Phosphorous Detector	NPD
Potential Daily Intake	PDI
Pre-Harvest Interval	PHI
Primary Secondary Amine	PSA
Poly Tetra Fluro Ethylene	PTFE
Quick, Easy, Cheap, Effective, Rugged and Safe	QuEChERS
Relative Standard Deviation	RSD
Response Surface Methodology	RSM
Retention Time Locked	RTL
Sher-e-Bangla Agricultural University	SAU
Stir Bar Sorptive Extraction	SBSE
Through Oven Transfer Adsorption Desorption	TOTAD
Ultra-High-Performance Liquid Chromatography-Tandem Mass Spectrometry	UHPLC-MS/MS
World Health Organization	WHO

CHAPTER I

INTRODUCTION

INTRODUCTION

Food is the basic necessity of human life and vegetables are one of the most important components of food. They are highly beneficial for the maintenance of human health (Walia *et al*., 2010). Fruits and vegetables play an essential role in a healthy diet by serving as a source of various phytonutrients and secondary metabolites such as carotenoids, cyclic compounds, indoles, polyphenols as well as micronutrients, vitamins and minerals assisting in performing multiple biological activities in day to day life (Santarelli *et al*., 2018). Globally, vegetables are recognized as "protective foods" since they supply adequate quantities of vitamins, minerals, organic acids like folic acids, essential amino acids, dietary fibers, carbohydrates and supplementary amount of proteins etc. The constituents of vegetables have therapeutic value due to anti-carcinogenic and antioxidant properties, reducing the risk of several life threatening ailments. In Bangladesh agriculture, vegetables play a significant role by providing food, nutritional and economic security and more importantly producing higher returns per unit area and time. Agriculture in our country is in the process of diversifying from subsistence rice production to higher value crops such as vegetables and fruits. Diversification in vegetable crops and increasing commercialization can support the development of the agriculture sector in several ways. One potential drawback associated with a shift toward more intensive vegetable production is the reliance of most vegetable producers on heavy application of pesticide (Hossain *et al*., 2000). Bangladesh is the third largest producer of vegetables in the world after China and India. Vegetables commonly grown in Bangladesh include cabbage, cauliflower, tomato, brinjal, potato, radish, country bean, bottle gourd, pumpkin, bitter gourd, teasle gourd, ribbed gourd, ash gourd, okra, yard long bean, spinach etc. (Hasan *et al*., 2017).

Tomato (*Solanum lycopersicum* L.) is one of the most palatable vegetables which usually occupies the maximum number of our daily dishes and also takes its possession in market. It is a remunerative vegetable crop grown in tropical and subtropical regions of the world for fresh market and processing, constituting an important part of human diet. It is considered as the apple of poor man. The consumption of tomato exceeds all vegetables and is next to Potato. Tomato is a flowering plant belongs to the family Solanaceae having chromosome number 2n = 24. It is a self-pollinated crop. The number of tomato cultivars cultivated worldwide will be about 25,000 (Hixson, 2015),

2

and they are diversified in terms of skin color, size, shape, leaf type, and disease resistance code etc. Tomato is the rich source of Vitamin-A, Vitamin-C and minerals and it keeps eye sight good. Night blindness occurs due to lack of Vitamin-A. Tomato contains lycopene pigment which is a vital anti-oxidant that helps to fight against cancerous cell formation as well as other kind of health complications and diseases (Kumavat and Chaudhari, 2013). It is also rich with Vitamin-K which plays a major role in blood clotting. Tomato is the main source of health-promoting compounds due to the balanced mixture of antioxidants including vitamins C and E, lycopene, beta-carotene, lutein and flavonoids, amino acids, proteins, fatty acids and carbohydrates (Heeb, 2005). These natural antioxidants improve the skin's ability to protect against harmful ultra violet rays and might be strongly protective against neurodegenerative diseases.

Bitter gourd *(Momordica charantia)* belongs to the family Cucurbitaceae, is one of the most popular vegetables in South Asia. The Latin name *Momordica* means "to bite" referring to the jagged edges of the leaves, which appear as if they have been bitten. It is regarded as one of the world's major vegetable crops and has great economic importance (Krishnendu and Nandini, 2016). It is also known as balsam pear, bitter melon and bitter cucumber etc. Bitter gourd contains 91.8% water, 0.20% fat, 4.2% carbohydrates and 1.4% fiber. It is a rich source of potassium, also contains calcium, sodium, magnesium, iron and zinc in trace quantities (Bangash *et al*., 2011). It is an important source of carbohydrate, proteins, vitamins, minerals and other nutrients in human diet which are necessary for maintaining proper health. It is an excellent source of vitamins B_1, B_2, B_3, Vitamin C, folic acid, zinc, phosphorus, manganese, and has high dietary fiber (Krawinkel and Keding, 2006). A triterpenoid compound called 'Charantin' present in bitter gourd is a potential substance used for the treatment of diabetes to lower blood sugar level. This vegetable has many medicinal applications. It is beneficial against piles, blood and respiratory disorders (Myojin *et al*., 2008). Moreover, the crude protein content (11.42 g kg^{-1}) of bitter gourd fruits is higher than that of tomato and cucumber (Gilden *et al*., 2010).

As the global populations are increasing, it would be an immense challenge for the farmers to increase agricultural productivity using limited environmental resources. Consequently, the use of pesticides is increasing especially in the overpopulated countries like China, India, Bangladesh, Pakistan, Thailand, Malaysia to grow more

food in a shortest possible time and to meet the demands of overpopulation (Bhandari *et al*., 2019). According to the World Ecology Report (Robson, 2019), roughly around 1.8 billion people in the world are directly engaged in agricultural production, and most of them use pesticides. It has also been estimated in the report that, annually, 5.6 billion pounds of pesticides are used by farmers in the world. Undoubtedly, pesticides application greatly assists in the crop protection and yield. It has been estimated that on an average more than 45 % of the world's food crops are destroyed due to attack of insect pests and plant diseases (Kolani *et al*., 2019). High pest infestation forces farmers to apply pesticides intensively to protect their crops. It is reported that the crop loss due to pest infestation can be as high as 100% if they are not controlled (Rajabu *et al*., 2017). Hence, pesticide application has become indispensable in increasing vegetable production because of its rapid effect, ease of application and availability. Vegetables are highly susceptible to the attack of insect pest and disease for being succulent and tender. Being a sub-tropical country, Bangladesh possesses a broad range of temperature and humidity in different seasons, which provide a privilege of multiplication and development to a vast array of insects. Since the manual control is costly, time consuming and laborious, farmers are likly to use chemical control methods in case of severe pest infestation in both tomato and bitter gourd. Consequently, pesticides are being used extensively for the economic production tomato and bitter gourd also as the market value of insect/disease infested tomato and bitter gourd are very much lower than the uninfested ones. Bangladesh has been using pesticides since 1950's in agriculture and public health. Now the number of registered pesticide is about 272 (Belonging to: Miticide = 8, Fungicide = 79, Insecticide = 117, Herbicide = 52, Biopesticide = 10, Strong grain products =4 and Rodenticide = 2) are commonly used in agriculture sector while 88 pesticides are commonly used in public sectors in Bangladesh (BCPA, 2016).

Although pesticides are manufactured under very strict regulations to function with logical certainty and minimal impact, excessive application of these pesticide results into bioaccumulation of their residues (Jallow *et al*., 2017). Pesticide residues are the deposit of the active constituent. Its metabolites or breakdown products are present in some component of the environment after its application, spillage or dumping (Rohan *et al*., 2012). The problem of residues accumulation needs more attention notably in vegetables because most of the time these are consumed either raw or without passing

4

recommended storage time. Indiscriminate use of pesticides particularly at fruiting stage and non-adoption of safe waiting period leads to accumulation of residues in consumable vegetables. Sometimes erroneous doses are applied because of the farmer's poor knowledge of pesticide handling (Elibariki and Maguta, 2017). Pesticide contamination poses a serious threat to food safety issue across the world, especially in a country like Bangladesh. These are characterized by pronounced persistency against chemical and biological degradation, high environmental mobility, strong tendency for bioaccumulation in human and animal tissues, and significant impacts on human health and the environment, even at extremely low concentrations. (Ibitomi *et al.*, 2016). Pesticides are among the leading causes of death by self-poisoning, particularly in low and middle-income countries like Bangladesh (WHO, 2018). Exposure to pesticide have been associated with acute (short-term exposure) to chronic (long-term exposure) toxicity with harmful effects on human health, especially on children and pregnant women who are more vulnerable to the toxic effects (Abd-Elhaleem, 2020). Dizziness, headaches, nausea, rashes, irritation, vomiting, diarrhea, abdominal pain, and hypersensitivity are repeatedly reported impacts of acute pesticide exposure. Chronic health impacts include reproductive defects, neurodegenerative disorders, organ damage (kidney/liver), mutagenic and carcinogenic transformation, and endocrine disruption (Beradda *et al.*, 2010). Continued exposure to sub-lethal quantities of pesticides for a persistent period (years to decades), results in chronic illness in humans. Incidences of chronic diseases have started to grow as a pesticide has become an increasing part of our ecosystem (PAN, 2012).

It is a direful concern that pesticide use is very unrestrained in Bangladesh. Due to lack of knowledge and high demand of fresh vegetables, farmers in our country do not follow the prescribed dosages and harvest treated vegetables by neglecting the withholding period or pre-harvest interval (PHI), which is defined as the number of days required to elapse between the date of final pesticide application and harvest, for residues to fall below the tolerance level established for that crop or for a similar food type (Prodhan *et al.*, 2018). The PHI allows enough time for the pesticide residue to breakdown before a treated crop is harvested. Most of the people of our country are indirect consumers of pesticides through food intake. In the context of food safety and public health, it is therefore necessary to assess the risks linked with food exposed to pesticides. Numerous indices can be used to predict pesticide residues. The maximum

residue limit (MRL) is one of such indices which represents the maximum amount of a pesticide that can be present in the food at the time of its sale. It is expressed as mg/kg. The MRL is being pursued to standardize international trade (Chowdhury *et. al.*, 2014). Health safety limits for human health are usually expressed as acceptable daily intake (ADI). The standard method to calculate human exposure with pesticides is based on the average consumption per person per day, average adult weight, and pesticide residue data (Seo *et al.,* 2013). The hazard risk index (HRI) is applied to evaluate the potential health risk from the consumption of foodstuff containing pesticide residues.

Quantification of pesticide residue in vegetables have become a consumers' safety issue. Various types of analytical methods are used to determine multiple pesticide residues in fruits and vegetables (Anastassiades *et al.*, 2003; Schenck *et al.*, 2008; Lehotay *et al.*, 2010; Dasika *et al.*, 2012; Singh *et al.*, 2012; Prodhan *et al.*, 2015; Prodhan *et al.*, 2015a; Prodhan *et al.*, 2016; Prodhan *et al.*, 2016a). The QuEChERS (quick, easy, cheap, effective, rugged, and safe) extraction techniques are widely used in the food testing laboratories among different extraction and clean-up methods used for different food matrices. This method was introduced in 2003 (Anastassiades *et al.*, 2003). Follow-up studies have further validated the method for more than 200 pesticides (Lehotay *et al.*, 2005), improved results for the remaining few problematic analytes (Lehotay *et al.*, 2005a), and tested it in fat-containing matrices (Lehotay *et al.*, 2005b). So, QuEChERS extraction techniques along with Gas Chromatography are used in this study to determine pesticide residues in tomato and bitter gourd.

All upazilas of Kishoreganj district excluding the Haor areas are very famous for vegetable production. Now a days farmers there have been using pesticides legally or illegally in an enormous quantity to control insect-pests of vegetables. Detailed information is not available about the level of pesticide residues finally remaining in different vegetables of the study area. Moreover, no substantial works have yet been done for the determination of pesticide residue level and the health risk assessment. So, it is essential to find out the actual scenario of selected pesticide residues in these two vegetables (tomato and bitter gourd) collected from selected upazilas of Kishoreganj district along with risk assessment.

Considering the aforementioned information, the present study was undertaken with the following objectives:

- ❖ To quantify the level of selected pesticide residues (if any) in tomato and bitter gourd collected from different markets of Kishoreganj district.
- ❖ To compare the level of detected pesticide residues along with the Maximum Residue Limit (MRL).
- ❖ To assess their chronic health risk for the consumers.

CHAPTER II

REVIEW OF LITERATURE

REVIEW OF LITERATURE

An effort has been made to review the available literatures to extend the knowledge regarding the existing status of research and information about the determination of pesticide residues in some vegetables and assessment of chronic risk associated with the residues. Available and accessible sources of relevant information have been systematically reviewed and summarized with essential comments as appropriately as possible. Although the review could not be made so comprehensive because of limited scope and facility, it is hoped that most of the relevant information available 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 different types of journals. Information of farmers' field condition are scanty. However, a significant number of study-reports on pesticide residues in vegetable crops conducted under farmers' field conditions are available. With this background, the information collected from different sources have been reviewed and presented below:

Afroze *et al*. (2021) have been developed an analytical method for the quantification of acetamiprid using gas chromatography coupled with electron capture detector (ECD). The calibration curve was prepared with different concentration of acetamiprid ranging from 0.025 to 0.200 mg/L. The linearity of the developed analytical method was very good and it was 0.999.

Ahmed *et al*. (2021) conducted a study to detect and quantify the residue of seven commonly used organophosphorus pesticides (acephate, chlorpyrifos, quinalphos, diazinon, malathion, dimethoate and fenitrothion) in eggplant and tomato samples collected from local market of commercially grown four different regions viz. Bogura, Narsingdi, Jeshore and Cumilla for the comparison between the detected residue level with maximum residue limit (MRL) set by European Union. From the 80 analyzed samples of eggplant and tomato, 21.25% of the total number of samples contaminated with acephate, chlorpyrifos, fenitrothion and diazinon residues which were above the EU-MRLs. Out of 40 analyzed samples of eggplant. 11 samples were contaminated with acephate, diazinon fenitrothion and chlorpyrifos residues. All of the contaminated samples (27.5% of the total number of samples) had chlorpyrifos (0.02-0.046), acephate (0.017-0-0.39), diazinon (0.11-0.47) and fenitrothion (0.20) residues which were above the EU-MRLs. The eggplant samples collected from Jeshore and Narsingdi received

9

more pesticides than Cumilla and Bogura regions. In case of 40 analyzed samples of tomato, 6 samples (15% of the total number of samples) had chlorpyrifos (0.27-0.43), diazinon (0.25) and fenitrothion (0.10) residues which were above EU-MRLs. Malathion, quinalphos and dimethoate residues were not found in any of the tested samples.

AlSaikhan *et al*. (2021) quantified the pesticide residues level in vegetables in the Unaizah city, Saudi Arabia. QuEChERS method following LC-MS/MS and GC-MS/MS were used for analysis. The results showed that 65% of samples contained 14 types of pesticides but pesticides residue level was below the maximum residue levels (MRL) whereas 30% samples were free from pesticides. A total 5% of the vegetables samples were found to exceed the maximum residue levels (MRLs). Moreover, the results indicate that the tomato samples with residue < MRL were 100%. Cucumber sample from farms showed insecticides were found to exceed the MRL and none of the fungicides detected exceeded the MRL. Acetamiprid was the most commonly detected pesticides and followed by imidacloprid. The results designated that most of the vegetable samples were contaminated with different types of pesticide residues.

Begum *et al*. (2021) analyzed pesticide residues in winter vegetables collected from Rajshahi, Bangladesh. They collected five types of winter vegetables like bean, brinjal, tomato, cauliflower and cabbage from six markets of Rajshahi District. Residues of commonly used pesticides (Acephate, Dimethoate, Diazinon, Fenotrothion, Malathion, Chlorpyrifos and Quinalphos) in winter vegetable samples were determined using Gas Chromatography-Flame Thermionic Detector (GC-FTD) procedures. A quick, easy, cheap, effective, rugged and safe (QuEChERS) method with acetate buffering was used for sample preparation. Out of 30 samples, pesticide residues were found only in one brinjal and two tomato samples. The result showed that tomato samples collected from Shaheb bazar and Kharkhari bazar of Rajshahi City contained 0.047 mg/kg and 0.139 mg/kg dimethoate residue, respectively. Brinjal sample collected from Shalbagan bazar, Rajshahi, contained 0.052 mg/kg dimethoate residues. The detected pesticide residue dimethoate of these three samples was higher than maximum residue level (0.01 mg/kg).

Habib *et al*. (2021) quantified residue levels of seven organophosphorus pesticides in two vegetables (eggplant and cauliflower) collected from major markets of Dhaka city, Bangladesh and assessed their health risks. A modified Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) extraction technique by Gas Chromatography coupled with Flame Thermionic Detector (GC-FTD) were used for the analysis. Among the 50 analyzed samples of the eggplant 12% samples contained residues of chlorpyrifos, 6% samples contained residue of dimethoate and 2% samples contained residue of diazinon. Whereas, among the 50 samples of cauliflower, 12% samples contained residues of chlorpyrifos, 8% samples contained residues of diazinon and 2% samples contained residues of quinalphos. The chlorpyrifos was found as the most frequently detected organophosphorus pesticide. Among the 21 contaminated samples, 20 were above EU-MRL. Short and long-term health risk assessment based on ARfD and ADI indicates that the intake risks of eggplant and cauliflower were in the acceptable range.

Hepsag and Kizildeniz (2021) conveyed a study to assess the health risks associated with pesticide residues in greenhouse grown tomato production in the Mediterranean Region of Turkey. A multiresidue method based on modified QuEChERS (quick, easy, cheap, effective, rugged, and safe) was used for sample preparation that is applied for pesticide detection from extraction of tomato samples. The outcome divulged that out of tomatoes cultivated in greenhouse demonstrate 61.5% of samples with one or various pesticide residues. The maximum permitted residue level of above the EU-DG Guideline was in 12.2% of the samples. The main determined pesticide residues on the tomatoes cultivated in greenhouse were identified as chlorpyrifos methyl, cyfluthrin, deltamethrin, and acetamiprid. Chlorpyrifos methyl (9.5%), cyfluthrin (6.6%), deltamethrin (5.5%), and acetamiprid (3.2%) were recognized as the most conducing residues to the hazard index (HI). The HI was 9.5% for adults and 11.02% for children (3 to <10 years). The major contributor of the HI was chlorpyrifos in both.

Prodhan *et al*. (2021) have been developed and validated a novel method in order to determine 8 pesticide residues (acephate, diazinon, malathion, fenitrothion, chlorpyrifos, quinalphos, dimethoate and cypermethrin) in betel leaf using quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction in combination to Gas Chromatography (GC) coupled with Flame Thermionic Detector (FTD) and Electron Captured Detector (ECD). In this study, the optimization of cleanup materials was done properly and found that 600 mg anhydrous $MgSO_4$, 150 mg activated charcoal powder,

and 120 mg PSA (Primary Secondary Amine) was the best combination for proper cleanup of betel leaf matrix. Recoveries for all the selected pesticides at fortification levels of 0.02, 0.1, and 0.3 mg/kg ranged from 86 to 108% with RSDr ≤ 9% and the matrix matched calibration curve showed good linearity (r2 ≥ 0.996). The limit of detection ranged from 0.003 to 0.005 mg/kg and the limit of quantification was 0.02 mg/kg, which was lower than the EU-MRLs. The matrix effects of the selected pesticides were also evaluated in this study and found that cypermethrin had a prominent matrix effect (+124%). The proposed method was applied successfully to analyze 110 fresh betel leaf samples and found that 12 were contaminated with cypermethrin, chlorpyrifos, and dimethoate at a level above EU-MRLs.

Prodhan *et al*. (2021a) performed a research to quantify pesticide residues and to estimate variability factors (VFs) in large size fruit crops of mango and guava. A total of 140 mango and 130 guava samples from different marketplaces in Bangladesh were collected to estimate the variability of pesticide residues (acephate, diazinon, malathion, fenitrothion, chlorpyrifos, quinalphos, dimethoate and cypermethrin) by in-house validated methods based on modified QuEChERS extraction and gas chromatography coupled with electron capture detector (ECD) and flame thermionic detector (FTD). A wide variation of residues was found in the analyzed samples. In the case of mango, the ranges of residues were 0.011–0.314, 0.015–0.04, and 0.05–0.291 mg kg^{-1}, respectively, for cypermethrin, chlorpyrifos, and dimethoate, while in the case of guava, the ranges were 0.04–0.113, and 0.03–0.290 mg kg^{-1}, respectively, for cypermethrin and acephate. The average VF for mango was 4.06 and it was 5.70 for guava. The estimated VFs were higher than the default values.

