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Human Health Risk Assessment Through the Detection of Organochlorine Pesticides in Vegetables and Fruits from Dhaka, Bangladesh by Gas Chromatography Tandem Mass Spectrometry (GC-MS/MS)

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Abstract

This study investigated the levels of Organochlorine pesticides (OCPs) in vegetables and fruits from local markets of Dhaka, Bangladesh using Gas Chromatography Tandem Mass Spectrometry(GC-MS/MS) and analyzed the possible health risks of peoples through consumption of those fruits and vegetables. A total of 100 vegetables and 100 fruits samples were analyzed and 45% of vegetable samples and 40% of fruit samples were found to be contaminated with OCPs residues. Aldrin, p,p-DDE (Dichlorodiphenyldichloroethylene), Cis-Chordane, p,p-DDT (Dichlorodiphenyltrichloroethane), Endrin, α-Endosulfan and Lindane-I were detected in vegetable samples while Aldrin, p,p-DDE, p,p-DDT, α-Endosulfan and Lindane-I were detected in fruit samples. The HI (Hazard Risk Index) values of Aldrin, p,p-DDE, Cis-Chordane, p,p-DDT, Endrin, α-Endosulfan and Lindane-I in vegetables were 0.1096, 0.0066, 0.3964, 0.0088, 0.1532, 0.8828 and 0.0198 respectively while HI values of Aldrin, p,p-DDE, p,p-DDT, α-Endosulfan and Lindane-I in fruit samples were 0.0155,0.0005, 0.0002, 0.0339, 0.0019respectively. The average concentration of detected OCPs residues were below the FAO's recommended maximum residue limits (MRL).It is therefore concluded that, even though OCPs residues are below the maximum tolerance value but, continuous accumulation in consumer body through consumption of such vegetables and fruits may lead to chronic effects.

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Introduction

In agricultural productions, pesticides are using worldwide to resist pest attacks and prevent diseases. The excessive use of pesticides is the cause of spreading environmental contamination in developing countries.[1,2] Recently, the determination of the traces of pesticide residues in food becoming the primary concern in pesticide research, to obtain a comprehensive assessment of food quality and to avoid potential health problems.[3]

OCPs are a broad category of extremely long-lasting contaminants. After being applied for a long time, they remain in the environment. Many OCPs are endocrine disruptors,which mean they have a mild harmful influence on the body's hormonal systems, resulting in adverse health outcomes.[4] OCPs are a significant source of worry worldwide due to their negative eco-toxicological consequences. OCPs are persistent organic pollutants because of their non-polar and semi-volatile properties and their persistence and bio-accumulative nature.[5,6] OCPs have been banned in several European nations, yet they have been found in several food samples in the recent decade.[7,8,9]