Odewale *et al*. (2021) implemented a study to assess human health risk associated with dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) residues in Nigeria. The residues of DDTs and HCHs in 48 composite fruit and vegetable samples (carrot, cucumber, tomato, and watermelon) were qualitatively and quantitatively determined using gas chromatography equipped with electron capture detector (GC-ECD). Safety indices such as the estimated average daily intake (EADI), cancer benchmark concentration (CBC), hazard quotient (HQ) and index (HI), and hazard ratio (HR) were also estimated. Results showed the predominance of HCH and its isomers in the fruits and vegetables as compared with the DDTs. The analysis showed that the levels of pesticide residues detected in 25 to 100% of the fruit and vegetable samples

were above the UK/European Commission Maximum Residue Limits (MRLs). The non-carcinogenic health risk estimates showed that only α-HCH in tomatoes and watermelon had HQ > 1 which indicates the possibility of systemic health risk in children consumers. The carcinogenic health risk showed that only α-HCH and γ-HCH in children and α-HCH in adults had HR > 1 for tomato and watermelon which implies the possibility of carcinogenic health risk from its consumption.

Omwenga *et al*. (2021) undertook a study to assess the levels of organophosphates and carbamates in vegetables in Kenya and to examine potential consumer health risks. A total of 90 samples were analysed by liquid chromatography/high-resolution tandem mass spectrometry. Residues of acephate, chlorpyrifos, methamidophos, omethoate and profenofos were found in 22% of the samples, ranging from 10 to 1343 μg/kg. The EU MRL was exceeded in 21%, 10%, 8% and 22% of the samples of French beans, kales, spinach and tomatoes, respectively. Chlorpyrifos in spinach had an acute HQ of 3.3 and 2.2 for children and adults, respectively, implying that potential health risks with respect to acute dietary exposure cannot be excluded. For chronic dietary exposure, all chronic HQs were below 1. The HI for the pesticides was 0.54 and 0.34 for children and adults.

Amjad *et al*. (2020) carried out a study to assess the pyrethroid residues in eggplant and okra along with their dietary intake assessment. The procured vegetables were quantified for pyrethroid residues by using gas chromatography (GC) equipped with an electron capture detector (ECD). Out of all analyzed samples for pyrethroid residues, 32% samples contained detectable residues and 6% samples exceeded their maximum residual limits (MRLs) established by the European Union (EU). Dietary intake assessment (mg kg^{-1} day^{-1}) was calculated as per their maximum permissible intake (MPI) values, i.e., bifenthrin (1.28), cyfluthrin (1.28), cypermethrin (3.20), deltamethrin (0.64), fenvalerate (1.28), lambda-cyhalothrin (0.064), and permethrin (3.20) respectively. Although some samples exceeded MRLs in selected areas, their safe consumption limit was found.

Chaikasem and Roi-et (2020) conducted a study to investigate the level of pesticide residues and the potential health risk associated with vegetables, surface water, and sediment obtained from the river basin area. The concentrations of 87 pesticides from four main groups namely; organophosphate, organochlorine, pyrethroid, and persistent

organic pollutants (POPs) were verified by triple quadrupole GC-MS/MS. The detectable pesticide residues were found in 95% of 20 vegetable samples. The positive of screening vegetables were most obviously contaminated with organophosphate (95%) followed by pyrethroid (40%), organochlorine (20%) and POPs (5%), respectively. The highest concentration of 0.04 mg kg^{-1} was recorded for Dicrotophos in Kitchen mint. Fenpropathrin recorded the lowest concentration in corn. The combined risk index of pesticide residues showed significant health risk to humans more than individual risk index.

Elgueta *et al*. (2020) initiated a research program to determinate health risks assessment of pesticide residues associated to tomatoes and lettuces produced in Metropolitan Region (MR). The findings revealed that tomatoes and lettuces cultivated in the MR showed more than 50% of samples with one or multiple pesticides residues. From the total samples, 16% were over the Chilean Maximum Residue Levels (MRLs). The main pesticides detected in tomatoes and lettuces were methamidophos, methomyl, difenoconazole, cyprodinil and boscalid. The results obtained using the official data of the Ministry of Health of Chile (MINSAL) compared to the World Health Organization (WHO), described relevant risks through the Estimated Daily Intakes (EDI), Hazard Quotients (HQ) and Hazard Index (HI) for the Chilean population due to high concentrations of methamidophos, methomyl and cyprodinil.

Gowda *et al*. (2020) estimated pesticide residues in carrot sample collected from five different districts of Karnataka, India. They used gas chromatographic technique equipped with Electron Capture Detector (ECD) and Flame Thermo ionic Detector (FTD) for different pesticide residues of organophosphate, organochlorine, synthetic pyrethroids and carbamates. Acephate was the mostly used pesticide and chlorpyrifos residue exceed the MRL value. Cyfluthrin-β is not detected in any districts and the concentration of monocrotophos, cyhalothrin-λ, cypermethrin and deltamethrin were found below the permissible limit in all the places.

Huong *et al*. (2020) conducted a research program to detect the pyrethroid residues in vegetables and their health risk assessment. The residues of λ-cyhalothrin, permethrin, cypermethrin, deltamethrin in four vegetable head mustard, leaf mustard, choy sum, bok choy were detected by GC/MS technique. 84 samples of four leafy vegetable in Brassicaceae family were collected from seven places (farms, stores, markets) in Ha

Nam Province. The levels of λ- cyhalothrin in three samples, cypermethrin in four samples, deltamethrin in four samples were above the maximum residue limit of Vietnam Government. There were no significant of health risk by these pesticides via digestion vegetable but the risk for kid was higher than for adult. Their health risk on cosumers using these vegetables were evaluated.

Ijeoma *et al*. (2020) conveyed a study to assess pesticide residues and associated health risks in tomatoes sold in Lagos state, Nigeria. The result obtained indicated the presence of alpha and delta lindane, heptachlor, heptachlor epoxide, endrin, endosulfan, endosulfan sulphate and ether. Mean concentrations (mg/kg) and estimated daily intake (EDI) (mg/kg/day) of the pesticide residues were in the range of 0.0042 to 0.336 mg/kg and 7.5E- 6 to 2.3E-4 mg/kg/day respectively. The mean concentration of most of the pesticide residues in the tomato samples were above their maximum residue limit (MRL) while some had estimated daily intake (EDI) above their established acceptable daily intake (ADI) and hazard quotients (HQ) above their safe value. The hazard indices (HI) and Incremental lifetime cancer risk (ILCR) for the pesticide residues were above their safe values.

Luo *et al.* (2020) dealt with an experiment on the residue analysis, risk assessment and processing factors of tebufenozide in okra fruits under field conditions. A simple LC-MS/MS method was applied and validated for determining the tebufenozide residues in okra fruits. The recoveries of tebufenozide in okra fruits were > 72% with relative standard deviations of 0.6%-6.1%. The dissipation rates of tebufenozide were different in okra fruits cultivated under open land and greenhouse field conditions because of the discriminating humidity and temperature conditions. The dietary intake of the tebufenozide residues from okra fruit consumption for Chinese shoppers was fairly low, with approximately no potential health risk.

Mao *et al*. (2020) carried out an analysis of organophosphorus and pyrethroid pesticides in organic and conventional vegetables using QuEChERS extraction combined with dispersive liquid-liquid micro extraction based on the solidification of floating organic droplet. The key parameters were optimized through orthogonal array experimental design and statistical analysis. The linearity of the calibration curves was satisfied in matrix-matched standard solution with R2 ≥ 0.99. The limits of detection and limits of quantification were 0.3–1.5 and 0.9–4.7 µg/kg, respectively. The average recoveries of

pesticides were 61.6–119.4% with relative standard deviations < 16.1%. Furthermore, the method was applied successfully to analyze the pesticides in 15 pairs of organic and conventional vegetables. These results showed the efficiency, reliability and robustness of the developed method.

Marete *et al*. (2020) determined seven commonly used pesticides residue in random samples of tomatoes, French beans, and kale collected from horticultural farms in Kenya. QuEChERS method for extraction followed by LC-MS/MS was used to determine the concentrations. The pesticide residue levels were extremely low and met the MRLs set by EU and other countries, except for carbendazim and metalaxyl in French beans, and posed no concern to human health. The health risk indices were subsequently extremely low for the detectable pesticide residues, indicating no health risk in the population, but their presence in these vegetables cannot be ignored as long-term exposure can cause health risks.

Nahar *et al*. (2020) conducted an experiment 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. They used modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction technique and GC-FTD (Gas Chromatography coupled with Flame Thermionic Detector) to analyze 80 vegetable samples for major organophosphorus insecticides namely acephate, chlorpyrifos, diazinon, dimethoate, fenitrothion, malathion and quinalphos used in that region. Results showed that 11 (6 cauliflower, 5 tomato) samples contained residues which were 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.

Otchere et al. (2020) performed a study to detect organochlorine, organophosphate and pyrethroid insecticide residues in cabbage collected from 3 major markets of Kumasi. The analysis was carried out using Multiple Reaction Monitoring by Gas Chromatography-Pulsed Flame Photometric Detector (GC-PFPD), Gas Chromatography-Electron Capture Detector (GC-ECD) and Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method to detect residues. Their outcome showed that no organochlorine was present in any of the samples and only Diazinon was present in the sample but below the MRL in case of 2 markets. In the samples of

other market Diazinon was found to exceed its established MRL (0.01 mg/kg) and so is more likely to pose danger to consumers health.

Ramadan *et al*. (2020) implemented a study to determine the pesticide residues in 10 different vegetable commodities from the Asir region, Saudi Arabia. They evaluated 211 vegetable samples 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 QuEChERS method. A total of 145 samples (68.7%) contained detectable pesticide residues at or lower than maximum residue limits (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.

Ratnamma *et al*. (2020) estimated pesticide residues in okra and determined potential health risk. They collected 90 different field and market samples of okra in North-Eastern Karnataka were contaminated with residues of organophosphate, synthetic pyrethroid, triazole, benzimidazole, neonicotinoid, abamectin, diamide, acetanilide and IGR group and analyzed using LC-MS/MS and GC-MS/MS. The most frequently detected pesticides were profenophos, acephate, triazophos, carbendazim, hexaconazole, imidacloprid, metolachlor, bifenthrin, emamectin benzoate and fenpyroximate. Pesticides reported above the MRL were profenophos (8 samples), acephate (29 samples), hexaconazole (14 samples), thiacloprid (2 samples), carbofuran (1 sample) and triazophos (15 samples). only few pesticides showed hazard index more than 1 while remaining pesticide residues estimated hazard indices being below 1.

Ahmed *et al*. (2019) carried out a study to analyze the amount of residue of six commonly used pesticides (e.g., chlorpyriphos, quinalphos, diazinon, acephate, dimethoate and fenitrothion) in vegetables viz., hyacinth bean and eggplant samples collected from local market of nine different locations. The samples were extracted through QuEChERS method and analyzed by GC-FTD technique. Among 36 analyzed samples of hyacinth bean six samples (16.67%) were contaminated with chlorpyriphos (0.082 mg/kg) and dimethoate residue (0.192 mg/kg - 0.961 mg/kg), all of them were above maximum residue limit. Out of 36 analyzed samples of eggplant 3 samples (8.33%) were contaminated with quinalphos (0.081mg/kg) and dimethoate residue

(0.032 mg/kg - 0.217 mg/kg) which were above MRL. Most of the samples contained with dimethoate residue in both the vegetables.

Bhandari *et al*. (2019) undertook a study in order to assess the pesticide residues in vegetables and examine the related human health risk. Therefore, residues of 23 pesticides (organophosphates, organochlorines, acaricides, fungicides, and insecticides of biological origin) were analyzed in the three main vegetable crops grown in Southern Nepal: 27 eggplant, 27 chilli and 32 tomato samples representing (i) conventional (N=67) and (ii) integrated pest management (IPM) fields (N=19). Pesticide residues were found in 93% of the eggplant samples and in all of the chilli and tomato samples. The most frequently detected pesticides in these vegetables were carbendazim and chloropyrifos. Pesticide residues in 4% of the eggplant, 44% of the tomato and 19% of the chilli samples exceeded the EU maximum residue limits (MRLs). The residues of triazophos, omethoate, chloropyrifos and carbendazim exceeded the EU MRLs. HQ>1 was observed for chloropyrifos, triazophos and carbendazim in eggplants; profenofos, triazophos, dimethoate, omethoate, chloropyrifos and carbendazim in tomatoes; and dichlorvos and chloropyrifos in chillies. Of all of the HQs, the highest acute HQ (aHQ) was for triazophos (tomato) in adolescents (aHQ=657) and adults (aHQ=677), showing the highest risks of dietary exposure. The concentration of pesticide residues in the vegetable crops from the IPM field was considerably lower.

Chu *et al*. (2019) conveyed a study to investigate the pesticide residues in bell peppers from Shandong Province, China. A total of 299 samples were collected from 17 cities. The concentrations of 26 pesticide residues were determined by gas chromatography with mass spectrometry (GC–MS). The results showed that there were 25 pesticides (15 OPs, 7 PYs, 3 CBs) found in 86 bell pepper samples, and the total number of positives was 120. The total frequency was 28.76%. The detection frequency for OPs, PYs and CBs was 16.39%, 12.37% and 3.01%, respectively. The most frequently detected pesticide was bifenthrin, with the frequency of 5.02%. 5.35% of samples contained pesticide residues above the maximum residue limits (MRLs) set by China. 7.36% of samples contained more than one pesticide. The values of %ADI were below 100, while the %ARfD of carbofuran and methidathion exceeded 100 for children. The cumulative risk was highest for OPs.

Hasan and Rahman (2019) investigated selected pesticides in selected vegetable samples using gas chromatography-mass spectrophotometry (GC-MS) procedures. They used quick, easy, cheap, effective, rugged and safe (QuEChERS) method for sample preparation. Pesticide residues above the maximum residue levels (MRLs) were found in 3 brinjal, 2 country bean and 1 tomato samples. The result revealed that country bean collected from Karwanbazar, Dhaka and Jessore sadar wet market contained 44.92 μg/kg and 38.65 μg/kg Dimethoate residue, respectively. Brinjal sample collected from Jatrabari, Dhaka, Khetlal bazar and Mithapukur bazar wet market contained 32.54 μg/kg, 25.82 μg/kg and 20.65 μg/kg Quinalphos residue respectively. Tomato sample collected from Narsingdi sadar wet market contained 8.50 μg/kg Quinalphos residue, which was lower than Maximum Residue Levels (10 μg/kg).

Islam et al. (2019) conducted the residual analyses of selected pesticides (Carbofuran, Cypermethrin, Mancozeb and Chlorpyrifos) in two varieties (BARI-8 and UTTARA) of brinjal, cultivated at Department of Environmental Science Field, Bangladesh Agricultural University, Mymensingh and the harvesting time was selected as 0 day, 3rd day and 7th day from the pesticide spray. 54 samples were collected and analyzed through GC-FID. The contents of pesticide residues were found higher in 0-day as compared to 3rd day and 7th day for both of the varieties. The incidences of pesticides in samples of 0 day for both varieties exceeded the MRL with the highest significant for all pesticide residues. On the 7 days interval the pesticide residues for all selected pesticide under the MRL of both varieties. UTTARA brinjal fruits had more trend to reduce the pesticide residue within day variation than the BARI-8 variety. This study also suggested brinjal should not be harvested less than 3-5 days as well as it may be consumed at approximately 7 days later from the spray.

Islam et al. (2019a) implemented a study to monitor the presence of seven organo-phosphorous 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. 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 65 analyzed samples, 8 (12.3% of the total number of samples) were contaminated with pesticide residues and all of them contained residues above Maximum Residue Limit (MRL). Another 57 samples

(87.7% of the total number of samples) contained no detectable pesticide residues of the sought pesticides.

Islam *et al*. (2019b) carried out a study to investigate the entity of seven Organophosphorus pesticide residues like acephate, dimethoate, fenitrothion, chlorpyrifos, quinalphos, diazinon and malathion in eggplant. 78 eggplant samples were collected from retail markets located at the surrounding area of Jahangirnagar University, Savar, Dhaka, Bangladesh. 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 78 analyzed samples, nine (11.5%) were contaminated by pesticide residues. Two of them were exceeded the EU-MRL. Another sixty-nine samples (88.5%) were free from the contamination of the sought pesticides.

Kumari and John (2019) conveyed a study to assess the health hazards associated with the presence of pesticide residues in fruits and vegetables sampled from farms and markets of Kinnaur district of Himachal Pradesh (India). After extraction through QuChERS method, gas chromatography quadrupole mass spectrometer (GC-MS/MS) were applied to analyze the residues of predominant pesticides used in the region, belonging to the group of organophosphates, pyrethroid and phthalimide. Results indicated varying concentrations of pesticide residue in market and farm samples with farm samples more contaminated than market samples. Chronic health hazards prediction indicated that organophosphorus groups (methyl parathion and triazophos) posed health risk to children in the study area.

Prodhan *et al*. (2019) performed a work to analyze four organophosphorus pesticides namely Chlorpyrifos, Diazinon, Fenitrothion and Quinalphos residues in cabbage collected from 5 vegetables markets of Dhaka. 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.

Tankiewicz (2019) carried out a study on the determination of selected priority pesticides in high water content fruits and vegetables by modified QuEChERS and GC-ECD with GC-MS/MS. 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.

Akhtar *et al*. (2018) carried out a study to determine selected pesticides namely bifenthrin, difenoconazole, paraquat, dimethomorph, imidacloprid, deltamethrin residual in fruit (guava) and vegetables (eggplant and round gourd) collected from shops in commercial market, Lahore. These samples were subjected to high pressure liquid Chromatography (HPLC) for detection of pesticide residues. The results showed that in Guava fruit concentration of bifenthrin, difenoconazole, paraquat, dimethomorph and imidacloprid were 5.13, 81.5, 6.6, 0.48 and 1.65 mg/kg respectively. In Egg Plant sample, bifenthrin, difenoconazole, paraquat, dimethomorph and deltamethrin detected residues were 3.53, 5.62, 4.58, 0.25 and 0.005 mg/kg respectively while imidacloprid residues were not detected. In Round Gourd, the values of bifenthrin, difenoconazole, paraquat, dimethomorph residues were 3.87, 61.53, 5.01 and 0.15 mg/kg respectively while imidacloprid and deltamethrin were not detected. Concentration of all pesticide in guava, eggplant and round gourd exceed the Maximum Residue Limit (MRL).

Forkuoh *et al*. (2018) implemented a study to assess the level of organochlorine pesticide (OCP) residues in fruits and to determine the potential health risks associated with the exposure to these pesticides. A total of 120 fruits (watermelon, pineapple, and banana) were collected from five communities and a local market within the Mampong Municipality and analyzed for organochlorine pesticide residues. The results showed

that levels of methoxychlor, Aldrin and gamma-hexachlorocyclohexane (HCH) exceeded the maximum residue limits in watermelon. Estimated health risk revealed that Aldrin in watermelon could pose potential toxicity to the consumer. Estimated average daily intake for Aldrin was above the acceptable average daily intake.

Golge *et al*. (2018) performed a research to identify pesticide residues in green pepper and cucumber marketed in Turkey along with consumer risk assessment of selected pesticides. They used liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) for analysis. Pesticide residues were detected in 12.9% of peppers and 13.5% of cucumbers but the levels were below the EU-MRL. Propamocarb and chlorpyrifos were the major contributors to hazard index. Hence, there was no reason to be concerned about cumulative exposure to residues from green pepper and cucumbers.

Ibrahim *et al*. (2018) conducted a study on the determination of Organochlorine Pesticide Residues in Pumpkin, Spinach and Sorrel Leaves Grown in Akwanga, Nasiriya State, Nigeria. They collected leafy vegetable samples of pumpkin leaves, spinach leaves, and sorrel leaves from a farm in Akwanga and tested for the presence of residues of organochlorine pesticides. The concentrations of all the pesticide residues in the vegetable samples were determined using GC/MS. Among the organochlorine pesticide p,p'-DDT was detected in pumpkin (0.75 mg/kg), spinach (0.319 mg/kg) and sorrel (0.219 mg/kg). θ-BHC and γ-BHC were detected only in pumpkin leaves (0.359 mg/kg and 0.647 mg/kg respectively). Dieldrin was detected in spinach and sorrel (0.124 mg/kg and 0.053 mg/kg respectively). Endrin was detected in pumpkin (0.732 mg/kg) and Aldrin in sorrel (0.095 mg/kg). All these values were above the maximum residue limit (MRL) value of the pesticides. Endosulfan II was detected in sorrel (0.306 mg/kg) below the MRL. The levels of most of the pesticide residues found in vegetables were above the maximum residue limits (MRLs) that call for laws to regulate the use and circulation of such chemicals.

Loughlin *et al*. (2018) investigated the presence of such residues in nationally produced fruits and vegetables for domestic consumption in order to evaluate the present state of the market. 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. Result revealed

that 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. Five pesticides were detected at frequencies above 10%, the highest being chlorpyrifos in 25.9% of the total samples.

Prodhan *et al*. (2018) 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 levels 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.* (2018a) 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.

Aktar *et al*. (2017) carried out a study to determine the pesticide residues in eggplant available in the local markets of Mymensingh Sadar, Mymensingh. 50 samples of eggplant were analyzed which were collected from 10 markets of Mymensingh Sadar, Mymensingh. A simple and efficient multiple pesticide residue analytical method (QuEChERS extraction) and gas chromatography-flame thermonized detector (GC-FTD) were used for the determination of pesticide residues. Among the 50 analyzed samples, 11 (22% of the total number of the samples) contained pesticide residues of diazinon, dimethoate, quinalfos, and chlorpyrifos, of which, 2 had multiple pesticide residues and 5 samples contained residue above the European Union maximum residue limit (EU-MRLs). Chlorpyrifos was detected as the most used pesticide in eggplant in the studied area. Eggplant samples collected from K.R market did not contain any residues of pesticides.

Elgueta *et al*. (2017) investigated the pesticide residue concentrations and potential human health risk in 118 leafy vegetable samples collected in 2014-2015 from the North Central agricultural areas of Chile using the multiresidue QuEChERS method using 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}, 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.

Hasan *et al*. (2017) conducted a research to analyze pesticide residues in country bean collected from different areas of Dhaka city. A simple and efficient multiple pesticide residue analytical method using Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) extraction technique and Gas Chromatography (GC) coupled with Flame Thermionized Detector (FTD) were used for the determination of pesticide residues in 50 country bean samples. Among the analyzed samples, 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) contain residue of Dimethoate.

Jallow *et al*. (2017) performed a study to assess the level of pesticide residues in commonly consumed fruits and vegetables in Kuwait. A total of 150 samples of different fresh vegetables and fruits were analyzed for the presence of 34 pesticides using the quick easy cheap effective rugged and safe (QuEChERS) multi-residue extraction, followed by gas chromatography-mass spectrometry (GC-MS) or liquid chromatography-tandem mass spectrometry (LC-MS/MS). The result revealed that pesticide residues above the maximum residue limits (MRL) were detected in 21% of the samples and 79% of the samples had no residues of the pesticides surveyed or contained residues below the MRL. Multiple residues were present in 40% of the samples with two to four pesticides, and four samples were contaminated with more than four pesticide residues. Of the pesticides investigated, 16 were detected, of which imidacloprid, deltamethrin, cypermethrin, malathion, acetamiprid, monocrotophos, chlorpyrifos-methyl, and diazinon exceeded their MRLs. Aldrin, an organochlorine pesticide, was detected in one apple sample, with residues below the MRL.

Mohammed and Boateng (2017) initiated a research to estimate the concentration of various pesticide residues in tomatoes, obtained from three market centers (namely Bantama, Central, and Ayigya Markets) in Kumasi, dealing with potential health risks for the consumers. Analyzed samples have revealed high percentage of organophosphate pesticide residues (45%) in Ayigya market with Bantama market recording high percentage of organochlorines and pyrethroid. Laboratory analysis of tomato samples for various pesticides residues has indicated that all the pesticide residues pose no threat to human's health with all estimated hazard indices being below 1; however, heptachlor (HI=0.85) and dieldrin (HI=0.74) have shown the highest risk levels in children.

Bempah *et al*. (2016) analyzed 400 fruit and vegetable samples obtained from open and closed markets in Accra, Ghana employing a multi-residue method based on solid-phase extraction followed by gas chromatography–mass spectrometry. The results obtained revealed that 20% of the fruit and vegetable samples were above MRL, 73% were below MRL and 7% contained no detectable level of the monitored pesticides.

Estimation of dietary intake of pesticides from fruit and vegetables revealed that, pesticides detected in fruits and vegetables did not cause dietary intake risks.

Prodhan *et al*. (2016) have been developed and validated an analytical method for the simultaneous determination of residues of five insecticides and two fungicides in cabbage. Pesticide residues were extracted by using QuEChERS extraction and the analysis was performed by liquid chromatography triple quadrupole mass spectrometry (LC-MS/MS). The method was applied for the residue analysis of 132 fresh cabbage samples collected from different market places in Thessaloniki, Greece. Among the analyzed samples, 41 (31 % of the total no. of samples) had pesticide residues, of which, two had multiple pesticide residues and 39 had a single pesticide residue. Only one sample was found contaminated with deltamethrin at a level above the European Union maximum residue levels (EU-MRLs).

Prodhan *et al*. (2016a) have been developed and validated a multiresidue analytical method for the determination of pesticide residues in cauliflower collected from different market places in Thessaloniki, Greece. The collected samples were extracted using the quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction technique, and the residues were determined by liquid chromatography-tandem mass spectrometry (LC-MS/MS). 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.

Zhang *et al*. (2016) developed and used a modified quick, easy, cheap, efficient, rugged and safe (QuEChERS) method coupled with gas chromatography with electron capture detection to determine eight pyrethroid pesticide residues in green, red and dehydrated red peppers. Pyrethroids were extracted with acetonitrile, partitioned with sodium chloride and purified with primary secondary amino and graphitized carbon black in hexane. Under the optimized conditions, the calibration curves for pyrethroid pesticides showed good linearities in the concentration range of 0.05-20 µg/mL. The limits of quantification of eight pyrethroids were 0.004-0.04 mg/kg for green and red pepper and 0.04-0.5 mg/kg for dehydrated red pepper. These values are below the suggested regulatory maximum residue limits. The developed method was successfully applied to commercial samples. Some samples were found to contain pyrethroid pesticides with levels below the legal limits.

26

Akoto *et al*. (2015) estimated the human health risk associated with the consumption of pesticide-contaminated vegetables from Kumasi, Ghana. Residue analysis was carried out using a GC equipped with PFPD for OP residues and ECD for OC and pyrethroid residues for eggplant, okra and tomato. The results revealed that organophosphates residues exceed the MRL in all sample, organochlorines residues exceeded their MRLs in okra samples whereas pyrethroid residues exceeded in eggplant samples. The combined risk index showed no health risk to consumers due to intake of pyrethroid OC and OP residue on these vegetables. The overall risk index for combined pesticides due to consumption of all the vegetables was higher than 1, which signifies potential health risk to consumers. OPs were the major risk contributor for both eggplant and tomatoes and OCs were the major risk contributor for the okra without carcinogenic risk.

Alam *et al*. (2015) investigated residual levels and associated health risk of seven frequently used pesticides in 140 samples of two common vegetables, eggplants and tomatoes, from agricultural fields in the Narayanganj district of Bangladesh. The analysis of pesticide residues was performed by high-performance liquid chromatography with photodiode array detection. Large percentage of the eggplants (50%) and tomatoes (60%) from the Narayanganj district were contaminated with pesticides, and all of the levels were above the maximum residual limit (MRL). Diazinon was the most common (35%) pesticide detected in the vegetable samples at a concentration of 45–450 times higher than the MRL. The health risk index for diazinon was highest for both eggplant and tomato samples, which may be due to its physiochemical properties. Fenitrothion and linuron are the two second most common types of pesticides detected in the vegetable samples.

Fakhruddin *et al*. (2015) used HPLC with a Photo Diode Array (PDA) detector to determine two organochlorines (methoxychlor and DDT), seven organophosphorus (acephate, chlorpyrifos, fenthion, fenitrothion, malathion, parathion, and ethion), two carbamate (carbaryl and carbofuran) and one pyrethroid (cypermethrin) pesticide residues in 15 samples of three common vegetables (Tomato, Lady's Finger and Brinjal). Except chlorpyrifos and cypermethrin, all of the pesticides were found at higher levels than the corresponding MRLs in all vegetable samples. Highest percentage of samples was found contaminated with chlorpyrifos. The highest health

index (5.7) was found for ethion in lady's finger, whereas health index for carbaryl in tomato, chlorpyrifos and carbofuran in brinjal were 1.09, 1.97 and l.17, respectively.

Fang *et al*. (2015) performed residue risk assessment in three hundred samples of celery collected from eight main growing regions in China. Pesticide residue analyses were performed using GC–MS/MS and LC-MS/MS methods. Both chronic and acute intake risk of pesticides were assessed. Out of these 300 samples, 175 were revealed to contain one or more pesticide residues. Most pesticides have a residue level lower than their maximum residue limit and pose low chronic and acute dietary intake risk except carbofuran.

Hossain *et al*. (2015) implemented a work with twenty-five vegetable samples which are three types- brinjal samples (BS), cucumber samples (CS) and tomato samples (TS) were collected from different Upazila of Bogura district in Bangladesh. Out of them eight samples were contaminated with pesticides residues, of which five samples exceeded the Maximum Residue Level (MRL). Moreover, eight samples contaminated with organophosphorus while only one (BS-3) with carbamate pesticide (Carbaryl). The highest concentration for carbaryl was found in BS-3 is 4.43 ppm and the highest level for Diazion in CS-5, TS-3 was estimated 0.18 ppm, 0.57 ppm respectively and for Chlorpyriphos in BS-7, CS-9 was detected 0.4 ppm, 0.33 ppm accordingly. Whereas, no Organochlorine pesticides such as DDT, endrin, aldrin, dieldrin, endosulfan etc. were found in the samples studied.

Prodhan *et al*. (2015) developed a simple and efficient multiple pesticide residue analytical method using quick, easy, cheap, effective, rugged, and safe (QuEChERS) extraction and liquid chromatography triple quadrupole-mass spectrometry and validated for the determination of ten insecticides and three fungicides in eggplant. The method was validated by evaluating the accuracy, precision, linearity, limit of detection, and limit of quantification. They applied this method for the residue analysis of 72 fresh eggplant fruit samples collected from different market places in Thessaloniki, Greece. Among the 72 analyzed samples, 34 (47 % of the total no. of samples) had pesticide residues, of which, 5 had multiple pesticide residues and 29 had single pesticide residue. Only one sample contained residue above the EU-MRLs.

Prodhan *et al*. (2015a) estimated seven insecticides (chlorpyrifos, dimethoate, deltamethrin, thiamethoxam, thiacloprid, pirimicarb and indoxacarb) and three fungicides (azoxystrobin, fluopicolide and propamocarb hydrochloride) in melon by developing a rapid, precise and efficient (modified) QuEChERS extraction method coupled with liquid chromatography triple quadrupole mass spectrometry. The method was validated by evaluating the accuracy, precision, linearity, limit of detection (LOD) and limit of quantification (LOQ). This method was applied for the residue analysis of 122 fresh melon samples collected from different markets of Thessaloniki, Greece. Among the 122 analyzed samples, 32 (26% of the total no. of samples) were found to have pesticide residues. None of the samples contained residues above the European Union-Maximum Residue Levels. The most frequently detected pesticides were fluopicolide and thiamethoxam.

Qin *et al*. (2015) analyzed 21 types of organophosphorus (OP) and pyrethroid (PYR) pesticide residues in 506 vegetables collected from local markets in western China from 2010 to 2013. The samples were determined by gas chromatography–mass spectrometry (GC–MS). Ten OP pesticides were found in concentrations ranging from 0.0008 to 4.0544 mg/kg. Five types of PYR pesticides were determined to have concentrations in the range of 0.0009 to 6.0827 mg/kg. There were no residues in 69.76% of the samples. A portion (25.49%) of the samples contained pesticide residues less than or equal to the maximum residue limits (MRLs), and 4.94% of samples contained pesticide residues greater than their MRLs.

Singh *et al*. (2015) conducted a study to observe the persistence pattern and risk assessment of cypermethrin in chili fruits following three applications of cypermethrin at 50 and 100 g a.i. ha^{-1} at 10-day interval. Residues of cypermethrin in chili were estimated by gas liquid chromatography (GLC) and were confirmed by gas chromatography-mass spectrometry (GC-MS). The average initial deposits of cypermethrin in chili fruits were found to be 1.46 and 3.11 mg kg^{-1}, at recommended and double the recommended dosages, respectively, following third application of the insecticide. Residues of cypermethrin declined below its limit of quantification (LOQ) of 0.05 mg kg^{-1} after 25 days at both the application dosages. Theoretical maximum residue contribution (TMRC) values were calculated from the residue data generated and were found to be below maximum permissible intake (MPI) even on 0 day.

Chowdhury *et al*. (2014) carried out a study to investigate the contamination and health risk assessment of pesticide residues in vegetables from agricultural fields of Gazipur district, Bangladesh. They analyzed ten vegetables for selected pesticides using HPLC with (photo diode array) PDA detector. None of the vegetable samples were contaminated with organochlorine pesticides. Lady's finger was found contaminated with ethion and fenitrothion residues. Health indices of acephate, cypermethrin and fenitrothion in brinjal were 0.363, 0.002 and 0.475 respectively and in lady's finger for ethion and fenitrothion were 10.350 and 0.490 respectively.

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 was 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.

Islam *et al*. (2014) performed a survey on three major vegetables like eggplant, cauliflower, and country bean. Total 42 samples collected from fields and market and multiple pesticide residue analysis was done by Gas Chromatography (GC) with Flame Thermionized Detector (FTD) and Electron Capture Detector (ECD). On the basis of questionnaires, under their supervision 23 farmers were interviewed. They record 8.33 to 45.00 percent farmers in two selected locations of Narsinghdi to apply different pesticides every day and in some cases even twice in a day on vegetables. They found 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.

Maher *et al*. (2014) monitored certain carbamate pesticide residues in tomatoes grown in Jordan valley by GC-NPD. Methomyl was found to be the most abundant carbamate pesticide and residues were found in 90% of the collected tomato fruits and 70% of these samples contained methomyl residues less than the maximum residue limit (MRL). Oxamyl residues were found in 20% of the fruits samples, however oxamyl residues were found to be less than the maximum residue limits (MRL).

Fakhruddin *et al*. (2013) carried out a study on "Determination of Cypermethrin, Chlorpyrifos and Diazinon Residues in Tomato and Reduction of Cypermethrin Residues in Tomato Using Rice Bran." It was found that out of 14 samples, 5 were found contaminated with cypermethrin and 1 with chlorpyrifos, but no residue of diazinon was detected in any of the tested samples. Only 7% of the samples were found contaminated with cypermethrin residue which was above the maximum residue level (MRL) adopted by the FAO/WHO. 0.45 mg/kg of cypermethrin spiked tomato samples were rubbed by rice bran paste for 5, 10 and 15min. Rubbing with rice bran paste for 10min, removed 97.73% and 97.4% in both trails, and whereas cypermethrin residue was not detected in tomato samples treated for 15 min. The removal efficiency was $97.56 \pm 0.22\%$ with the adsorbent rice bran rubbing for 10min. The result showed that cypermethrin residues of tomato sample could easily be decontaminated through absorption of rice bran.

Chowdhury *et al*. (2013) undertook a study to identify the bioaccumulation and the ascertain level of chlorinated pesticide residues in some winter vegetables viz. tomato, spinach, potato and carrot collected from Dhaka city market. The samples were analyzed by capillary column of Gas Chromatograph Mass Spectrometry (GC-MS) with Electron Impact Ionization (EI) method for the detection of chlorinated pesticide. They found that collected samples of tomato, potato and spinach were contaminated with some chlorinated substances. But carrot was free of contamination with organochlorine pesticide.

Łozowicka *et al*. (2013) implemented a research program to evaluate the residues of insecticides, fungicides and herbicides in fruit from Poland and their health risks assessment. Accredited multiresidue methods based on gas and liquid chromatography, and spectroscopic technique were used to determine the concentrations above 160 pesticides. In 48.2% of samples no residues were found, 45.9% of samples contained

pesticide residues at or below the EU-MRL, and 5.9% of samples contained pesticide residues above MRL. Sour cherries (66%) and apples (63%) were the commodities in which pesticide residues the most frequently occurred. Thirty-one different pesticides were detected in total. Dithiocarbamate, captan, cyprodinil and boscalid were the pesticide most frequently found. Multiple pesticides (>1 pesticide) were detected in about 30.1% samples. Data obtained were used for estimating the potential health risks associated with the exposures to these pesticides. The highest estimated daily intakes (EDIs) for children were: 22% for di-methoate and 112% for diazinon of the ADI. The most critical commodity was apple, contributing 1.30 to the acute Hazard Index for flusilazole.

Saeid and Selim (2013) conducted multi residue analysis of 86 pesticides used in non-leafy vegetables (cold pepper, eggplant, carrot cucumber, hot pepper, tomato, squash bean, okra, onion, cauliflower and greenhouse tomato). The result revealed that the pesticide residues were above maximum residue limits (MRL) in 15.89% of the total samples (168 from 1057 samples), but 83.90% of the total samples (887 from 1057 samples) did not record any residues or contained pesticide residues at or below MRL.

Sheikh *et al*. (2013) monitored insecticide residues in vegetables collected from markets of Sindh, Pakistan and observed that 7 vegetables namely okra, bitter gourd, brinjal, tomato, onion, cauliflower and chilies were heavily contaminated with chlorpyrifos, profenofos, endosulfun, imidaclorid, emamectin benzoate, lufenuron. bifenthrin, diafenthiuron and cypermethrin. Moreover, every vegetable was contaminated with more than one insecticide and majority of the samples violated the Japanese MRLs.

Bempah *et al*. (2012) conducted a study to investigate the organochlorine, organophosphorus and synthetic pyrithroid residues in fruit and vegetables collected from markets in Ghana. The result showed that 39.2% of the fruits and vegetable samples contained no detectable level of monitored pesticides, 51.0% of the samples contained trace levels of pesticide residues below the maximum residue limit (MRL), while 9.8% of the samples possessed residues above the MRL.

Chauhan *et al*. (2012) evaluated the pesticide residues present in vegetable samples (brinjal, okra, tomato, sweet pepper, cabbage and cauliflower) collected from five different districts of Uttarakhand. The result revealed that most of the vegetables possessed endosulfun residues above maximum residue limit (MRL) followed by carbendazim, chlorpyrifos, imidacloprid, and cypermethrin respectively.

Bhupendor *et al*. (2011) monitored selected vegetables (cauliflower, radish, tomato, carrot, spinach and eggplant) in West Bengal for organochlorine pesticide (OCP) residues and found that the residue levels of OCPs were below maximum residue limits (MRLs) indicating minimal risk to the consumers.

Chowdhury *et al.* (2011) undertook an experiment to identify the bioaccumulation and the ascertain level of chlorinated pesticide residues in some vegetables collected from market baskets of New market, Dhaka, Bangladesh namely potato, tomato and carrot. The samples were randomly collected from different shops and analyzed using Gas Chromatograph Mass Spectrometry (GC-MS) with Electron Impact Ionization (EI) method for the detection of chlorinated pesticide. They found that collected samples of potato, tomato, red amaranth and spinach were contaminated with some chlorinated substances. But Indian spinach and carrot were free of contamination with organochlorine pesticide.