In the developed countries, organochlorine pesticides are banned and they are strictly regulated in those countries. However, it has been reported that, several developing countries still using these OCPs.[10,11,12] According to the agricultural statistical review, about 40% of the previously used pesticides were organochlorine pesticides (FAO, 2005; Gupta, 2004). After application, the pesticide residues can stay in the environment for longer time. These pesticide residues have the ability to bio accumulate in both plant and animal tissues. The present of these pesticide residues in food chains poses serious human health hazards.[13] The majority of OCPs have been outlawed due to their great persistence as insecticides, yet their residues continue to pollute food and the environment.[14] OCPs have been discovered in both raw and cooked foods. Permissible levels of persistent organic pollutants type OCPs in foods are getting stricter as people become more aware of the hazardous risks they represent to humans.[15] For acute and chronic exposure to OCPs, carcinogenic, neurological, endocrinal, natal and neonatal disorders are growing. OCPs, including hexachlorocyclohexanes (HCHs) and dichlorodiphenyltrichloroethanes (DDTs), were widely utilized in agriculture, industry, and public health initiatives late 1940s.[16] DDT breakdown products or metabolites include DDD (Dichlorodiphenyldichloroethane) and DDE. Human faced preterm birth and spontaneous abortion due to DDT exposure. At high plasma DDE concentration, one nested case-control study showed a fourfold increased risk of breast cancer in the United States. In 1970, Sweden firstly banned OCPs for agricultural use and then extended it to other countries.[17] Pesticides are employed in agricultural areas to reduce crop loss by eliminating the physiological activities of target organisms. OCPs can contaminate water, soil, and air because of their lipophilicity, bioaccumulation, long half-life, and long-range transportability. Pesticides are harmful for living organisms in the aquatic ecosystem such as plants, fishes, microorganisms and invertebrates.[18,19,20] Because of their low cost and activity against a variety of organisms, pesticides including DDT, HCH (Hexachlorocyclohexane), aldrin, and dieldrin are utilized in most Asian developing countries.[21,22] As a result, pesticide residues may damage final consumers, particularly when these commodities are consumed fresh. Pesticide residues on agricultural commodities are known to be carcinogens and/or toxins, therefore reducing their total daily intake are preferred. Maximum residue limits (MRLs), which are defined by each country and can lead to controversies since residual levels that are acceptable in one country may be unacceptable in another, are regulated by MRLs. The required rates of application may range from country to country and within regions within the same country, depending on agricultural and climatic factors.[23,24] Pesticide residues on treated crops are being closely monitored and controlled in many countries. Analytical procedures are required to screen, quantify, and confirm pesticide residues in fruits and vegetables for both research and regulatory applications. Pesticide residues in fruit and vegetables have been confirmed by GC–MS.[25],[26,27,28,29] Gas chromatography is used in conjunction with either electron capture detection (ECD) or mass spectrometry (MS) in the majority of OCP determination procedures.

Our work aimed to assess the amount of OCPs in ten types of vegetables and fruits from Dhaka's local market. In this determination, we used Gas Chromatography Tandem Mass Spectrometry

(GC-MS/MS). This method is a sensitive and selective methodology for determining and identifying a wide range of pesticides at the trace level. Better understanding the level of OCPs in fruits and vegetables, we can quickly analyze the possible risks to human health after consumption of those vegetables and fruits.

Materials and Methods

Sampling

Various fruits and vegetables samples were purchased from largest local market for fruits and vegetables in Dhaka named Kawran Bazar. Sampling was done between February, 2021 to May, 2021. The samples were taken to the lab and stored at 4°C until further analysis. The vegetable and fruit samples were extracted and analyzed for the detection of OCPs within 24 hours after collection. Samples were collected on three replicates and a total of 10 types of fruits and 10 types of vegetables were collected randomly. The vegetables analyzed for the present study were cabbage (*Brassica oleraceavarcapitate*), cauli flower(*Brassica oleraceavar* botrytis), Radish (*Raphanussativus*), Hyacinth bean (*Lablab niger*), Sweet gourd (*Cucurbita maxima*), Cucumber (*Cucumissativus*), Bitter gourd (*Momordicacharantia*), Brinjal (*Solanummelongena*), Tomato (*Lycopersiconesculentum*) and Chilli (*Capsicum species*). The fruits analyzed for this study were Banana (*Musa sapientum*), Mango (*Mangiferaindica*), Litchi (*Litchi chinensis*), Papaya (*Carica papaya*), Guava (*Psidiumguajava*), Orange (*Citrus chrysocarpa*), Grape Fruit (*Citrus grandis*), Pineapple (*Ananascomosus*), Watermelon (*Cucumismelo*) and Lemon (*Citrus limon*). This research was conducted at the Institute of Food Science and Technology (IFST), Bangladesh council for Scientific and Industrial Research (BCSIR), Dhaka, Bangladesh.

Extraction of Sample and Clean-up

Sample extraction was done according to the method[30] with slight modification. In short, frozen samples were homogenized and thawed to room temperature. About 10 g of sample was transferred to 50 ml polypropylene tube and 10 ml of acetonitrile was added with it. The samples and the solution were homogenized with vortex mixer at high speed for 1 minute. Then, 4 g anhydrous magnesium sulphate and 1g of sodium chloride was added and shaken for 1 minute. Then, centrifuged for 5 minutes and 4 ml of organic layer supernatant was collected and eluted with two portions of 5 ml acetonitrile in a 50 ml flask (pear- shaped). The elute was then evaporated using a rotary evaporator (RE100 Pro, DLAB, USA) with 80 rpm speed at 40◦C The concentrated extract was dissolved in 2 ml ethyl acetate and finally transferred to 2ml standard vial for GC-MS/MS analysis.