Crentsil *et al*. (2011) analyzed a total of 350 locally produced vegetables (okra, cabbage, tomato, lettuce, carrot, green pepper, onion, cucumber) from 6 main markets in Kumasi for pesticide residues and found that 37.5% of the fruit and vegetable samples contained no detectable level of the monitored pesticides, 19.0% of the samples had residues above the MRL, while 43.5% of the samples contained residues below the MRL.

Srivastava *et al*. (2011) conducted a work on 20 vegetables including leafy, root, modified stem, and fruity vegetables like bitter gourd, jack fruit, french-bean, onion, colocassia, pointed gourd, capsicum, spinach, potato, fenugreek seeds, carrot, radish, cucumber, beetroot, brinjal, cauliflower, cabbage, tomato, okra, and bottle gourd. 48 pesticides including 13 organochlorines (OCs), 17 organophosphates (OPs), 10 synthetic pyrethroids (SPs), and eight herbicides (H) were analyzed. A total number of 60 samples, each in triplicates, were analyzed using Quick, Easy, Cheap, Effective, Rugged, and Safe method. The quantification was done by GC-ECD/NPD. Twenty-

three pesticides were detected from total 48 analyzed pesticides in the samples. The detected pesticides were: Σ-HCH, Dicofol, Σ-Endosulfan, Fenpropathrin, Permethrin-II, β-cyfluthrin-II, Fenvalerate-I, Dichlorvos, Dimethoate, Diazinon, Malathion, Chlorofenvinfos, Anilophos, and Dimethachlor. In some vegetables like radish, cucumber, cauliflower, cabbage, and okra, the detected pesticides (Σ-HCH, Permethrin-II, Dichlorvos, and Chlorofenvinfos) were above maximum residues limit (MRL); however, in other vegetables the level of pesticide residues was below detection limit or MRL.

Chowdhury *et al*. (2010) undertook a study to detect and quantify the residue level of chlorpyrifos, diazinon of organophosphorus group and carbaryl, carbofuran of carbamate group in brinjal and tomato samples collected from different local markets of Dhaka city. Analysis was done by high performance liquid chromatography (HPLC) technique. Out of 8 samples, 6 brinjal samples were found to be contaminated with diazinon and carbaryl residues while 5 tomato samples were with chlorpyrifos and carbaryl. Carbofuran was not found in any samples studied. The range of chlorpyrifos, diazinon and carbaryl residues were 0.157-0.31, 0.17-0.35 and 0.22-0.39 μg/kg respectively which were below the maximum residue limits (MRL) recommended by FAO/WHO.

Baig *et al*. (2009) performed an experiment to evaluate and determine residues of three pesticides of Organophosphate group (Triazophos, Profenofos and Chlorpyrifos) in vegetables. Samples were analyzed for pesticide residues using multi-residue analysis by High-Performance Liquid Chromatography (HPLC) equipped with UV detector. It was observed that 33.0% of the samples were contaminated with any of the above three pesticides. The results showed that 8% of the samples tested contained residues higher than the MRLs. Based on observations made in these studies; it is proposed that more extensive monitoring investigations covering all vegetables from different agroclimatic regions of the state be carried out to find the exact position of pesticide residues.

Kabir *et al*. (2008) conveyed a study to detect and quantify the left over residue of Diazinon and Carbosulfan in brinjal and Quinalphos in yard long bean under supervised field trial and to compare between the detected residue level with maximum residue level (MRL) set by FAO. 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 up to 6 days after spray (DAS), and up to 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 up to 3 DAS. Left over residue of Quinalphos in yard long bean sample was detected up to 6 DAS and up to 4 DAS the level of residue was above the MRL.

Kabir *et al*. (2007) dealt with a work 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). 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
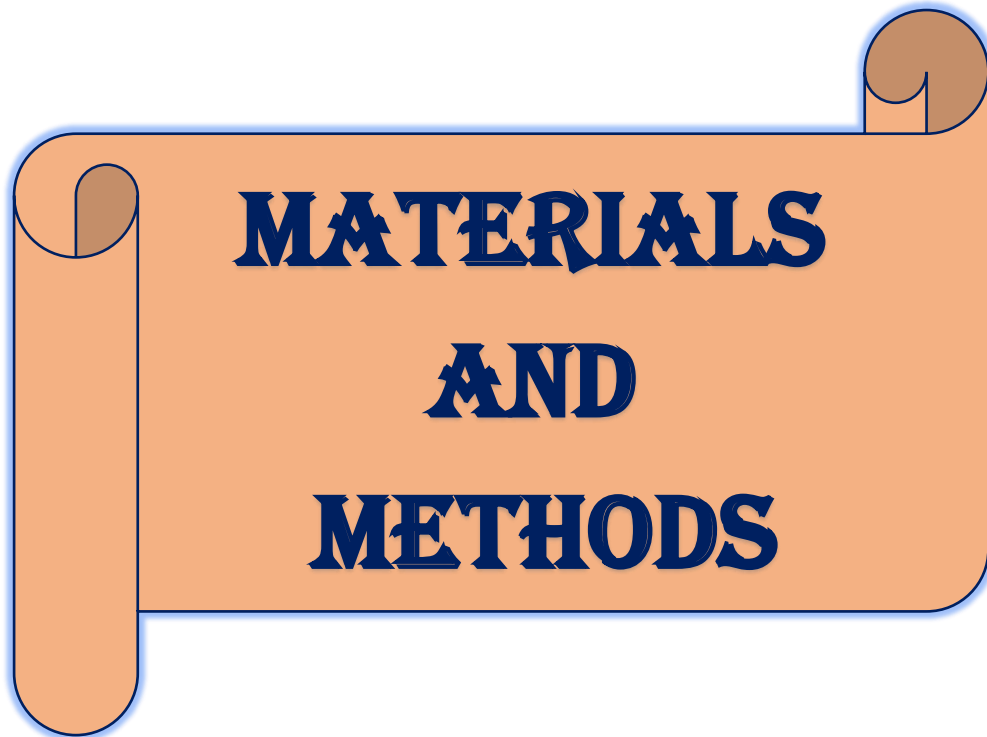
METHODS

MATERIALS AND METHODS

The samples of Tomato and Bitter gourd were collected from several markets of five upazilas of Kishoreganj district. Seven samples were collected randomly from each upazila and carried to the Pesticide Analytical Laboratory, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Joydebpur, Gazipur. Procedures followed for sample collection to final analysis are narrated below:

3.1 Location of the study

The study was carried out with samples collected from five vital markets of five upazilas of Kishoreganj district namely Kishoreganj Sadar, Katiadi, Bajitpur, Kuliarchar and Bhairab. The area of Kishoreganj district is 2731.21 sq km, lies in between 24°02' and 24°39' north latitudes and in between 90°35' and 91°15' east longitudes. It is bounded by Netrokona and Mymensingh districts on the north, Narsingdi and Brahmanbaria districts on the south, Sunamganj and Habiganj districts on the east, Gazipur and Mymensingh districts on the west. The region has a tropical monsoon climatic condition with an average annual temperature of 24.7 °C while annual average precipitation is about 2250 mm. Figure 1 shows the map of Kishoreganj district and sampling locations.

3.2 Collection of the samples

Fresh and ripen samples of tomato and green fruits of bitter gourd were purchased from the five markets (Kishoreganj Sadar, Katiadi, Bajitpur, Kuliarchar and Bhairab) for this investigation. At each market, seven samples of tomato and seven samples of bitter gourd i.e., a total 70 samples were collected randomly from different vendors. The amount of every sample was 0.5 kg for both tomato (*Lycopersicon esculentum*) and bitter gourd (*Momordica charantia*). The samples were kept in distinct transparent polyethylene bags in order to protect them from moisture and to avoid cross contamination. The bags were sealed and labelled with unique sample identifying marks before transferred to the laboratory. The details of the samples are given in Table 1 and Table 2.
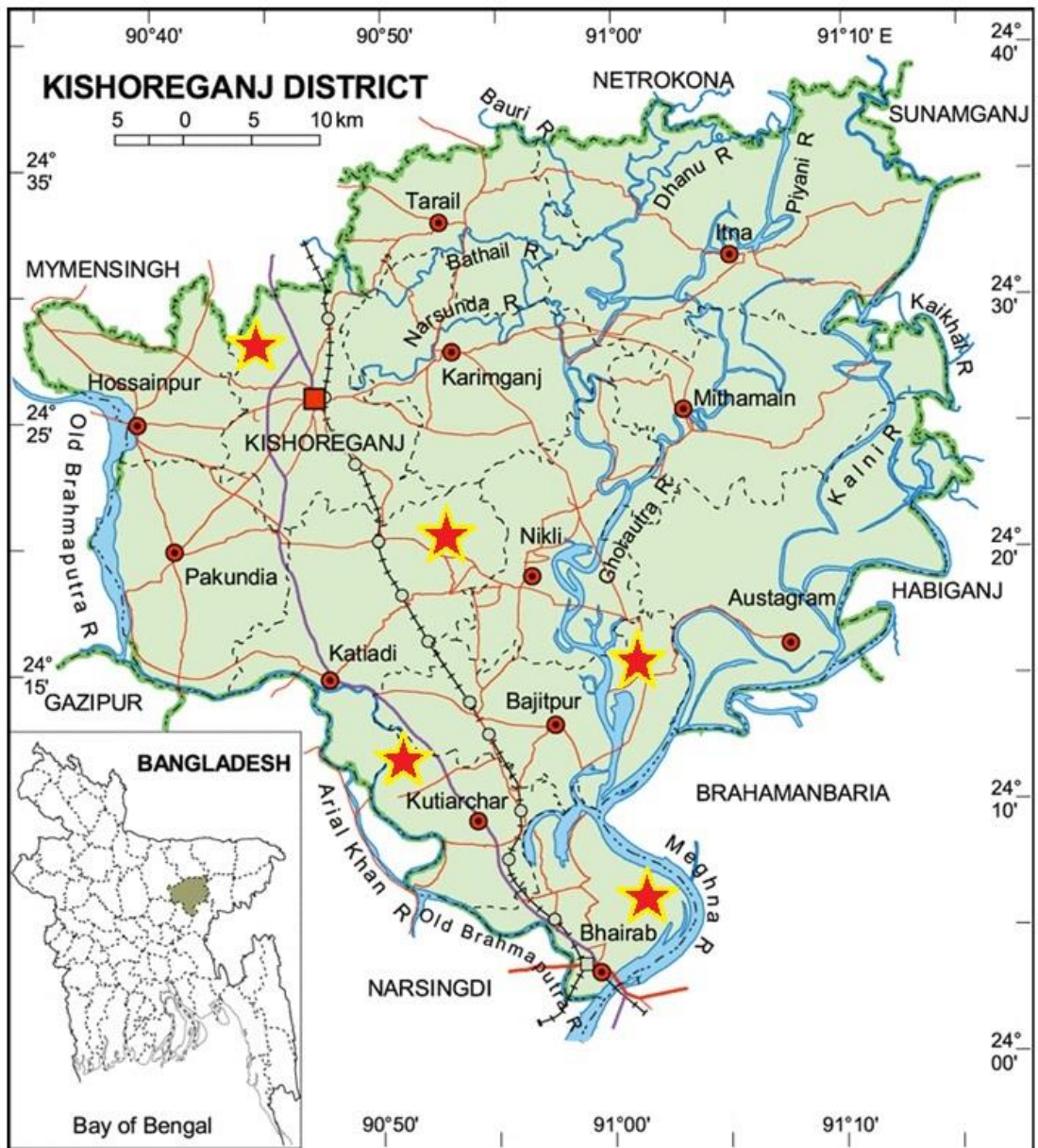
Figure 1. Map showing the locations of sample collection in Kishoreganj district and indicated by red star marks

Table 1: Locations and sources of tomato samples collection

Location of collection	Sample ID	Source
Kishoreganj Sadar	KGTo-01	Different vendors of Kishoreganj Sadar market under Kishoreganj district
	KGTo-02	
	KGTo-03	
	KGTo-04	
	KGTo-05	
	KGTo-06	
	KGTo-07	
Katiadi	KGTo-08	Different vendors of Katiadi Upazila market under Kishoreganj district
	KGTo-09	
	KGTo-10	
	KGTo-11	
	KGTo-12	
	KGTo-13	
	KGTo-14	
Bajitpur	KGTo-15	Different vendors of Bajitpur Upazila market under Kishoreganj district
	KGTo-16	
	KGTo-17	
	KGTo-18	
	KGTo-19	
	KGTo-20	
	KGTo-21	
Kuliarchar	KGTo-22	Different vendors of Kuliarchar Upazila market under Kishoreganj district
	KGTo-23	
	KGTo-24	
	KGTo-25	
	KGTo-26	
	KGTo-27	
	KGTo-28	
Bhairab	KGTo-29	Different vendors of Bhairab Upazila market under Kishoreganj district
	KGTo-30	
	KGTo-31	
	KGTo-32	
	KGTo-33	
	KGTo-34	
	KGTo-35	

Table 2: Locations and sources of bitter gourd samples collection

Location of collection	Sample ID	Source
Kishoreganj Sadar	KGBg-01	Different vendors of Kishoreganj Sadar market under Kishoreganj district
	KGBg-02	
	KGBg-03	
	KGBg-04	
	KGBg-05	
	KGBg-06	
	KGBg-07	
Katiadi	KGBg-08	Different vendors of Katiadi Upazila market under Kishoreganj district
	KGBg-09	
	KGBg-10	
	KGBg-11	
	KGBg-12	
	KGBg-13	
	KGBg-14	
Bajitpur	KGBg-15	Different vendors of Bajitpur Upazila market under Kishoreganj district
	KGBg-16	
	KGBg-17	
	KGBg-18	
	KGBg-19	
	KGBg-20	
	KGBg-21	
Kuliarchar	KGBg-22	Different vendors of Kuliarchar Upazila market under Kishoreganj district
	KGBg-23	
	KGBg-24	
	KGBg-25	
	KGBg-26	
	KGBg-27	
	KGBg-28	
Bhairab	KGBg-29	Different vendors of Bhairab Upazila market under Kishoreganj district
	KGBg-30	
	KGBg-31	
	KGBg-32	
	KGBg-33	
	KGBg-34	
	KGBg-35	

3.3 Preparation and preservation of sample for analysis

The acquired samples were transported to the Pesticide Analytical Laboratory, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipur on the day of collection. The whole amount of each sample was chopped into small pieces and mixed thoroughly with a blender. The chopped samples were put into clean airtight polythene bags and preserved in refrigerator at - 20°C until extraction and cleanup process started.

3.4 Chemicals and solvents

The standard grade of pesticides: acetamiprid, cypermethrin and lambda-cyhalothrin were obtained from Sigma-Aldrich (St Louis, MO, USA) via Bangladesh Scientific Pvt. Ltd. Dhaka, Bangladesh. The purities of all pesticide standards were >99.6%. Solvents such as 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 Pesticide standard solution preparation

Pesticide standard stock solutions of acetamiprid, cypermethrin and lambda-cyhalothrin were prepared separately in acetonitrile (MeCN) at a concentration of 1000 mg/L and stored at -20°C until use. A mixed standard solution of 50 mg/L in MeCN 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 the addition of acetone. An intermediate mixed standard solution of 10 mg/L in MeCN 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 MeCN 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 freezer at -20°C until use.

3.6 Required analytical apparatus

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) Gas Chromatography-2010, Shimadzu corporation, Japan (Plate 4)

Plate 1. Electric balance

Plate 2. Vortex mixture

Plate 3. Centrifuge Machine

Plate 4. Gas Chromatograph

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

- Centrifuge tube

- Conical flask

- Scissors

- Measuring cylinder

- Volumetric flask

- Tray

- Knife

- Spatula

- Funnel

- Test tube

- Micro pipette

- Aluminum foil

- Para film

3.6.1 Some pictorial view related to sample preparation:

Plate 5. Chopping of sample

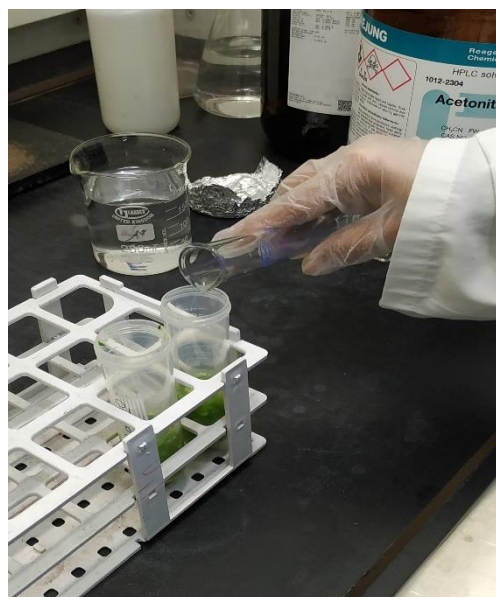**Plate 6. Homogenization of sample**

Plate 7. Addition of acetonitrile

Plate 8. Weighing of salts

(NaCl and anhydrous MgSO4)

Plate 9. Shaking of sample

Plate 10. Weighing of PSA

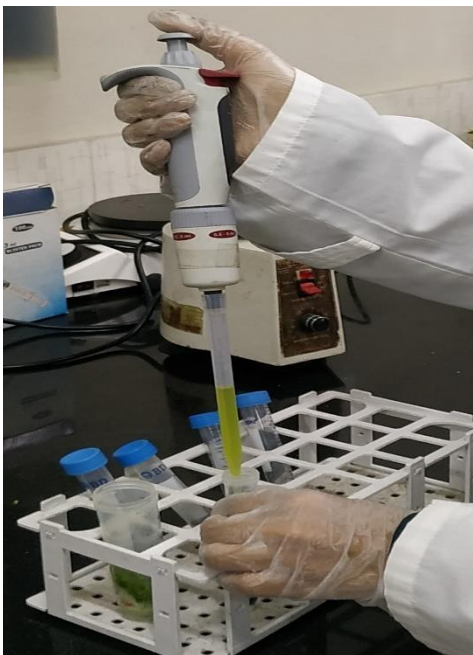**Plate 11. Centrifuging the sample**

Plate 12. Taking supernatant to the test tube

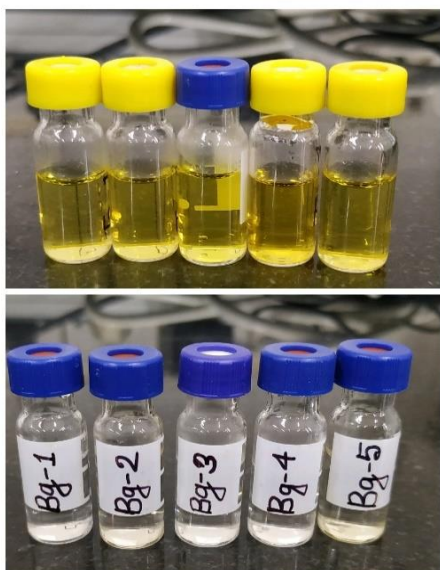**Plate 13. Filtration through PTFE filter**

Plate 14. Sample extract ready for injection

Plate 15. Sample placed in GC for analysis

3.7 Extraction and clean-up

QuEChERS extraction method is one of the latest extractions 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 g) 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), gas chromatography-electron capture detector (GC-ECD) or liquid chromatography tandem mass spectrometry (LC-MS/MS) with proper dilution.

46

The QuEChERS extraction technique was subsequently modified by Prodhan *et al.* (2015) and was used for the extraction and clean-up of the samples of the present study. The chopped samples were grounded thoroughly with a fruit blender. A 10g portion of firmly homogenized sample was weighted in a 50 mL polypropylene centrifuge tube followed by adding 10 mL of acetonitrile (MeCN). The centrifuge tube was closed properly and oscillated for 30 seconds with a vortex mixer. Then 4g of anhydrous $MgSO_4$ and 1 g of NaCl were added into the centrifuge tube which was shaken immediately by the vortex mixer for 1 minute to prevent the formation of magnesium sulfate aggregates. Afterwards, the extract was centrifuged at 5000 rpm for 5 minutes. Then 3 mL aliquot 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 seconds and centrifuged for 5 minutes at 4000 rpm (Laboratory Centrifuges, Sigma-3K30, Germany). Eventually, 1.0 mL of supernatant was filtered using a 0.2 μm PTFE filter and taken into a clean GC vial for injection.

3.8 Detection and quantification of residues in samples

The concentrated extracts were subjected to analysis by GC-2010 (Shimadzu) with Electron Capture Detector (ECD) for the detection of acetamiprid, cypermethrin, lambda-cyhalothrin. The capillary column was AT-1, length was 30m, ID was 0.32mm and film thickness was 0.25μm. Nitrogen gas was used as carrier and make up gas for ECD. The identification of suspected pesticide was performed by peak retention times in samples to those of peaks in the pure analytical standards. A typical chromatogram containing selected insecticides is presented in Figure 2 to Figure 4. The instrument conditions are described in Table 3 to Table 6.
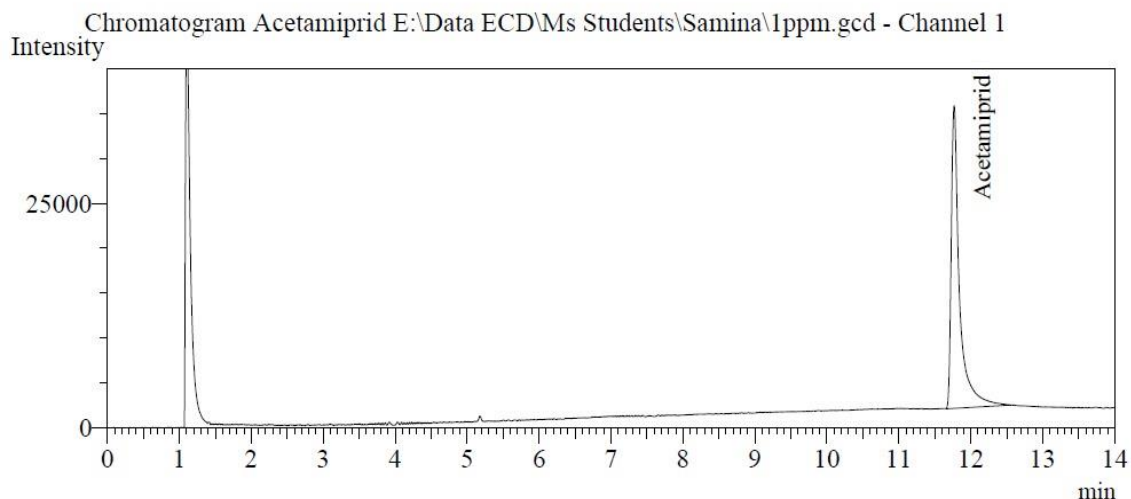
Figure 2. Chromatogram of acetamiprid standard prepared with the help of GC-ECD
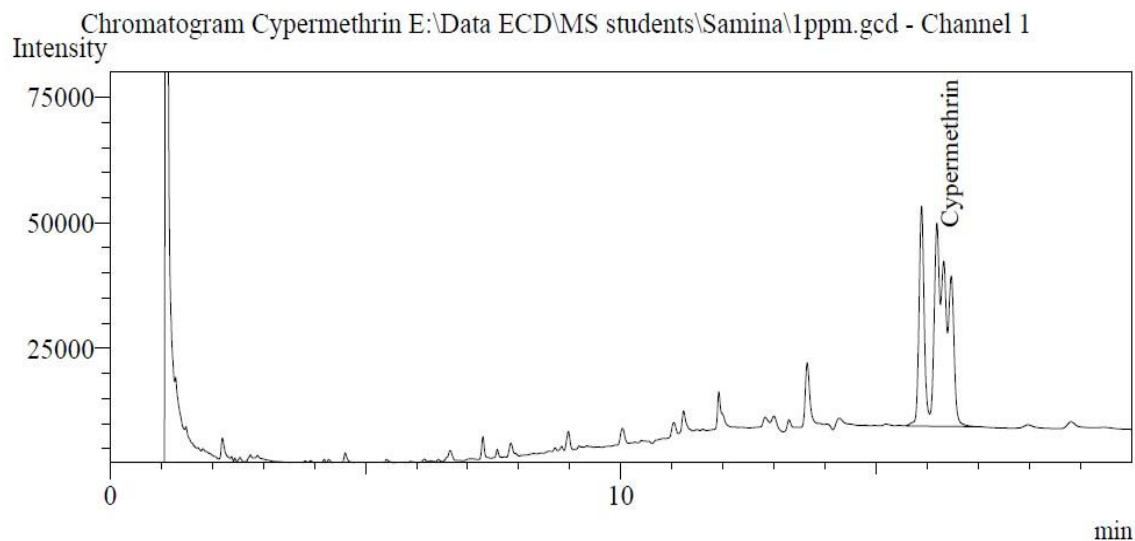
Figure 3. Chromatogram of cypermethrin standard prepared with the help of GC-ECD
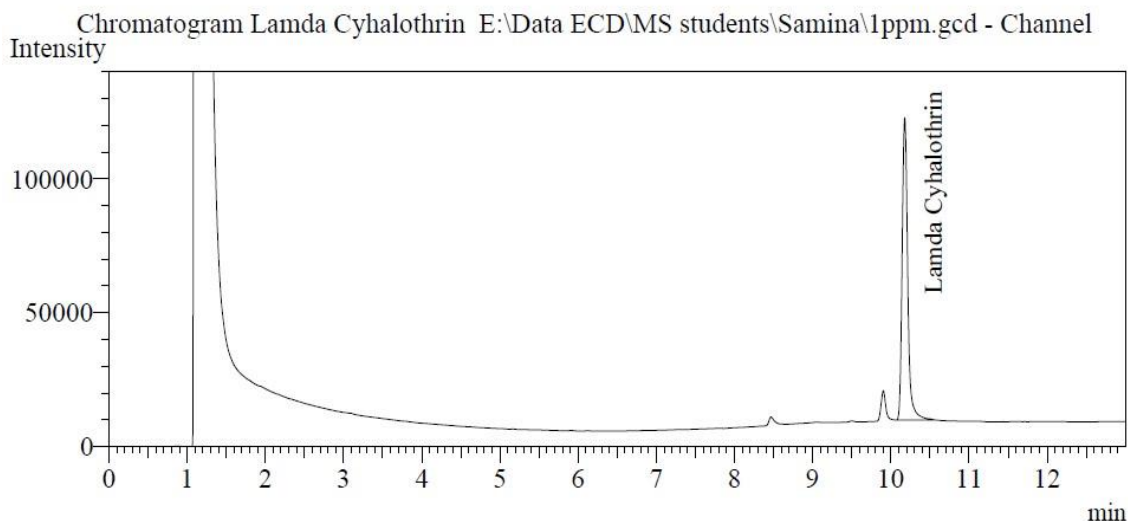
Figure 4. Chromatogram of lambda-cyhalothrin standard prepared with the help of GC-ECD

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 ($^\circ$C)	Hold time (min)
Initial temperature: 160°C	-	160	0
	15.0	220	0
	10.0	250	0
	5.0	270	3

49

Table 5. Conditions for column oven temperature for cypermethrin determination

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

Table 6. 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 Preparation of calibration curve

Prior to the injection of the sample extract, different concentrations level of standard solutions of each pesticide were prepared and injected with suitable instrument parameters. The samples were calibrated (retention time, peak area etc.) against four pointed calibration curve of standard solution of concerned pesticide (Figure 5 to Figure 7). Each peak was distinguished by its signatory retention time. The results were automatically expressed in mg/kg of sample by the gas chromatography software.

Calibration Curve - Analytical Line 1 - Channel 1 E:\Data ECD\Acetamiprid\29-01-2020\25ppb.gcd
ID#:1   Name:Acetamiprid

f(x)=7.40651694574e-004*x+0.333317269096
R=0.999999011298   R^2=0.999998022596
MeanRF:7.44907690127e-004   RFSD:2.73321464836e-006   RFRSD:0.366919912976
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard
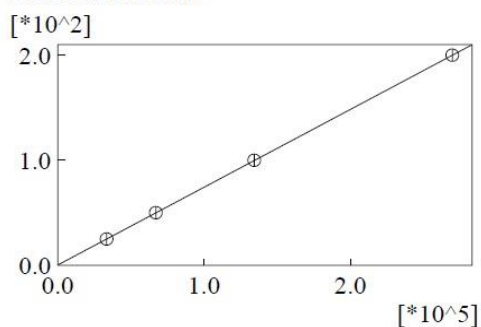
[*10^2]		No.	Conc.	Area
		1	200.000	269671
		2	100.000	134354
		3	50.000	67074
		4	25.000	33412

Figure 5. Calibration curve prepared for acetamiprid made with different concentrations ranging from 10 µg/L to 100 µg/L.

Calibration Curve - Analytical Line 2 - Channel 1
ID#:1   Name:Cypermethrin

f(x)=9.72861566278e-005*x+9.9950013555e-003
R=0.999966763424   R^2=0.999933527952
MeanRF:9.88583736873e-005   RFSD:9.19328503897e-007   RFRSD:0.929945000719
CurveType:Linear
ZeroThrough:Not through
WeightedRegression:None

External Standard

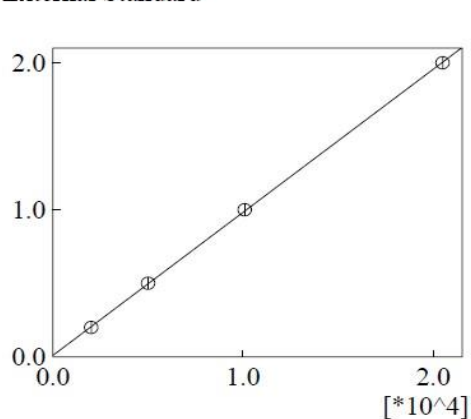|		No.	Conc.	Area
		1	0.020	2020
		2	0.050	5011
		3	0.100	10096
		4	0.200	20494

Figure 6. 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 E:\Data ECD\Lamda Cyhalothrin\12-01-2021\Std 500ppb.gcd
ID#:1 Name:Lamda 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
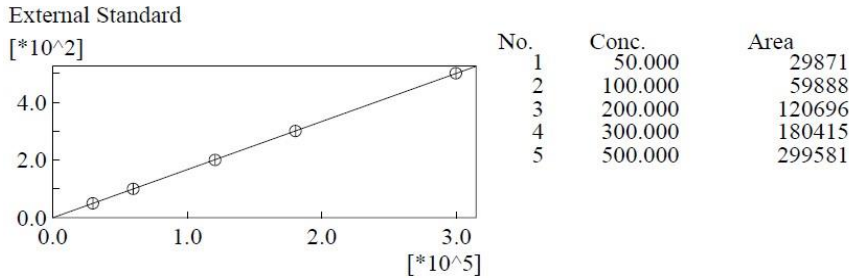WeightedRegression:None

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

3.10 Health risk assessment

The potential health risk associated with pesticide residues from dietary intake of selected vegetables per person were estimated based on the model recommended by the United States Environmental Protection Agency (USEPA). The estimated daily intake (EDI, mg/kg/day) was calculated for selected pesticides with the help of following equation proposed by USEPA (2005).

$$EDI = \frac{C \times FCR}{BW} \quad mg/Kg \text{ body weight/day}$$

Where, EDI stands for the estimated daily intake of each pesticide, C is the mean residual concentration of that pesticide, FCR is the food consumption rate and BW is the human body weight.

According to the final report on the Household Income and Expenditure Survey (HIES, 2016), the consumption rate of vegetables in Bangladesh was considered. An EDI value was calculated by considering average vegetable consumption of 0.1673 kg/person/day in Bangladesh (HEIS, 2016). Body weights of adults and children were considered to be 60 kg and 10 kg, respectively (USEPA, 2005).

52

The chronic health risk indices (HRI) of pesticide residues were evaluated by the ratio of estimated daily intake (EDI) and acceptable daily intake (ADI) as shown in the following equation (USEPA, 2005).

$$HRI = \frac{EDI}{ADI}$$

A value of HRI greater than 1 reveals that consumption of vegetables with measured level of pesticide is unsafe for human health (Darko and Akoto, 2008; Akoto *et al.,* 2015).

CHAPTER IV

RESULTS

AND
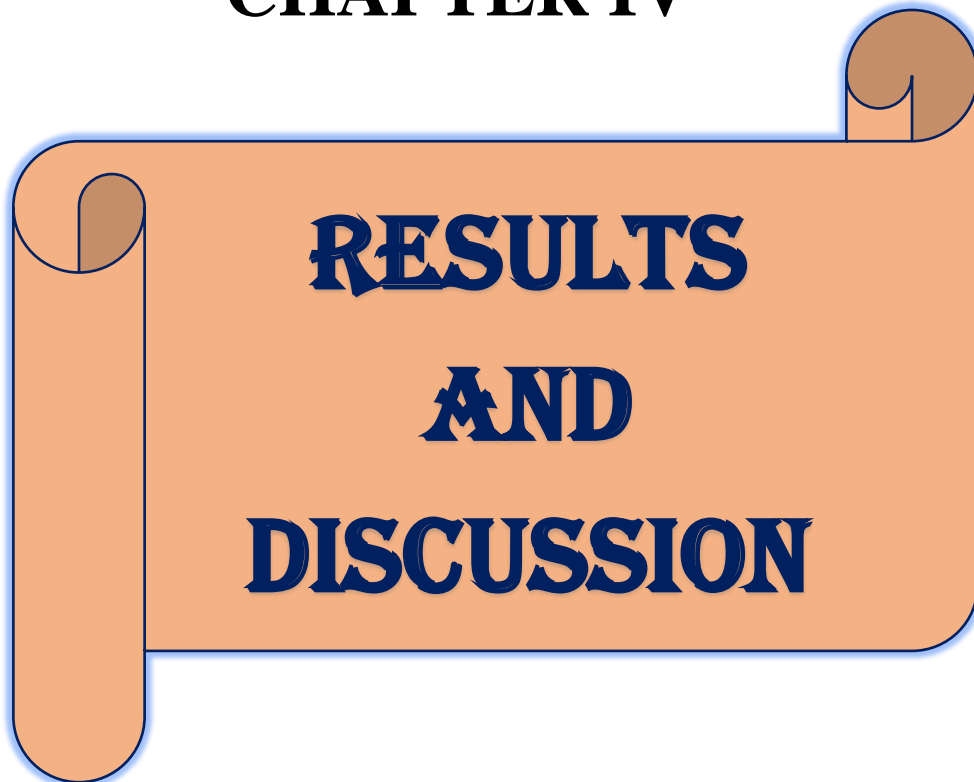
DISCUSSION

RESULUTS AND DISCUSSION

Seventy (70) vegetable samples (35 tomato and 35 bitter gourd samples) were collected from five leading markets of five upazilas (Kishoreganj Sadar, Katiadi, Bajitpur, Kuliarchar, Bhairab) of Kishoreganj district to detect and estimate selected pesticide residues and to assess the associated health risk. The findings obtained from this study are presented and narrated in this chapter using figures and tables.

4.1 Pesticide residues in tomato

The concentrated extracts of tomato samples collected from various markets of Kishoreganj were subjected to analyze by GC-2010 (Shimadzu) with Electron Capture Detector (ECD) with the pre-set parameters. Figure 08 to Figure 10 show the chromatograms of the injected extracts of tomato samples containing detected pesticides.
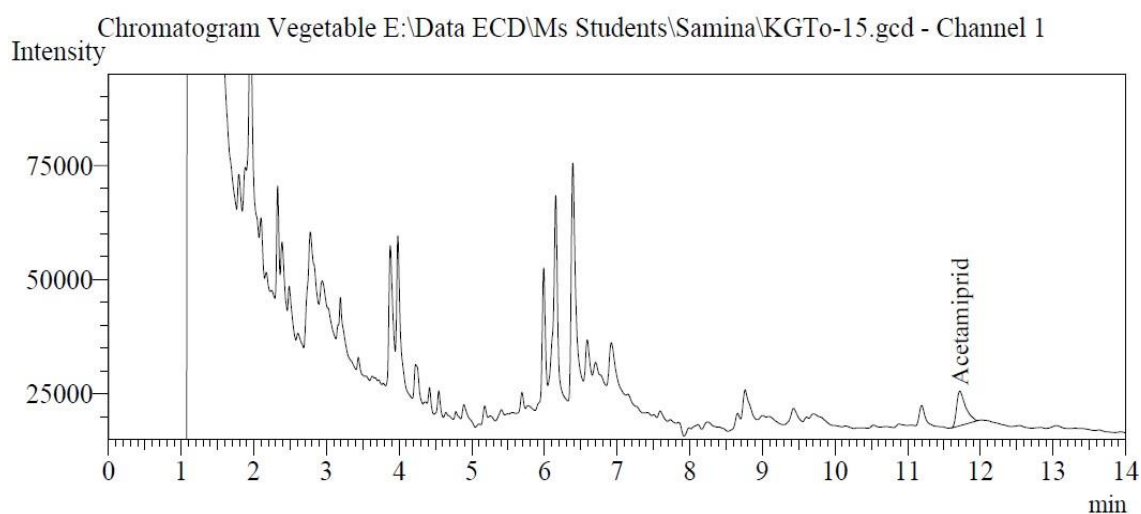
Figure 8. Chromatogram of acetamiprid found in one of tomato sample (KGTo-15) collected from Bajitpur upazila
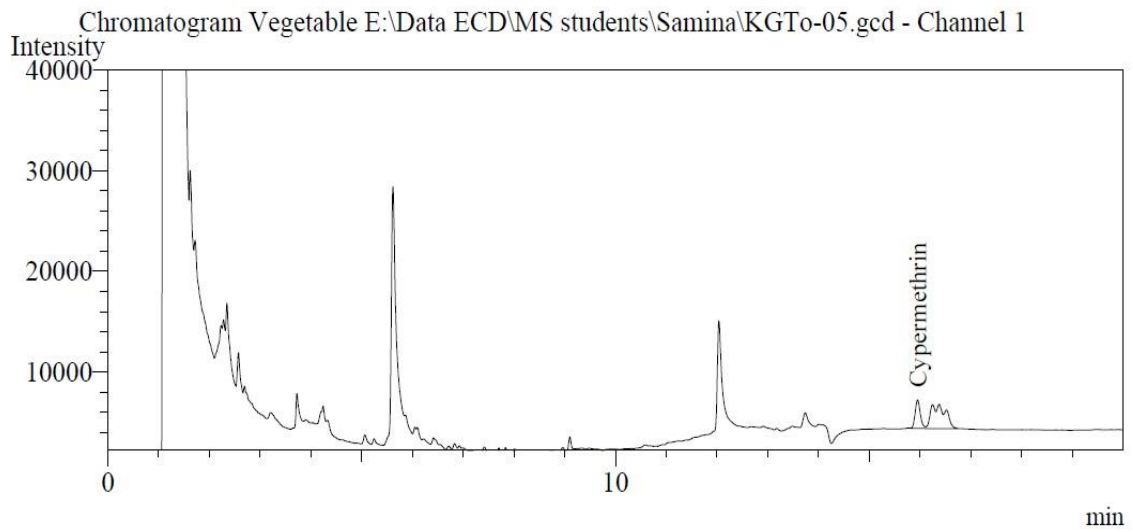
Figure 9. Chromatogram of cypermethrin found in one of tomato sample (KGTo-05) collected from Kishoreganj Sadar
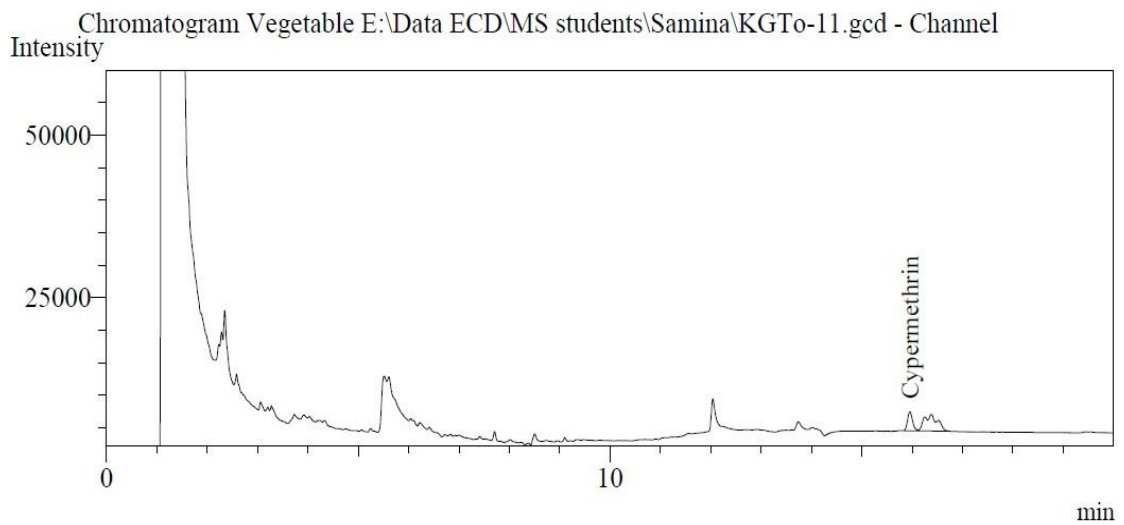
Figure 10. Chromatogram of cypermethrin found in one of tomato sample (KGTo-11) collected from Katiadi upazila

The extent of pesticide residues obtained by analyzing the tomato samples and their maximum residue levels are outlined in Table 7.