GC-MS/MS

The analysis was performed in GC-MS/MS (Model: TRACE 1310, Thermo Fisher Scientific, USA) equipped with Thermo Scientific™ Trace GOLD™ TG-5MS GC Column (0.25 mm X 0.25 µm X 0.25 m) and 5% phenyl phase. Helium was used as the carrier gas in this experiment, with a constant flow rate of 1.2 ml/min. The injection port had a temperature of 230 degrees Celsius. The temperature profile for GC was ranged from 80◦C to 290◦C. The inject volume was 2 µL. Spectral detection was performed by Mass Spectrometer (Model: TSQ DUO, Thermos Scientific, USA).

Calibration, recovery performance, limit of detection (LOD) and imit of quantification (LOQ) Reference standard (98% purity) containing a cocktail of 19 different OCPs (Lindane I, Lindane II, Lindane III, Lindane IV, Heptachlor, Aldrin, Heptachlor epoxide, trans-chlordane, α-endosulfan, cis-chlordane, p',p'-DDE, Endrin, β-Endosulfan, Endrin-Ketane, Methoxychlor, Endosulfan sulfate, p',p'-DDT, Phthalic acid, p',p'-DDD), Acetonitrile (HPLC grade) and Ethyl acetate were purchased Sigma Aldrich (Germany). Analytical grade anhydrous magnesium sulphate (98% purity) and sodium chloride was purchased from Merck. (Darmstadt, Germany). Before starting the analysis, the column performance was checked by running only the blank samples. The stock solution of OCPs pesticides containing a cocktail of 19 pesticides was used as standard solution. For the standard calibration curve construction, five different concentrations ranging from 5 ppb to 200 ppb were prepared and injected on the column and all the standards showed a linear range from 5 ppb to 200ppb. The coefficient values (R2) obtained was ranged from 0.94 to 0.99 for all 5 standards. Recovery performance evaluation was used to confirm the method's precision results. For the purpose of the recovery performance

evaluation, pesticides were spiked with two known concentrations (0.5µg/L and 1 µg/L). The spiked samples were extracted and analyzed exactly using the same procedure of sample analysis. The following equation was used to determine the mean percentage recoveries of the OCPs

Pi= (Si/Ti) × 100Pi= (Si/Ti) × 100

Here, Pi represents the percent recovery, Si represents results from laboratory controls and Ti represents the percentage recovery from the spiked samples of known concentrations. Recovery tests were repeated at least two times for each OCPs and the mean percentage value, standard deviation (SD) was detected and presented in the table 2. Average blank value method was applied to determine LOD and LOQ. LOD and LOD values were determined by running several blank samples. The LOD value of the OCPs was calculated based on the signal to noise ratio (3:1). LOD is defined as the lowest concentration of OCPs that produced a chromatographic peak that was 3 times larger than the noise background (during the same retention time). The 10 times value of baseline noise in the chromatogram of the blank samples was used to compute the LOQ value.

Determination of Estimated Daily Intake (EDI) of OCPs

According to the Codex Alimentarius Commission Procedural Manual,[31] the exposure assessment can be defined as "the qualitative and/or quantitative evaluation of the likely intake of biological, chemical, and physical agents via food, as well as exposures from other sources if relevant." For each pesticide exposure the life time exposure dose (mg/kg/day) can be obtained through multiplication of residual pesticide concentration (mg/kg) in food items with the daily food consumption rate (per capita consumption) (kg/day) and dividing the result by the body weight (kg). The per capita consumption of vegetables and fruits in Bangladesh are 167.30 g/person/day and 35.78 g/person/day respectively.[32] Dietary exposure was determined by the following formula:

EDI = (FCC ×DFC) /BW

Here, EDI represents Estimated daily intake (EDI) (mg/(kg/day)); FCC indicated food chemical concentration (mg/kg); DFC is stand for daily food consumption (kg/day) and BW is used for Body weight (kg). The hypothetical assumption of body weight for adults (70 kg) considered for the dietary exposure calculation.[33,34]

Hazard Risk Index (Hi) Calculation

Consumers' health risk assessment from pesticide-contaminated vegetables and fruits was expressed as a Health Risk index (HI). The HI was calculated by multiplying the estimated daily intake (EDI) by the corresponding appropriate daily intake (ADI) values as given by WHO/FAO[35] and indicated by the equation:

HI = EDI/ADI.

For vegetables,

HI_v= Estimated daily intake of vegetables (EDI_v)/ADI_v

Here, EDI_v stands for EDI of vegetables and ADI_v stands for acceptable daily intake of vegetables.
For fruits,

HI_f= Estimated daily intake of fruits (EDI_F)/ADI_f
Here, EDI_f stands for EDI of fruits and ADI_f stands for acceptable daily intake of fruits.

If the value of HI is greater than 1, then it can be said that, the population consuming OCPs containing fruits and vegetables are safe from any health hazards.

Data Analysis

The obtained results were summarized, organized, tabulated and analyzed through Microsoft Office Excel 2007 and Statistics 10 (for statistical analysis). Duncan's multiple-range test was used to identify the differences between variables (DMRT).

Results and Discussion

Method Validation

Evaluation of recovery performance

For the method evaluation, recovery performance was carried out. The recovery rate was determined by the concentrations of the standard samples. Both fruit and vegetable samples were spiked with known two concentrations: 0.5 µg /Kg and 1 µg/Kg. The spiked samples were compared with that of blank samples because, the real blanks samples

never could be acquired without target samples. Table 2 represents the obtained recovery (%) of those pesticide residues by using this method. The recovery of the OCPs was varied from 87.2% to 99.27% for vegetables and 89.54% to 100.3% for fruits samples respectively. The Chromatogram of the standard mixture containing 19 OCPs is presented in Fig.1.

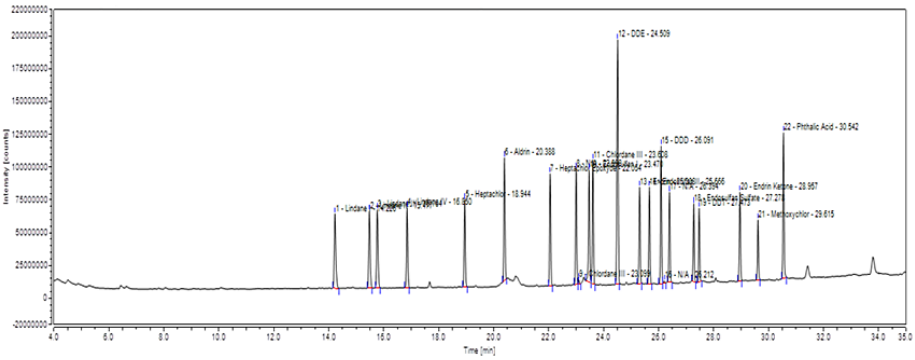

Fig. 1: GC-MS/MS chromatogram of standard OCPs mixture used in the present study. A total of 19 pesticides were analyzed with different retention times (RT) for each pesticides. 1: Lindane –I; 2: Lindane-II; 3: Lindane –III; 4: Lindane –IV; 5: Heptachlor; 6: Aldrin; 7: Heptachlor Epoxide; 8: Trans-Chlordane; 9: α- Endosulfan; 10: Cis-Chlordane; 11: p.p' -DDE; 12: Endrin; 13: β-Endosulfan; 14: Endosulfan Sulfate; 15: p.p'-DDT; 16: Endrin Ketone; 17: Methoxychlor; 18: Phthalic Acid and 19: p,p'-DDD.

Determination of LOD and LOQ

LOD was detected after injecting standard samples of three different concentrations at least six times of each sample. Then, mean standard deviation (SD) was determined for each residue. Figure 1 illustrates the chromatogram of standard samples. The LOD values were detected in the range of 0.019 to 0.033 µg/kg for vegetable samples and 0.017 to 0.038 µg /kg for fruit samples respectively. The LOQ values were detected in the range of 0.048 to 0.081 µg/kg for fruit samples and 0.049 to 0.088 µg / kg for vegetable samples. Table 1 shows the Retention time of each standard pesticides, LOD and LOQ values.

Table 1: Pesticides, their retention times, limit of detection (LOD) and Limit of quantification (LOQ) in vegetable and fruit samples.

		LOQ	LOD	LOQ	LOD
OCPs	**Retention time (Tr) (Min)**	**Vegetables (µg/Kg)**		**Fruits (µg/Kg)**	
Aldrin	20.39	0.053	0.023	0.048	0.019
p,p-DDE	24.51	0.072	0.019	0.063	0.023
Eldrine ketone	28.96	0.087	0.038	0.078	0.033
p,p-DDD	25.8	0.053	0.026	0.059	0.027
Cis-Chordane	23.61	0.088	0.019	0.072	0.022
Heptachlorepoxide	22.05	0.049	0.028	0.064	0.025
Heptachlor	18.94	0.069	0.024	0.078	0.029
p,p-DDT	27.2	0.074	0.029	0.077	0.032

Methoxychlor	26.92	0.066	0.024	0.069	0.031
Endrin	25.31	0.068	0.017	0.073	0.022
Endosulfan sulfate	27.28	0.072	0.021	0.078	0.026
α-Endosulfan	23.47	0.062	0.025	0.069	0.028
β-Endosulfan	25.67	0.058	0.022	0.063	0.027
Lindane-I	14.23	0.083	0.028	0.087	0.025
Lindane-II	15.48	0.058	0.017	0.062	0.022
Lindane -III	15.76	0.067	0.024	0.073	0.028
Lindane-IV	16.85	0.076	0.027	0.079	0.031
Trans-Chordane	23	0.078	0.019	0.064	0.023
Phthalic Acid	30.54	0.056	0.021	0.081	0.027

Table 2: Mean Recovery percentage ± relative standard deviation (RSD) of 19 OCPs extracted from fortified vegetable and fruit samples.

	0.5 µg/Kg	1 µg/Kg	0.5 µg/Kg	1 µg/Kg
OCPs	**Vegetables**		**Fruits**	
Aldrin	93.1±2.13	95.2±4.58	99.32±4.38	92.6±3.43
p,p-DDE	97.4±3.03	93.2±5.48	92.09±3.03	94.3±3.72
Eldrine ketone	99.1±3.04	91.6±4.16	96.16±4.37	95.45±3.29
p,p-DDD	91.3±4.22	96.2±3.80	89.54±4.70	99.0±3.37
Cis-Chordane	87.2±7.40	90.21±5.20	91.25±6.23	93.87±5.3
Heptachlorepoxide	87.9±3.19	92.3±4.15	97.23±5.38	92.5±2.48
Heptachlor	92.1±3.67	92.0±5.37	94.4±4.32	85.2±3.58
p,p-DDT	91.5±4.07	99.4±4.92	89.64±4.39	89.24±3.98
Methoxychlor	89.2±3.23	90.23±4.58	92.6±4.63	94.5±3.08
Endrin	96.2±4.21	88.4±5.39	91.17±4.20	92.12±3.72
Endosulfan sulfate	96.2±3.98	98.7±4.52	95.23±4.80	95.0±4.28
α-Endosulfan	98.54±6.3	90.48±4.09	95.43±4.28	93.4±3.28
β-Endosulfan	92.52±3.97	95.25±4.21	97.23±4.98	99.23±2.39
Lindane-I	98.13±3.28	88.4±5.39	91.17±4.20	92.12±3.72
Lindane-II	95.12±4.97	99.27±4.52	96.53±3.30	97.2±3.27
Lindane -III	98.04±3.12	93.48±3.34	96.17±2.48	89.4±3.28
Lindane-IV	93.23±4.32	89.28±3.17	94.48±3.37	97.42±4.39
Trans-Chordane	91.50±2.91	93.15±3.32	96.23±3.37	96.43±4.37
Phthalic Acid	90.32±3.27	95.14±3.47	94.23±3.82	93.27±4.93