56

Table 7. The content of residues (mg/kg) of different pesticides found in the analyzed tomato samples collected from five upazilazs of Kishoreganj district

Areas of collection	Sample ID	Name of detected pesticide	Level of residue (mg/kg)	MRLs (mg/kg)
Kishoreganj Sadar	KGTo-01	ND		
	KGTo-02	ND		
	KGTo-03	ND		
	KGTo-04	ND		
	KGTo-05	Cypermethrin	0.129	0.5
	KGTo-06	ND		
	KGTo-07	ND		
Katiadi	KGTo-08	ND		
	KGTo-09	ND		
	KGTo-10	ND		
	KGTo-11	Cypermethrin	0.098	0.5
	KGTo-12	ND		
	KGTo-13	ND		
	KGTo-14	ND		
Bajitpur	**KGTo-15**	Acetamiprid	0.056	0.5
	KGTo-16	ND		
	KGTo-17	ND		
	KGTo-18	ND		
	KGTo-19	ND		
	KGTo-20	ND		
	KGTo-21	ND		
Kuliarchar	KGTo-22	ND		
	KGTo-23	ND		
	KGTo-24	ND		
	KGTo-25	ND		
	KGTo-26	ND		
	KGTo-27	ND		
	KGTo-28	ND		
Bhairab	KGTo-29	ND		
	KGTo-30	ND		
	KGTo-31	ND		
	KGTo-32	ND		
	KGTo-33	ND		
	KGTo-34	ND		
	KGTo-35	ND		

MRL values are according to the EU Pesticide Database (European Commission, 2019)

Thirty five samples of tomato collected from five major markets of five Upazila (Kishoreganj Sadar, Katiadi, Bajitpur, Kuliarchar, Bhairab) of Kishoreganj district were analyzed to find out the presence of left-over residue of three pesticides (cypermethrin, acetamiprid and lambda-cyhalothrin). Out of 35 samples of tomato, only 3 samples (8.57% of the total number of samples) contained acetamiprid and cypermethrin residues and 32 samples (91.43% of the total number of samples) contained no detectable residues of the sought pesticides. Cypermethrin was the most frequently detected pesticide in tomato. These 35 samples of tomato contained no residue of lambda-cyhalothrin.

The findings of present study can be compared with findings of Ahmed *et al.* (2021). They found that in case of 40 analyzed samples of tomato, 6 samples (15% of the total number of samples) had chlorpyrifos (0.27-0.43), diazinon (0.25) and fenitrothion (0.10) residues which were above EU-MRLs. They further reported that malathion, quinalphos and dimethoate residues were not found in any of the tested samples. The outcomes of this study are also supported by Marete *et al.* 2020). They analyzed random samples of tomato, french bean and kale for seven pesticide residues. The pesticide residue levels were extremely low and met the MRLs set by EU except for carbendazim and metalaxyl in French beans, and posed no concern to human health. The results of this study are also in a good agreement with Begum *et al.* (2021). They analyzed 30 samples of five different vegetables for pesticide residues and found in one brinjal and two tomato samples i.e., 10% samples contained residues. The detected pesticide residue was of dimethoate in these 3 samples and was higher than maximum residue level (0.01 mg/kg) whereas in the present study, out of 35 analyzed samples only 3 samples contained residues and were below the EU-MRL. The variation of results may occur due to the sampling area, types of pesticide, methods used etc.

Status of pesticide residue in the tomato samples collected from selected upazilas of Kishoreganj district

Kishoreganj Sadar upazila

From Kishoreganj Sadar upazila, seven tomato samples were obtained. Among them only one sample (KGTo-05) contained cypermethrin residues at a level of 0.129 mg/kg, which was below EU-MRL (0.5 mg/kg). The other six samples contained no detectable level of sought pesticide residue.

Katiadi upazila

Out of seven samples collected from Katiadi upazila, one sample (KGTo-11) contained pesticide residue. This sample contained residue of cypermethrin with a level of 0.098 mg/kg. The level was lower than EU-MRL (0.5 mg/kg). The remaining six samples were free from detectable residues of sought pesticides.

Bajitpur upazila

Only one sample (KGTo-15) contained residue of acetamiprid and the other six samples contained no detectable residues of selected pesticides among the seven samples collected from Bajitpur upazila. The level of detected residue was 0.056 mg/kg which was below the EU-MRL (0.5 mg/kg).

Kuliarchar upazila

In case of the seven samples collected from Kuliarchar upazila, there were no detectable amount of residue of sought pesticides.

Bhairab upazila

No detectable amount of residues of the sought pesticides were found in the samples collected from Bhairab upazila.

4.2 Pesticide residues in bitter gourd

The concentrated extracts of bitter gourd samples collected from different markets of Kishoreganj district and were analyzed by GC-2010 (Shimadzu) with Electron Captured Detector (ECD) with the pre-set parameters. Figure 11 to Figure 14 shows the chromatograms of the injected extracts of bitter gourd sample containing detected pesticides.
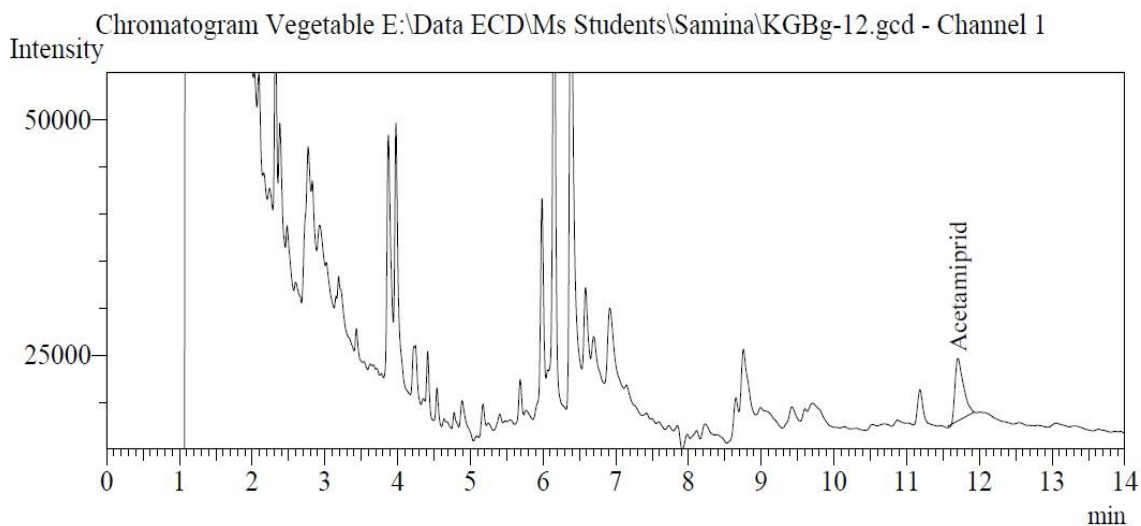
Figure 11. Chromatogram of acetamiprid found in one of bitter gourd sample (KGBg-12) collected from Katiadi upazila
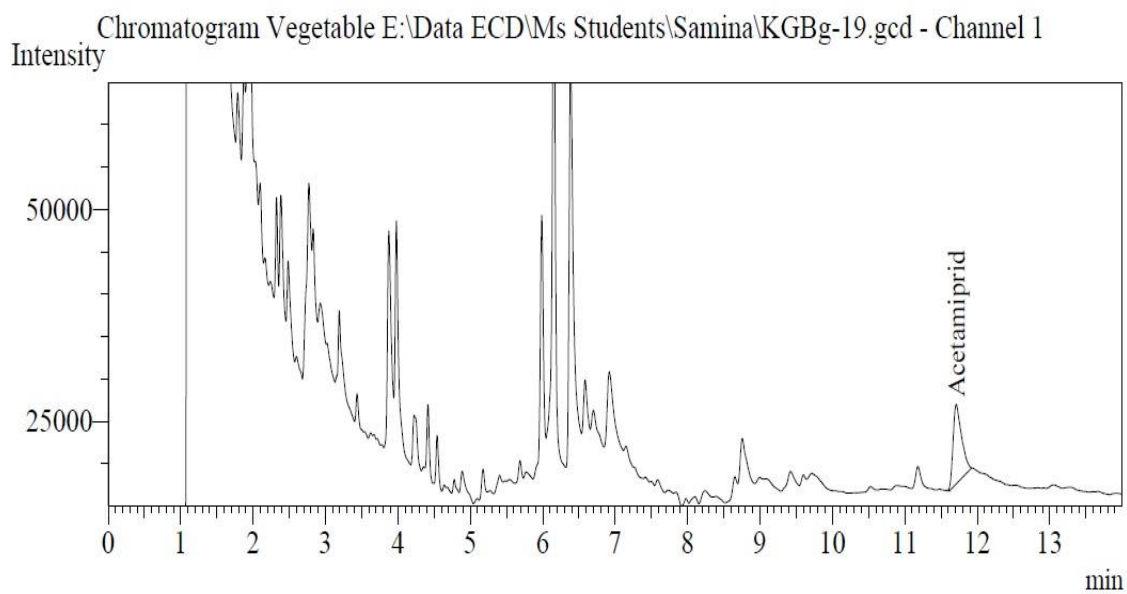
Figure 12. Chromatogram of acetamiprid found in one of bitter gourd sample (KGBg-19) collected from Bajitpur upazila
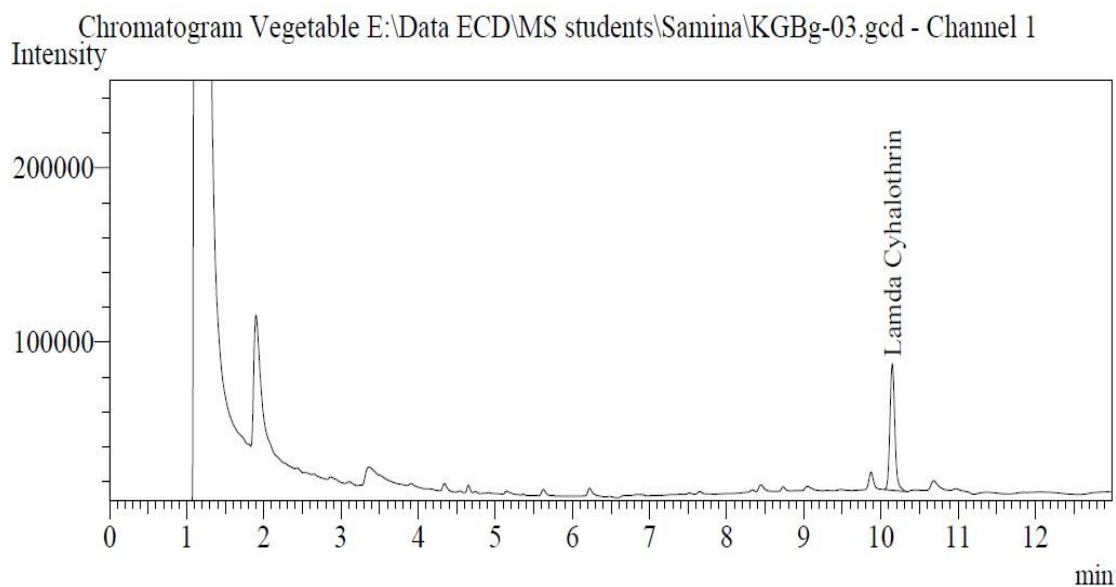
Figure 13. Chromatogram of lambda-cyhalothrin found in one of bitter gourd sample (KGBg-03) collected from Kishoreganj Sadar
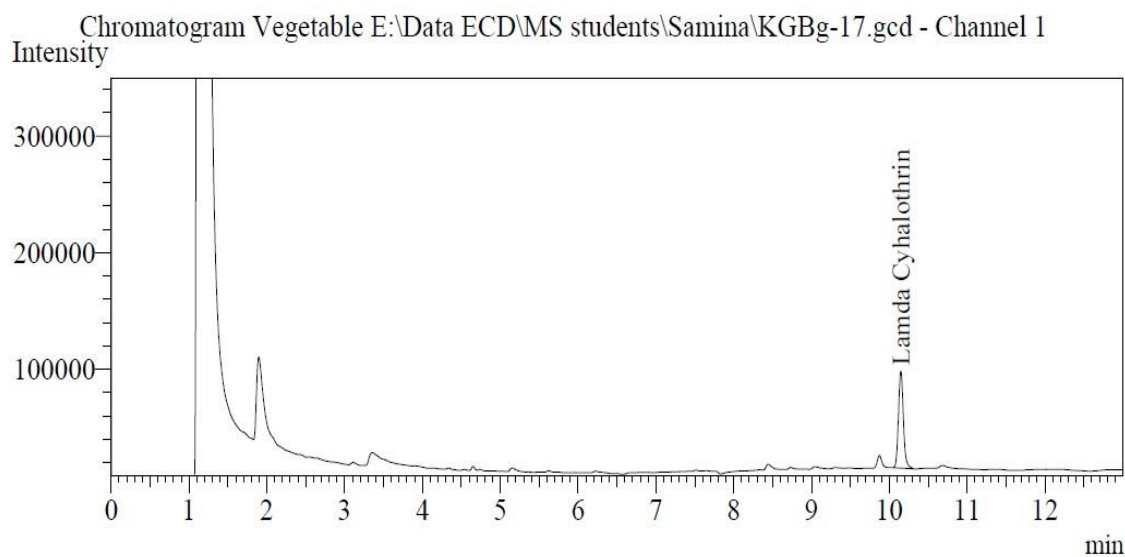
Figure 14. Chromatogram of lambda-cyhalothrin found in one of bitter gourd sample (KGBg-17) Bajitpur upazila

The level of pesticide residues obtained by analyzing the bitter gourd samples and their maximum residue levels are presented in Table 8.

Table 8. The content of residues (mg/kg) of different pesticides found in the analyzed bitter gourd samples collected from five upazilas of Kishoreganj district

Areas of collection	Sample ID	Name of detected pesticide	Level of residue (mg/kg)	MRLs (mg/kg)
Kishoreganj Sadar	KGBg-01	ND		
	KGBg-02	ND		
	KGBg-03	Lambda-cyhalothrin	**0.207**	0.15
	KGBg-04	ND		
	KGBg-05	ND		
	KGBg-06	ND		
	KGBg-07	ND		
Katiadi	KGBg-08	ND		
	KGBg-09	ND		
	KGBg-10	ND		
	KGBg-11	ND		
	KGBg-12	Acetamiprid	0.109	0.3
	KGBg-13	ND		
	KGBg-14	ND		
Bajitpur	KGBg-15	ND		
	KGBg-16	ND		
	KGBg-17	Lambda-cyhalothrin	**0.152**	0.15
	KGBg-18	ND		
	KGBg-19	Acetamiprid	0.137	0.3
	KGBg-20	ND		
	KGBg-21	ND		
Kuliarchar	KGBg-22	ND		
	KGBg-23	ND		
	KGBg-24	ND		
	KGBg-25	ND		
	KGBg-26	ND		
	KGBg-27	ND		
	KGBg-28	ND		
Bhairab	KGBg-29	ND		
	KGBg-30	ND		
	KGBg-31	ND		
	KGBg-32	ND		
	KGBg-33	ND		
	KGBg-34	ND		
	KGBg-35	ND		

MRL values are accortding to EU Pesticide Database (European Commission, 2019)

Thirty five samples of bitter gourd collected from five major markets of five Upazila (Kishoreganj Sadar, Katiadi, Bajitpur, Kuliarchar and Bhairab) of Kishoreganj district were analyzed to find out the presence of left-over residue (if there any) of three pesticides (cypermethrin, acetamiprid and lambda-cyhalothrin). Out of 35 bitter gourd samples, 4 samples (11.43% of the total number of samples) contained pesticide residues and 31 samples (88.57% of the total number of samples) contained no detectable residues of the sought pesticides. Of all the 35 bitter gourd samples, there were no detectable residue of cypermethrin.

The outcomes of present investigation indicate much similarity with that of Islam *et al.* (2019a) They analyzed 65 bitter gourd samples for 7 organophosphorus pesticide residues obtained from Savar, Dhaka. Among the 65 analyzed samples, 8 (12.3% of the total number of samples) were contaminated with pesticide residues and all of those contained residues above Maximum Residue Limit (MRL). Rest 57 samples (87.7% of the total number of samples) contained no residues of sought pesticides. The results of the present study can also be compared with that of Prodhan *et al.* (2019). They analyzed 50 samples collected from five vegetable markets of Dhaka, of which 6 samples (12%) contained pesticide residues and all of those were above the MRLs set by European Commission. Among the four organophosphorus insecticides they tested only Chlorpyrifos and Diazinon were detected above the MRLs.

Status of pesticide residue in the bitter gourd samples collected from selected upazilas Kishoreganj district

Kishoreganj Sadar upazila

Among the seven samples of bitter gourd collected from Kishoreganj Sadar, one sample (KGBg-03) contained residues of pesticide. This sample contained residues of lambda-cyhalothrin, where the level of this residue was 0.207 mg/kg. The level of detected pesticide was higher than the EU-MRL (0.15 mg/kg). The other six samples contained no detectable pesticide residues.

Katiadi upazila

One sample (KGBg-12) of bitter gourd contained residue of acetamiprid among the seven samples collected from Katiadi upazila. The extent of this residue was 0.109 mg/kg, which was below the EU-MRL (0.3 mg/kg). Rest of the samples contained no residues of sought pesticides.

Bajitpur upazila

Seven bitter gourd sample were obtained from the Bajitpur upazila. One sample (KGBg-17) contained lambda-cyhalothrin residue at a level of 0.152 mg/kg, which exceeded the EU-MRL (0.15 mg/kg). Another sample (KGBg-19) contained acetamiprid with a level of 0.137 mg/kg, which exhibited the level of residue was lower than the EU-MRL (0.3 mg/kg).

Kuliarchar upazila

No detectable residues of the sought pesticides were found in the samples, which were collected from Kuliarchar upazila.

Bhairab upazila

Among the seven samples collected from Bhairab upazila, any of the samples contained no detectable residue of selected pesticides.

4.3 Health risk assessment

The potential health risk associated with long-term pesticide exposure from tomato and bitter gourd consumption by people of the study area were estimated. For adult and children, chronic health risk indices were calculated dividing EDI (mg/kg bw/day) by the corresponding values of ADI (mg/kg/day) established by European Commission for the detected pesticides. The findings are summarized in Table 9.