n=3 replicates

Detection of Ocps Residues In Vegetables and Fruit Samples

Total 100 samples from each category (vegetables and fruits) were analyzed. Mean residue levels of OCPs in vegetables and fruits are depicted in tables 3 and 4 respectively. Almost all of the samples were contaminated with OCPs residues. However, none of the sample contained residues of any OCPs above maximum residue limits FAO/WHO fixed maximum residue limits (MRL).

Among the vegetable samples, maximum Aldrin content was detected in radish (5.42±1.32 µg/kg) with minimum detection in brinjal (1.13±0.65 µg/kg), maximum p,p-DDE content detected in Bitter gourd (5.65±1.09 µg/kg) with minimum

Table 3: OCPs residue levels (µg/Kg ± SD) detected in 10 different vegetable samples.

OCPs	Cabbage	Cauliflower	Radish	Hyacinth bean	Sweet gourd	Cucumber	Bitter gourd	Brinjal	Tomato	Chilli
Aldrin	2.68 ± 0.55	1.21±0.76	5.42±1.32	2.03±0.28	2.55±0.54	3.54±0.29	1.83±0.29	1.13±0.65	1.57±0.87	0.98±0.39
p,p-DDE	2.12±0.93	2.28±0.45	3.21±1.13	2.22±0.57	2.34±0.98	3.33±0.76	5.65±1.09	2.29±0.76	1.43±0.15	2.98±0.76
Cis-Chordane	0.85±0.15	1.21±0.31	0.96±0.21	ND	ND	1.45±0.12	2.28±0.98	3.67±1.01	2.09±0.27	0.76±0.31
p,p-DDT	4.89±1.21	3.89±0.67	3.89±1.29	2.28±0.69	3.98±1.06	1.04±0.45	4.67±1.87	5.90±1.87	4.87±1.45	1.56±2.20
Endrin	ND	ND	2.56±0.31	ND	ND	3.34±0.45	4.32±1.21	3.34±1.23	3.39±0.29	2.29±0.28
α-Endosulfan	7.74±2.45	0.77±0.34	4.67±1.76	ND	1.42±0.67	2.24±0.91	3.98±5.43	ND	6.64±2.89	2.09±0.32
Lindane-I	2.93±0.98	1.87±0.64	1.57±0.67	1.23±0.12	1.36±0.76	1.53±0.98	1.34±0.45	1.76±0.87	1.97±0.31	1.08±0.39

n= 3 replicates; ND= Not detected; SD= Standard Deviation

Table 4: OCPs residue levels (µg/Kg ± SD) in 10 different fruits samples.

OCPs	Banana	Mango	Litchi	Papaya	Guava	Orange	Grape Fruit	Pineapple	Watermelon	Lemon
Aldrin	1.09±0.56	ND	ND	0.98±0.43	ND	ND	0.93±0.47	0.94±0.34	3.67±1.98	ND
p,p-DDE	0.98±0.34	ND	ND	ND	0.38±0.21	ND	0.77±0.32	ND	2.25±1.07	ND
p,p-DDT	0.328 ±0.18	ND	ND	ND	ND	ND	ND	ND	0.61 ±0.29	ND
β-Endosulfan	0.89±0.39	ND	ND	ND	ND	ND	ND	ND	0.87±0.45	0.23±0.03
Lindane-I	1.03±0.79	ND	ND	0.53±0.32	ND	ND	0.87±0.32	0.67±0.26	0.74±0.26	ND