Table 9. Results showing the assessment of health risk of detected pesticides on tomato and bitter gourd based on ADI for adult and children population of selected areas of Kishoreganj district

Sample ID	Location	Detected Pesticide	ADI mg/kg/d	BW kg		EDI mg/kg/d	HRI	HR Remark
				Tomato				
KGTo-05	Kishoreganj Sadar	Cypermethrin	0.05	Adult		0.00036	0.007	No
				Children		0.00215	0.043	No
KGTo-11	Katiadi	Cypermethrin	0.05	Adult		0.00027	0.005	No
				Children		0.00164	0.033	No
KGTo-15	Bajitpur	Acetamiprid	0.07	Adult		0.00016	0.002	No
				Children		0.00094	0.013	No
				Bitter gourd				
KGBg-03	Kishoreganj Sadar	Lambda-cyhalothrin	0.0025	Adult		0.00058	0.232	No
				Children		0.00346	**1.384**	**Yes**
KGBg-12	Katiadi	Acetamiprid	0.07	Adult		0.00030	0.004	No
				Children		0.00182	0.026	No
KGBg-17	Bajitpur	Lambda-cyhalothrin	0.0025	Adult		0.00042	0.168	No
				Children		0.00254	**1.016**	**Yes**
KGBg-19	Bajitpur	Acetamiprid	0.07	Adult		0.00038	0.005	No
				Children		0.00229	0.033	No

In this study, out of 70 samples (35 tomato samples and 35 bitter gourd samples) only 7 samples were contaminated with the residues of sought pesticides. The result revealed that all the samples expressed the HRI values lower than the threshold limit (HRI<1) for adult: hence, safe for consumption. Only lambda-cyhalothrin in two samples (KGBg-03 and KGBg-17) indicated health risk for children in the studied areas as HRI values exceeded 1. The findings of the present study are also supported by Nahar *et al.* (2020). They found that out of 80 samples only 11 (6 cauliflower, 5 tomato) samples contained residues which were about 14% of the total number of samples. They further noted that most of the samples contaminated with diazinon at a level above EU-MRLs. However, health risk assessment based on ADI indicated that the contaminated samples were safe. The results of current study are also in a good agreement with Kumari and John (2019). In their findings chronic health hazards prediction indicated that organophosphorus groups (methyl parathion and triazophos) posed health risk to children in the study area. The outcomes of this investigation can also be compared with Mohammed and Boateng (2017). They analyzed tomato sample for organophosphate, organochlorine and pyrethroid residues. Laboratory analysis of tomato samples for various pesticides residues has indicated that all the pesticide residues posed no threat to human health with all estimated hazard indices being below 1; however, heptachlor (HI=0.85) and dieldrin (HI=0.74) have shown the highest risk levels in children.

CHAPTER V

SUMMARY

AND
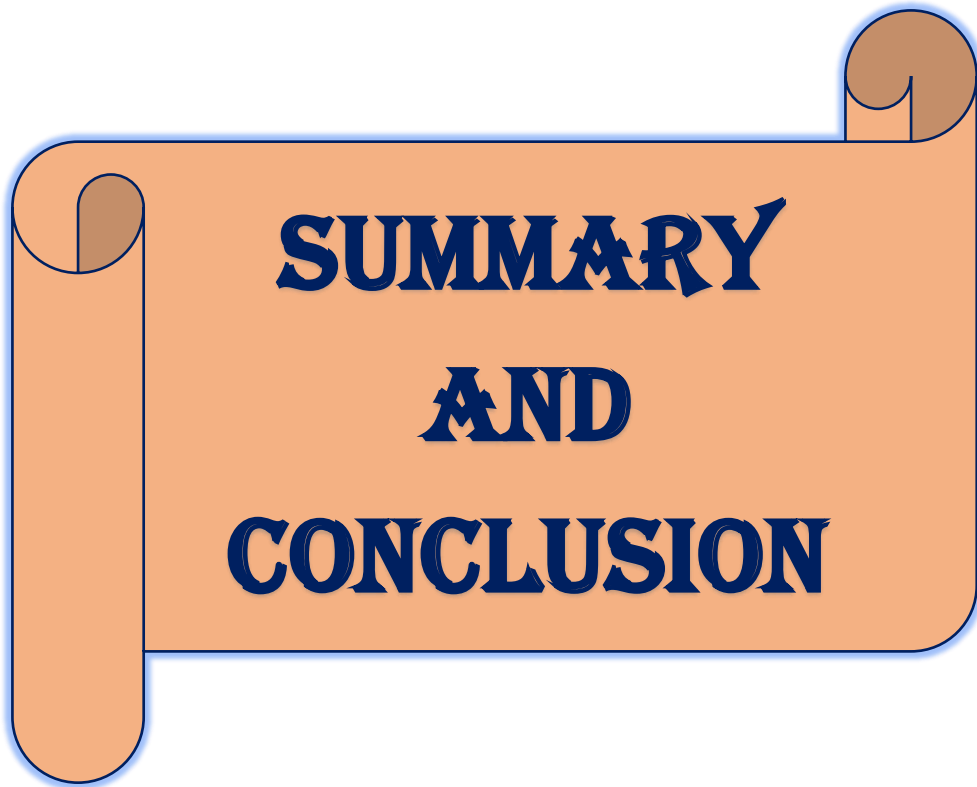
CONCLUSION

SUMMARY AND CONCLUSION

The present research work was intended to quantify the level of selected pesticide residues in samples of tomato and bitter gourd procured from several local markets of Kishoreganj district and to evaluate the associated chronic health risk of these pesticides to the population. On account of this, thirty five (35) samples of tomato and thirty five (35) samples of bitter gourd were collected from five major markets of five upazila (Kishoreganj Sadar, Katiadi. Bajitpur, Kuliarchar and Bhairab) of Kishoreganj district and carried to the Pesticide Analytical Laboratory, Entomology Division, Bangladesh Agricultural Research Institute (BARI), Gazipur, Bangladesh. The modified QuEChERS extraction technique was applied for the extraction and cleanup of the collected sample. Gas chromatography associated with electron capture detector (ECD) was used to identify and quantify the level of pesticide residues present in the extracted samples. Three most commonly used pesticides i.e. cypermethrin, acetamiprid and lambda - cyhalothrin were selected for this study. Health risk indices (HRI) were estimated based on the acceptable daily intake (ADI) and estimated daily intake (EDI) of the corresponding vegetables for adult and children.

Out of 70 samples analyzed, only 7 samples (10% of total sample) were contaminated with the residues of sought pesticides. Among 35 samples of tomato 3 samples (8.57% of the total number of tomato samples) contained residues of cypermethrin and acetamiprid and 32 samples (91.43% of the total number of tomato samples) contained no detectable residues of the sought pesticides. All the three contaminated sample contained residues of pesticide below the maximum residue limits (EU-MRLs). Out of 35 bitter gourd samples, 4 samples (11.43% of the total number of bitter gourd samples) contained residues of acetamiprid and lambda-cyhalothrin and 31 samples (88.57% of the total number of bitter gourd samples) contained no detectable residues of the sought pesticides. Among the 4 contaminated samples, 2 samples containing lambda-cyhalothrin exhibited residue level above the EU-MRL and other 2 samples containing acetamiprid expressed the residue level below the EU-MRL.

The estimated chronic health risk indices revealed that hazard indices of all contaminated samples were less than one for adult. Hence, consumption of these vegetables did not pose health risk for adult population. But higher health risk indices (>1) of lambda-cyhalothrin in case of children, indicated higher vulnerability to

68

pesticide contamination in the studied area. In this study processing factors like peeling, cooking and boiling before consumption were ignored which might result in an overestimation of the actual exposure of pesticide residues.

The outcome of the study will help to increase public awareness about health risk associated with pesticide residues and also help the policy planners to take necessary steps for the reduction of residue load in tomato and bitter gourd.

Recommendations for further research

Even though the detected residue level and chronic risk indices are low in the studied area, it does not imply complete safety for all the time. Residues could accumulate and bio-magnify over a period of time and this could have posed chronic effect on the consumers; therefore, routine monitoring of pesticides in tomato and bitter gourd is recommended. This research was executed only in five markets of five upazila of Kishoreganj district of Bangladesh. More research work should be performed in other areas of Kishoreganj district and for that matter all over Bangladesh in order to find out the proper scenario of pesticide residue load in different vegetables grown in this district and elsewhere. This investigation was accomplished only for two vegetables (tomato and bitter gourd), more investigation with different vegetables should be done. Additional research work should be carried out with other types of pesticides used in this area. This study concentrated on the chronic health effects, so it is recommended to conduct research for estimating acute health risks of the pesticides also.

CHAPTER VI

REFERENCES

REFERENCES

Abd-Elhaleem, Z.A. (2020). Pesticide residues in tomato and tomato products marketed in Majmaah province, KSA, and their impact on human health. *Environ. Sci. Pollut. Res. Int.* **27**(8): 8526-8534.

Afroze, M., Prodhan, M.D.H. and Begum, A. (2021). Development of analytical method for the determination of acetamiprid using gas chromatography. DOI:10.13140/RG.2.2.15108.35201. .

Ahmed, M.S., Begum, A., Prodhan, M.D.H., Afroze, M. and Sarkar, D. (2021). Organophosphorus pesticide residues detected in eggplant and tomato samples collected from different regions of Bangladesh. *Asian-Australas. J. Food Saf. Secur.* **5**(1): 27-31.

Ahmed, M.S., Begum, A., Prodhan, M.D.H. and Sarker, D. (2019). Analysis of pesticide residue in vegetables collected from nine different regions of Bangladesh using gas chromatography. *Asian-Australas. J. Food Saf. Secur.* **3**(1): 23-26.

Akhtar, S., Yaqub, G., Hamid, A., Afzal, Z. and Asghar, S. (2018). Determination of pesticide residues in selected vegetables and fruits from a local market of Lahore, Pakistan. *Curr. World Environ.* **13**(2): 242-250.

Aktar, M.A., Khatun, R. and Prodhan, M.D.H. (2017). Determination of pesticide residues in eggplant using modified QuEChERS extraction and gas chromatography. *Int. J. Agron. Agri. Res.* **11**(2): 22-31.

Akoto, O., Gavor, S., Appah, M.K. and Apau, J. (2015). Estimation of human health risk associated with the consumption of pesticide contaminated vegetables from Kumasi, Ghana. *Environ. Monit. Assess.* **187**(5): 1-9.

Akoto, A.Z., Hasan, M., Karim, N., Fakhruddin, A.N.M., Hossain, S., Chowdhury, A.K.M.A., Akhter, H. and Alam, K. (2014). Contamination and health risk assessment of pesticide residues in vegetables from agricultural fields of Gazipur District, Bangladesh. *Am-Euras. J. Agric. and Environ. Sci.* **14** (5): 421-427.

71

Alam, M.N., Chowdhury, M.A.Z., Hossain, M.S., Rahman, M.M., Rahman, M.A., Gan, S.H. and Khalil, M.I. (2015). Detection of residual levels and associated health risk of seven pesticides in fresh eggplant and tomato samples from Narayanganj District, Bangladesh. *J. Chem*. Article ID: 243574 (111): 1-7.

AlSaikhan, W.H., Almatroodi, S.A., Almatroudi, A., Alsahli, M.A. and Rahmani, A.H. (2021). Pesticide residue measurement in commonly used vegetables using the QuEChERS method. *Pharmacogn. J*. **13**(1): 142-149.

Amjad, A., Randhawa, M.A., Javed, M.S., Mhammad, Z., Adhraf, M., Ahmed, Z. and Murtaza, S. (2020). Dietary intake assessment of pyrethroid residues from okra and eggplant grown in peri-urban areas of Punjab, Pakistan. *Environ. Sci. Pollut. Res*. **27**: 39693–39701. https://doi.org/10.1007/s11356-019-06037-6.

Anastassiades, M., Lehotay, S.J., Stajnbaher, D. and Schenck, F.J. (2003). Fast and easy multiresidue method employing acetonitrile extraction/partitioning and dispersive solid phase extraction for the determination of pesticide residues in produce. *J. AOAC Int*. **86**: 412-431.

Baig, S.A., Akhtera, N.A., Ashfaq, M. and Asi, M.R. (2009). Determination of the organophosphorus pesticide in vegetables by high-performance liquid chromatography. *American-Eurasian J. Agric. Environ. Sci*. **6** (5): 513-519.

Bangash, J.A., Arif, M., Khan, F., Rahman, A. and Hussain, I. (2011). Proximate composition, minerals and vitamins content of selected vegetables grown in Peshawar. *J. Chem. Soc. Pak*. **33**:118-122.

BCPA, Bangladesh Crop Protection Association. (2016). Annual Report, 2016. Pp. 1-182. http://www.bcpabd.com/pdf/RegisteredPesticidesList.pdf.

Begum, S., Sultana, S., Ahmed, M., and Azad, M. (2021). Pesticide residue analysis from winter vegetables collected from six markets of Rajshahi, Bangladesh. *J. Environ. Sci. Nat. Res*. **12**(1-2): 43–50.

Bempah, C.K., Agyekum, A.A., Akuamoa, F., Frimpong, S. and Buah-Kwofie, A. (2016). Dietary exposure to chlorinated pesticide residues in fruits and vegetables from Ghanaian markets. *J. Food Compos. Anal*. **46**: 103-113.

Bempah, C.K., Asomaning, J. and Boateng, J. (2012). Market basket survey for some pesticide residues in fruits and vegetables from Ghana. *J. Microbiol. Biotechnol. Food Sci*. **2**(3): 850-871.

Berrada, H., Fernández, M., Ruiz, M.J., Moltó, J.C., Mañes, J. and Font, G. (2010). Surveillance of pesticide residues in fruits from Valencia during twenty months (2004/05). *Food Control*. **21**(1): 36-44.

Bhandari, G., Zomer, P., Atreya, K., Mol, H.G.J., Yang, X. and Geissen, V. (2019). Pesticide residues in Nepalese vegetables and potential health risks. *Environ. Res*. **172**: 511–521.

Bhupendor, K., Mukherjee, D.P., Sanjay, K., Mishra, M., Richa, G., Prakash, D., Singh, S.K. and Sharma, C.S. (2011). Occurrence and distribution of pesticide residues in selected vegetables from West Bengal. *Arch. Appl. Sci. Res*. **3**(5): 85-93.

Chaikasem, S. and Na Roi-et, V. (2020). Health risk assessment of pesticide residues in vegetables from river basin area. *Appl. Environ. Res*. **42**(2): 46–61.

Chauhan, S., Swati, N., Singh, N., Gunjan, B. and Srivastava, A. (2012). Monitoring of pesticide residues in farmgate vegetables of Uttarakhand, India. *Wudpecker J. Agric. Res*. **2**(7): 250-256.

Chowdhury, A.Z., Hasan, M., Karim, N., Fakhruddin, A.N.M., Hossain, S., Chowdhury, A.K.M.A., Akhter, H. and Alam, K. (2014). Contamination and health risk assessment of pesticide residues in vegetables from agricultural fields of Gazipur District, Bangladesh. *Am-Euras. J. Agric. and Environ. Sci*. **14** (5): 421-427.

Chowdhury, M.A.Z., Paul, D.K., Mondal, M.Z.H. and Alam, M.M. (2010). Study of selected pesticide residues in vegetable samples from different local markets of Dhaka city area. *J. Appl. Sci. Tech*. **7**(1): 45-48.

Chowdhury, M.T.I., Razzaque, M.A., Sultana, N., Mustafiz, S.S.B., Akter, S., Akter, A. and Islam, M.R. (2013). Chlorinated pesticide residue status in some winter vegetables. *Int. J. Agri Crop Sci*. **6** (11): 667-675.

Chowdhury, M.T.I., Razzaque, M.A. and Khan, M.S.I. (2011). Chlorinated pesticide residue status in tomato, potato and carrot. *J. Expt. Sci*. **2**(1):1-5.

Crentsil, K.B., Archibold, B.K., Dzifa, D., Jacob, A. and Anita, O.T. (2011). Monitoring of pesticide residues in fruit and vegetables and related health risk assessment in Kumasi, Ghana. *Res. J. Environ. Earth Sci*. **3**(6): 761-771.

Chu, Z., Zhuang, M., Li, S., Xiao, P., Li, M., Liu, D., Zhou, J., Chen, J. and Zhao, J. (2019). Residue levels and health risk of pesticide residues in bell pepper in Shandong. *Food. Addit. Contam. Part A Chem. Anal. Control. Expo. Risk Assess*. **36**(9): 1385-1392.

Darko, G. and Akoto, O. (2008). Dietary intake of organophosphorus pesticide residues through vegetables from Kumasi, Ghana, *Food Chem. Toxicol*. **46**(12): 3703–3706.

Dasika, R., Tangirala, S. and Naishadham, P. (2012). Pesticide residue analysis of fruits and vegetables. *J. Environ. Chem. Ecotoxicol*. **4**(2): 19-28.

Elgueta, S., Valenzuela, M., Fuentes, M., Meza, P., Manzur, J.P., Liu, S., Zhao, G. and Correa, A. (2020). Pesticide residues and health risk assessment in tomatoes and lettuces from farms of Metropolitan Region Chile. *Molecules*. **25**(2): 355.

Elgueta, S. Moyano, S., Sepúlveda, P., Quiroz, C. and Correa, A. (2017). Pesticide residues in leafy vegetables and human health risk assessment in North Central agricultural areas of Chile. *Food Addit. Contam. Part B*. **10**(2): 105-112.

Elibariki, R. and Maguta, M.M. (2017). Status of pesticides pollution in Tanzania - a review. *Chemosphere*. **178**: 154–164.

EU Pesticide Database. https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/mrls/?event=search.pr. Accessed on 19 March 2021.

Fakhruddin, A.N.M., Chowdhury, M.A.Z., Rahman, M.A. Alam, M.K. and Hossain, M.S. (2015). Health risk assessment of selected pesticide residues in locally produced vegetables of Bangladesh. *Int. Food Res. J*. **22**(1): 110-115.

Fakhruddin, A.N.M., Chowdhury, M.A.Z., Bhattacharjee, S., Islam, M.N., and Alam, M.K. (2013). Determination of cypermethrin, chlorpyrifos and diazinon residues in tomato and reduction of cypermethrin residues in tomato using rice bran. *World J. Agric. Res*. **1**(2): 30-35.

Fang, L., Zhang, S., Chen, Z., Du, H., Zhu, Q., Dong, Z. and Li, H. (2015). Risk assessment of pesticide residues in dietary intake of celery in China. *Regul. Toxicol. Pharmacol*. **73**(2): 578-586.

Forkuoh, F., Boadi, N.O., Borquaye, L.S. and Afful, S. (2018). Risk of human dietary exposure to organochlorine pesticide residues in fruits from Ghana. *Sci. Rep*. **8**: 16686.

Gilden, R.C., Huffling, K. and Sattler, B. (2010). Pesticides and health risks. *J. Obstet. Gynecol. Neonatal. Nurs*. **39**: 103-110.

Golge, O., Hepsag, F. and Kabak, B. (2018). Health risk assessment of selected pesticide residues in green pepper and cucumber. *Food Chem. Toxicol*. **121**: 51-64.

Gowda, A., Reddy, A.S.R.K, and Ramesh, H.L. (2020). Analysis of pesticide residues in carrot retailed in vegetable markets in five districts of Karnataka, India. *GSC Biol. Pharm*. Sci, **10**(3): 27-38.

Habib, M., Kaium, A., Khan, M.S.I., Prodhan, M.D.H., Begum, N., Chowdhury, M.T.I. and Islam, M.A. (2021). Residue level and health risk assessment of organophosphorus pesticides in eggplant and cauliflower collected from Dhaka city, Bangladesh. *Food Res*. **5**(3): 369-377.

Hasan, M., and Rahman, A. (2019). Pesticide residues in selected vegetable collected from wet markets of Bangladesh. *Adv. Soc. Sci. Res. J*. **6**(5): 15-23.

Hasan, R., Prodhan, M.D.H., Rahman, S.M.M., Khanom, R. and Ullah, A. (2017). Determination of organophosphorus insecticide residues in country bean collected from different markets of Dhaka. *J. Environ. Anal. Toxicol*. **7**(4): 489.

Heeb, A. (2005). Organic or mineral fertilization, effects on tomato plant growth and fruit quality. Doctoral Thesis. Swedish University of Agricultural Sciences, Uppsala, Sweden.

HIES, Household Income and Expenditure Survey. (2016). Statistical Yearbook of Bangladesh-2020, BBS. Pp. 532.

Hepsağ, F. and Kizildeniz, T. (2021). Pesticide residues and health risk appraisal of tomato cultivated in greenhouse from the Mediterranean region of Turkey. *Environ. Sci. Pollut. Res. Int*. **28**(18): 22551-22562.

Hixson, J.E. (2015). Growing tomatoes like a pro: how to grow juicy, colorful, tasty, organic tomatoes in your backyard & in containers. Living Plus Healthy Publishing. Pp. 106.

Hossain, M.S., Rahman, M.M., Kabir, K.H., Miah, M.R.U. and Prodhan, M.D.H. (2014). Determination of Pre-Harvest Interval (PHI) for cypermethrin and acephate in yard-long bean under supervised field trial. *Bangladesh J. Entomol.* **24** (1): 101-115.

Hossain, M.I., Shively, G. and Mahmoud, C. (2000). Pesticide expenditure in a rice vegetable farming system: evidence from low-income farms in Bangladesh. IPM-CRSP working paper. November 2000, Office of International Research, Education, & Development (OIRED), Virginia Tech, 526 Prices Fork Road, Blacksburg, VA 24061-0334. Pp. 120.

Hossain, S., Chowdhury, M.A.Z., Alam, M., Islam, M.N., Rashid, M.H. and Jahan, I. (2015). Determination of pesticide residues in brinjal, cucumber and tomato using gas chromatography and mass spectrophotometry (GC-MS). *Adv. Biochem. Biotechnol.* **1**(1): 1-16.

Huong, D.T.V., Nga, T.T.H and Ha, D.T.T. (2020). Residue pesticides (Pyrethroid group) in vegetable and their health risk assessment via digestion on consumers in Ha Nam Province, Vietnam. 6th International Conference on Environment and Renewable Energy. February 24-26, Hanoi, Vietnam. *IOP Conf. Ser.: Earth Environ. Sci*. **505**: 012052.

Ibitomi, M.O. and Mohammed, F. (2016). Determination of pesticide residues in fruits and vegetables in Kaduna metropolis, Nigeria. *Int. J. Environ. Sci. Toxic. Res*. **4**(10): 185-189.

Ibrahim, E.G., Yakubu, N., Nnamonu, L. and Yakubu, J.M. (2018). Determination of organochlorine pesticide residues in pumpkin, spinach and sorrel leaves grown in Akwanga, Nasarawa State, Nigeria. *J. Environ. Prot*. **9**(5): 508-515.

Ijeoma, K.H., Aboila, O.O. and Daniel, A. (2020). Human health risk assessment of pesticide residues in *Solanum lycopersicum* fruit sold in Lagos Metropolis, South-West Nigeria. *Commun. Phys. Sci*. **5**(4): 533-543.

Islam, M.A., Yeasmin, M., Rahman, M.A., Hossen, M.S. (2019). Quantitative analysis of selected pesticide residues in brinjal using gas chromatography. *Int. J. Sci. Res. Sci. Technol*. **5**(4): 157-167.

Islam, M.S., Prodhan, M.D.H. and Uddin, M.K. (2019a). Analysis of the pesticide residues in bitter gourd using modified QuEChERS extraction coupled with gas chromatography. *Asia Pac. Environ. Occup. Health J*. **5**(3): 6-15.

Islam, M.S., Prodhan, M.D.H. and Uddin, M.K. (2019b). Determination of major organophosphorus pesticide residues in eggplant using QuEChERS extraction and gas Chromatography. *Int. J. Innov. Sci. Res. Technol*. **4**(8): 212-219.

Islam, M.W., Dastogeer, K.M.G., Hamim, I., Prodhan, M.D.H. and Ashrafuzzaman, M. (2014). Detection and quantification of pesticide residues in selected vegetables of Bangladesh. *J. Phytopath. Pest Manag*. **1**(2): 17-30.

Jallow, M.F.A., Awadh, D.G., Albaho, M.S., Devi, V.Y. and Ahmed, N. (2017). Monitoring of pesticide residues in commonly used fruits and vegetables in Kuwait. *Int. J. Environ. Res. Public Health*. **14**(8): 833.

Kabir, K.H., Rahman, M.A., Ahmed, M.S., Prodhan, M.D.H. and Akon, M.W. (2008). Determination of residue of diazinon and carbosulfan in brinjal and quinalphos in yard long bean under supervised field trial. *Bangladesh J. Agril. Res*. **33**(3): 503-513.

Kabir, K.H., Abdullah, M., Prodhan, M.D.H., Ahmed, M.S. and Alam, M.N. (2007). Determination of carbofuran residue in the samples of sugarcane and soil of sugarcane field. *The Agriculturist.* **5**(1 & 2): 61-66.

Kolani, L., Mawussi, G. and Sanda, K. (2019). Assessment of organochlorine pesticide residues in vegetable samples from some agricultural areas in Togo. *Am. J. Anal. Chem*. **7**(4):332.

Krawinkel, M.B. and Keding, G.B. (2006). Bitter gourd (*Momordica charantia*): a dietary approach to hyperglycemia. *Nutr. Rev*. **64**(7): 331–337.

Krishnendu, J.R. and Nandini, P.V. (2016). Nutritional composition of bitter gourd types (*Momordica charantia* L.). *Int. J. Adv. Eng. Res. Sci*. **3**(10): 96-104. DOI: 10.22161/ijaers/3.10.1.

Kumari, D. and John, S. (2019). Health risk assessment of pesticide residues in fruits and vegetables from farms and markets of Western Indian Himalayan region. *Chemosphere*. **224**: 162-167.

Kumavat, S.D. and Chaudhari,Y.S. (2013). Lycopene and it's role as prostate cancer chemo preventive agent. *Int. J. Res. Pharm. Chem*. **3**(3): 545-551.

Lehotay, S.J., Kyung, A.S., Kwon, H., Koesukwiwat, U., Fu, W., Mastovska, K., Hoh, E. and Leepipatpiboon, N. (2010). Comparison of QuEChERS sample preparation methods for the analysis of pesticide residues in fruits and vegetables. *J. Chromatogr. A*. **1217**(16): 2548-2560.

Lehotay, S.J., de Kok, A., Hiemstra, M. and Bodegraven, P.V. (2005). Validation of a fast and easy method for the determination of residues from 229 pesticides in fruits and vegetables using gas and liquid chromatography and mass spectrometric detection. *J. AOAC Int*. **88**(2): 595-614.

Lehotay, S.J., Mastovská, K. and Lightfield, A.R. (2005a). Use of buffering to improve results of problematic pesticides in a fast and easy method for residue analysis of fruits and vegetables. *J. AOAC Int*. **88**(2): 615-629.

Lehotay, S.J., Mastovska, K. and Yun, S.J. (2005b). Evaluation of two fast and easy methods for pesticide residue analysis in fatty food matrices. *J. AOAC Int*. **88**(2): 630-638.

Loughlin, T.M.M., Peluso, M.L., Etchegoyen, M.A., Alonso, L.L, and Marino, J.G. (2018). Pesticide residues in fruits and vegetables of the Argentine domestic market: Occurrence and quality. *Food Control*. **93**: 129-138.

Łozowicka, B., Kaczyński, P., Rutkowska, E., Jankowska, M. and Hrynko, I. (2013). Evaluation of pesticide residues in fruit from Poland and health risk assessment. *Agric. Sci*. **4**(5B): 106-111.

Luo, X., Qin, X., Chen, D., Liu, Z., Zhang, K. and Hu, D. (2020). Determination, residue analysis, risk assessment and processing factors of tebufenozide in okra fruits under field conditions. *J. Sci. Food Agric*. **100**(3): 1230-1237.

Maher, M.D., Tawfiq, A. and Asma, S. (2014). Monitoring of certain carbamate pesticide residues in tomatoes grown in Jordan valley by GC-NPD. *Wulfenia J*. **21**(4): 235-246.

Mao, X., Wan, Y., Li, Z., Chen, L., Lew, H. and Yang, H. (2020). Analysis of organophosphorus and pyrethroid pesticides in organic and conventional vegetables using QuEChERS combined with dispersive liquid-liquid microextraction based on the solidification of floating organic droplet. *Food chem*. **309**: 125755.

Marete, G.M., Shikuku, V.O., Lalah, J.O., Mputhia, J. and Wekesa, V.W. (2020). Occurrence of pesticides residues in French beans, tomatoes, and kale in Kenya, and their human health risk indicators. *Environ. Monit. Assess.* **192**: 692. https://doi.org/10.1007/s10661-020-08662-y.

Mohammed, M. and Boateng, K.K. (2017). Evaluation of pesticide residues in tomato (*Lycopersicum esculentum*) and the potential health risk to consumers in urban areas of Ghana. *Pollution*. **3**(1): 69-80.

Myojin, C., Enami, N., Nagata, A., Yamaguchi, T., Takamuba, H. and Matoba, T. (2008). Changes in the radical-scavenging activity of bitter gourd (*Momordica charantia* L.) during freezing and frozen storage with or without blanching. *Food Chem*. **73**(7): 546–550.

Nahar, K.M., Khan, M.S.I., Habib, M., Hossain, S.M., Prodhan, M.D.H. and Islam, M.A. (2020). Health risk assessment of pesticide residues in vegetables collected from northern part of Bangladesh. *Food Res*. **4**(6): 2281-2288.

Odewale, G.O., Sosan, M.B., Oyekunle, J.A.O. and Adeleye, A.O. (2021). Human health risk assessment of dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) pesticide residues in fruits and vegetables in Nigeria. *Environ. Sci. Pollut. Res*. **28**: 33133–33145.

Omwenga, I., Kanja, L., Zomer, P., Louisse, J., Rietjens, I.M.C.M. and Mol, H. (2021). Organophosphate and carbamate pesticide residues and accompanying risks in commonly consumed vegetables in Kenya. *Food Addit. Contam. Part B Surveill*. **14**(1): 48-58.

Otchere, K.G., Adam, J.I., Larbi, J.A., Basil, S.A. and Banunle, A. (2020). Analysis of insecticide residues in cabbage (*Brassica oleracea var. capitata*) from three major markets in Kumasi. *Ann. Environ. Sci. Toxicol*. **4**(1): 19-23.

PAN Germany. Pesticide and health hazards-facts and figures. (2012). [Online] Available from: http//www.pan-germany. org/download/Vergift_EN-201112-web.pdf [Accessed 9 September 2019]

Prodhan, M.D.H., Afroze, M., Begum, A., Ahmed, M.S. and Sarker, D. (2021). Optimization of a QuEChERS based analytical method for the determination of organophosphorus and synthetic pyrethroid pesticide residues in betel leaf. *Int. J. Environ. Anal. Chem.* https://doi.org/10.1080/03067319.2021.1873311.

Prodhan, M.D.H., Afroze, M., Begum, A. and Sarker, D. (2021a). Determination of organophosphorus and synthetic pyrethroid pesticide residues and their variability in large size fruit crops. *J. Sci. Food Agric*. **101**(11): 4847-4854.

Prodhan, M.D.H., Islam, M.A., Ullah, A., Habib, M., Chowdhury, M.T.I., Khan, M.S.I. and Kaium, A. (2019). Determination of major organophosphate insecticide residues in cabbage samples from different markets of Dhaka. *Asia Pac. Environ. Occup. Health J.* **5**(2): 30-35.

Prodhan, M.D.H., Akon, M.W. and Alam, S.N. (2018). Determination of pre-harvest interval for quinalphos, malathion, diazinon and cypermethrin in major vegetables. *J. Environ. Anal. Toxi.* **8**: 553.

Prodhan, M.D.H., Papadakis, E.N. and Papadopoulou-Mourkidou, E. (2018a). Variability of pesticide residues in eggplants units collected from a field trial, and market places in Greece. *J. Sci. Food Agric.* **98**(6): 2277-2284

Prodhan, M.D.H., Papadakis, E.N. and Papadopoulou-Mourkidou, E. (2016). Analysis of pesticide residues and their variability in cabbage using QuEChERS extraction in combination with LC-MS/MS. *Food Anal. Methods.* **9**(12): 3470-3478.

Prodhan, M.D.H., Papadakis, E.N. and Papadopoulou-Mourkidou, E. (2016a). Variability of pesticide residues in cauliflower units collected from a field trial, and market places in Greece. *J. Environ. Sci. Health.* **51**(9): 644-653.

Prodhan, M.D.H., Papadakis, E.N. and Papadopoulou-Mourkidou, E. (2015). Determination of multiple pesticide residues in eggplant with liquid chromatography mass spectrometry. *Food Anal. Methods.* **8**: 229-235.

Prodhan, M.D.H., Papadakis, E.N and Papadopoulou-Mourkidou, E. (2015a). Analysis of pesticide residues in melon using QuEChERS extraction and liquid chromatography triple quadrupole mass spectrometry. *Int. J. Environ. Anal. Chem.* **95**(13): 1219-1229.

Qi, H., Huang, Q. and Hung, Y.C. (2018). Effectiveness of electrolyzed oxidizing water treatment in removing pesticide residues and its effect on produce quality. *Food Chem.* **239**: 561–568.

Qin, G., Li, Y., Chen, Y., Sun, Q., Zuo, B., He, F., Shen, N., Jia, G. and Ding, G. (2015). Pesticide residues determination in China vegetables in 2010–2013 applying gas chromatography with mass spectrometry. *Food Res. Int.* **72**: 161-167.

81

Rajabu, J., Tarimo, M. and Hangali, T. (2017). Health effects, trends and knowledge on pesticide use in Tanzania; Review. *Int. J. Sci. Res. Innov. Technol*. **4**(1):100-122.

Ramadan, M.F.A., Abdel-Hamid, M.M.A., Altorgoman, M.M.F., Algaramah, H.A., Alawi, M.A., Shati, A.A, Shweeta, H.A. and Awwad, N.S. (2020). Evaluation of pesticide residues in vegetables from the Asir Region, Saudi Arabia. *Molecules*. **25**(1): 205. DOI:10.3390/molecules25010205.

Ratnamma, N.H., Pallavi, M.S., Pavankumar, B.M. and Prabhuraj, A. (2020). Estimation of pesticide residues in okra (*Abelmoschus esculentus* L.) and risk assessments. *J. Farm Sci*. **33**(1): 105-112.

Robson, M.G. (2019). World Ecology Report Vol. 29. New York, NY 10016: World Information Transfer, Inc.

Rohan, D., Siddharth, T. and Padmaja, N. (2012). Pesticide residue analysis of fruits and vegetables. *J. Environ. Chem. Ecotoxicol*. **4**(2): 19-28.

Saeid, M.H. and Selim, M.T. (2013). Multiresidue analysis of 86 pesticide using gas chromatography mass spectrometry. *J. Chem*. **13**(1): 1-10.

Santarelli, G.A., Migliorati, G., Pomilio, F., Marfoglia, C., Centorame, P., D'Agostino, A. and Aprea, G. (2018). Assessment of pesticide residues and microbial contamination in raw leafy green vegetables marketed in Italy. *Food Control*. **85**: 350–358.

Schenck, F.J., Brown, A.N., Podhorniak, L.V., Parker, A., Reliford, M. and Wong, J.W. (2008). A rapid multiresidue method for determination of pesticides in fruits and vegetables by using acetonitrile extraction/partitioning and solid-phase extraction column cleanup. *J. AOAC Int*. **91**(2): 422-38.

Seo, Y.-H., Cho, T.-H., Hong C.-K., Kim, M.-S., Cho, S.-J., Park, W.-H. and Hwang, I.-S. (2013). Monitoring and risk assessment of pesticide residues in commercially dried vegetables. *Prev. Nutr. Food Sci*. **18**(2): 145–149.

Sheikh, S.A., Nizamani, S.M., Panhwar, A.A. and Mirani, B.N. (2013). Monitoring of pesticide residues in vegetables collected from markets of Sindh, Pakistan. *Food Sci. Technol. Lett*. **4**(1): 41-45.

Singh, B., Kar, A., Mandal, K., Kumar, R. and Sahoo, S.K. (2012). Development and validation of QuEChERS method for estimation of chlorantraniliprole residue in vegetables. *J. Food Sci*. **77**(12): T208-T215.

Singh, Y., Mandal, K. and Singh, B. (2015). Persistence and risk assessment of cypermethrin residues on chilli (*Capsicum annuum* L.). *Environ. monit. Assess*. **187**(3): 120.

Srivastava, A.K., Trivedi, P., Srivastava, M.K., Lohani, M. and Srivastava, L.P. (2011). Monitoring of pesticide residues in market basket samples of vegetable from Lucknow City, India: QuEChERS method. *Environ. Monit. Assess*. **176**(1-4): 465-472.

Suleiman, F., Nuhu, A.A., Omoniyi, I.K. and Yashim, I.Z. (2021). Health risk assessment of organochlorine and synthetic pyrethroid pesticide residues via dietary intake of field grown fruits and vegetables. *Nigerian J. Pharm. Appl. Sci. Res*. **10**(1): 10-14.

Tankiewicz, M. (2019). Determination of selected priority pesticides in high wwater fruits and vegetables by modified QuEChERS and GC-ECD with GC-MS/MS confirmation. *Molecules*. **24**(3): 417.

USEPA, United States Environmental Protection Agency. (2005). Supplementary guidance for conducting health risk assessment of chemical mixtures. Risk Assessment Forum Technical Panel, Washington DC.

Walia. S., Boora, P. and Kumari, B. (2010). Effect of processing on dislodging of cypermethrin residue on brinjal. *Bull. Environ. Contam. Toxicol*. **84**: 465–468.

WHO, World Health Organization. (2018). Pesticide residues in food. Available at. https://www.who.int/news-room/fact-sheets/detail/pesticide residues in food.

Zhang, Y., Hu, D., Zeng, S., Lu, P., Zhang, K., Chen, L. and Song, B. (2016). Multiresidue determination of pyrethroid pesticide residues in pepper through a modified QuEChERS method and gas chromatography with electron capture detection. *Biomed. chromatogr*. **30**(2): 142–148.
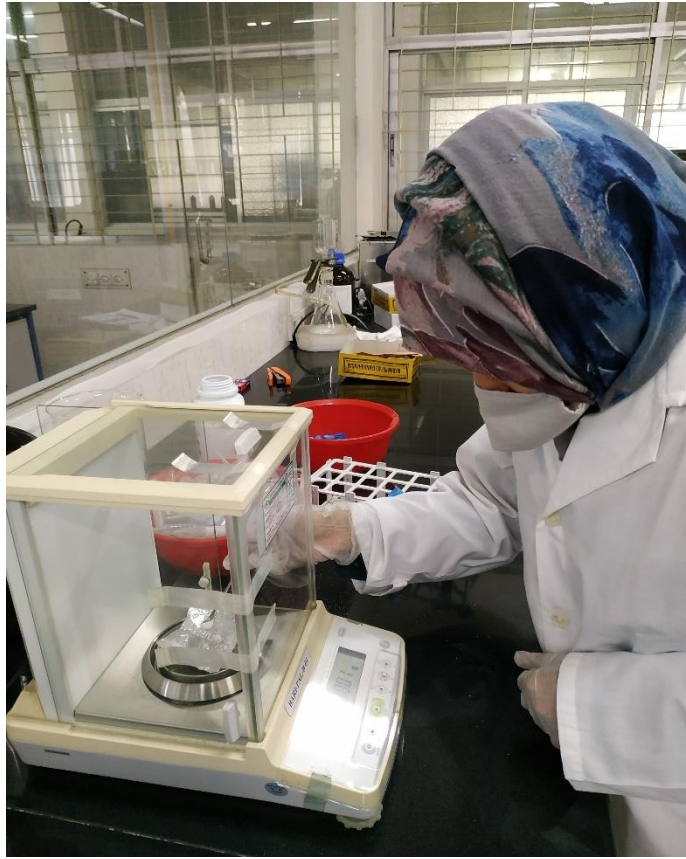
APPENDICES

Collecting samples from different vendors

Collecting samples from different vendors

Samples in transparent polythene bags with labeling

Weighing PSA

Taking supernatant

Sample analysis using GC-ECD