n=3 replicates; ND= Not detected; SD= Standard Deviation

in tomato (1.43±0.15 µg/kg), maximum Cis-Chordane content was detected in brinjal (3.67±1.01 µg/kg) with minimum in cabbage (0.85±0.15 µg/kg), maximum p,p-DDT content was detected again in brinjal (5.90±1.87 µg/kg) with minimum in cucumber (1.04±0.45 µg/kg), maximum endrin content was detected in bitter gourd (4.32±1.21 µg/kg) with minimum in chilli (2.29±0.28 µg/kg), maximum α-Endosulfan was detected again in cabbage (7.74±2.45 µg/kg) with minimum in cauliflower (0.77±0.34 µg/kg) and maximum Lindane-I content was detected in cabbage (2.93±0.98 µg/kg) with minimum detection in chilli (1.08±0.39 µg/kg). Further, Cis-Chordane content was not detected in Hyacinth bean and sweet gourd, Endrin was not detected in cabbage, cauliflower, Hyacinth bean and sweet gourd, α-Endosulfan was not detected in Hyacinth bean and brinjal samples.

Among the fruits samples, maximum Aldrin was detected in water melon (3.67±1.98 µg/kg) with minimum detected in grape fruit (0.93±0.47 µg/kg), maximum p,p-DDE content was detected again in water melon (2.25±1.07 µg/kg) with minimum detected in guava (0.38±0.21 µg/kg), maximum p,p-DDT was detected in water melon (0.61 ±0.29 µg/kg) with minimum detection in banana (0.328 ±0.18 µg/kg), maximum β-Endosulfan was detected in banana (0.89±0.39 µg/kg) with minimum detection in lemon and maximum Lindane-I was detected in banana (1.03±0.79 µg/kg) with minimum detection in papaya (0.53±0.32 µg/kg). Further, Aldrin content was not detected in mango, litchi, guava, orange and lemon samples, p,p-DDE was not detected in mango, litchi, guava, orange, papaya, pineapple and lemon samples, p,p-DDT content was not detected in mango, litchi, guava, orange, papaya, grape fruit, pineapple and lemon samples, β-Endosulfan was not detected in mango, litchi, guava, orange, papaya and grape fruit samples and Lindane-I was not detected in mango, litchi, guava, orange and lemon samples.

Several other researchers throughout the world have studied the presence of OCPs in vegetables and fruits.[36,37,38,39,40] Previous study showed that, the OCPs level of vegetable samples from market was lower than those from farm, the vegetable samples from market are found to be less contaminated than the samples from the farm.[41] This may be because of several washing and sorting of unnecessary vegetable parts. Other processing steps such as washing, cooking and peeling reduce the pesticide concentrations in the vegetable and fruit samples.[46,47] Water is an important cleaner as one study has reported that washing with water may reduce the contamination risk of 40%-90%.[42] Rain may be another important source of pesticide residues cleaning from the surface of vegetables. Several studies have reported that, low pesticide residues were detected because of rain water in rainy season.[43,44,45] As we know, several OCPs are banned in some developed countries. The OCPs residues detected from the vegetable and fruit samples may be due to the sporadic use of these pesticides in agricultural fields or may be past extensive use of these pesticides for agricultural production. From this analysis it is also found that some of the vegetables and fruits were contaminated with more than one OCP. There may have several reasons for this such as farmers may mix more than one pesticides at the same time of application. Other possible reasons may be contamination by water, soil or air. As the vegetables and fruits have similar contamination ranges therefore it suggests that those vegetables or fruits were contaminated from almost similar sources.

Although the concentration of pesticides residues are below the FAO/WHO recommended MRL but continuous exposure of OCPs residues through consumption of those vegetables and fruits can accumulate in the consumers body and later may develop chronic effects in human population for long term. The study also supports that the farmers specially the vegetables growers are using those pesticides which is responsible for the contamination of those vegetables. Fruit cultivars might also use pesticides for better production or those fruits may be contaminated from the other vegetables or fruits. This study also suggests that farmers from those regions are not properly following good Agricultural practices (GAP). Farmers should be trained properly to enhance their knowledge on pests, their ecological casualties, non-chemical alternatives and proper management of pesticides.

Health Risk from Consuming these Fruit and Vegetable Samples

Risk assessment is an important procedure to quantify the potential health risks and provides information to the risk managers to control the overuse of OCPs. The EDI (Estimated daily

intake) and HI (Health risk index) values analyzed from this study are presented in Table 5 and 6 for vegetables and fruits respectively. Theoretically, if Health risk index is greater than 1, then the responsible pesticide may cause potential health risks for systemic effects.[48,49] The HI values of Aldrin, p,p-DDE, Cis-Chordane, p,p-DDT, Endrin, α-Endosulfan and Lindane-I in vegetables were 0.1096, 0.0066, 0.3964, 0.0088, 0.1532, 0.8828 and 0.0198 respectively. The HI values of Aldrin, p,p-DDE, p,p-DDT, α-Endosulfan and Lindane-I in fruit samples were 0.0155,0.0005, 0.0002, 0.0339, 0.0019 respectively. Risk analysis shows that, there have no potential health risks through consumption of vegetables and fruits from those areas of Bangladesh but long term exposure can cause serious health problems. The HI values of detected OCPs are within the range of safe levels. Moreover, peoples can exposure OCPs from other sources like contaminated water, fish, milk, eggs, meat etc.

Table 5: Calculated Estimated daily intake (EDI) values and Heal risk Index (HI) values of vegetable samples.

OCPs	Mean concentration (mg/kg)	EDI	ADI	HI
Aldrin	0.002294	0.00548266	0.05	0.1096532
p,p-DDE	0.002785	0.00665615	1	0.00665615
Cis-Chordane	0.00165875	0.003964413	0.01	0.39644125
p,p-DDT	0.003697	0.00883583	1	0.00883583
Endrin	0.003206667	0.007663933	0.05	0.153278667
α-Endosulfan	0.00369375	0.008828063	0.01	0.88280625
Lindane-I	0.001664	0.00397696	0.2	0.0198848

EDI= Estimated daily intake; ADI= Acceptable daily intake; HI= Heal risk Index

Table 6: Calculated EDI values and HI values of fruit samples.

OCPs	Mean concentration (mg/Kg)	EDI	ADI	HI
Aldrin	0.0015232	0.000778573	0.05	0.015571456
p,p-DDE	0.001095	0.000559701	1	0.000559701
p,p-DDT	0.000469	0.000239726	1	0.000239726
β-Endosulfan	0.000663333	0.000339058	0.01	0.03390581
Lindane-I	0.00076	0.000388469	0.2	0.001942343

EDI= Estimated daily intake; ADI= Acceptable daily intake; HI= Heal risk Index

This study shows that, several vegetables and fruits samples were contaminated with OCPs residues. Although OCPs were banned many years ago in Bangladesh but still the traces are detected in food samples which might be because of the longer lasting nature of the pesticide residues. However, the levels of the residues in the tested fruits and vegetables were below those previously reported in other studies.[50,51,52] In summary, our study indicated that, there have no potential health risks due to consumption of vegetables and fruits from the studied area. In this study, HI values of OCPs were lower than the risk level. This calculation was based on the national per capita consumption.

This HI values may vary if there have difference in the per capita consumption rate in any particular area. However, the OCPs exposure must be controlled to reduce the human health risks.

Conclusions

The concentration of OCPs residues in fruits and vegetable samples from Dhaka, Bangladesh is determined through GC-MS/MS. From this analysis, several OCPs residues including Aldrin, p,p-DDE, Cis-Chordane, p,p-DDT, Endrin, α-Endosulfan and Lindane-I were detected in vegetable samples and Aldrin, p,p-DDE, p,p-DDT, α-Endosulfan and Lindane-I were detected in fruit samples. Detected OCPs residual concentrations were below the FAO's recommended maximum residue limits (MRL). Human health risk assessment suggested no potential health risks through consumption of vegetables and fruits from the studied area but long term exposure can cause serious health problems. This study provided estimation about the occurrence of OCPs residues in fruits and vegetables and further studies are suggested to ensure the safety of consumers.

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Conflict of Interest

The authors declare that they have no known conflict of interest.

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