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Assessment of organochlorine pesticide residues in edible oil

Habibur Rahman[1*], Md. Mahbubur Rahman[1], Md. Mofazzal Hossain[2], Zannatul Ferdous[1], Sajia Rahman[3] and Md. Quamrul Ahsan Talukder[4]

[1]Department of Entomology, Bangabandhu Sheikh Mujibur Rahman Agricultural University, Gazipur 1706, Bangladesh
[2]Department of Horticulture, Bangabandhu Sheikh Mujibur Rahman Agricultural University, Gazipur 1706, Bangladesh
[3]Department of Plant Genetics Research Centre (PGRC), Bangladesh Agricultural Research Institute, Gazipur 1701, Bangladesh
[4]Statistics and Information Division, Porishankhan Bhaban, Agargaon, Dhaka, Bangladesh.

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ABSTRACT

Organochlorine pesticides (OCP) are persistent in nature, highly toxic, and bio-accumulative. Their presence in different food items is a serious health concern for human being. Therefore, a total of ten edible oils were collected from the local market of Gazipur and Bogura districts of Bangladesh to assess the contamination of OCP residues. Modified AOAC version 2009.01 method was used to extract and clean up the sample. Detection and quantification of residue was done by gas chromatograph equipped with electron capture detection system. On an average 26.87% of the oil samples were found contaminated with at least one OCP residues. A total of sixteen organochlorine pesticides were detected such as α-BHC, ß-BHC, γ-BHC, δ-BHC, heptachlor, heptachlor epoxide, α-chlordane, γ-chlordane, α-endosulfan, aldrin, dieldrin, endrin, p,p′-DDD, p,p′-DDE, o,p′-DDT, and p,p′-DDT. Residues of α-chlordane, ß-BHC, heptachlor and heptachlor epoxide were detected in ≥ 40% of the total samples of edible oils. However, the residue levels were either very small (less than 0.02 ppm) or not detected at all in sesame, sunflower, rice bran, coconut, groundnut and palm oils. The majority of the OCPs contamination observed in oils of mustard, soybean, rice bran, olive and black cumin. The levels of heptachlor in soybean oil (0.021 mg.kg^{-1}) was found slightly higher than the recommended MRL (0.02 mg.kg^{-1}). Whereas the heptachlor epoxide in olive oil (0.10 mg.kg^{-1}) was found much higher than the recommended limit. Both alpha and gamma chlordane were found equal to the recommended limit (0.020 mg.kg^{-1}) in soybean oil. DDTs residues were observed in mustard, soybean, rice bran and black cumin oils but their individual occurrence was found below the MRL. But their cumulative DDTs (i.e ΣDDT = p,p′-DDD + p,p′-DDE + o,p′-DDT + p,p′-DDT) was found higher than the recommended limit in soybean oil (0.085 mg.kg^{-1}) only. Coconut, groundnut and palm oil did not have any OCP residues. The tolerable daily intake (TDI) was measured for impact assessment of ΣBHC, Σheptachlor, Σchlordane, ΣDDTs and ΣOCPs and found that the daily intake level of these OCPs by the people was found below the TDI. Therefore, the tested edible oils are safe for human consumption. However, the study suggested for periodical monitoring to ensure safe consumption of edible oils.

[*]**Corresponding Author:** Department of Entomology, Bangabandhu Sheikh Mujibur Rahman Agricultural University, Gazipur 1706, Bangladesh. Email: hrahman@bsmrau.edu.bd

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Introduction

Edible oils produced from numerous oil seeds are important sources of human nutrition. But the lipid content of edible oils is an accumulator of lipophilic organochlorine pesticides (OCPs), especially HCH, DDT, Endosulfan, BHC Aldrin, Dieldrin and Heptachlor. Most of the OCPs have substantial mutagenic and carcinogenic properties. Some OCPs are endocrine disruptors Colborn *et al*., 1993; Kalpana, 1999 and carcinogens Surendranath *et al*., 1998 and have effects on liver function, the nervous system and so on Kaushik & Kaushik, 2007; Steinberg *et al*., 2007; Soto & Sonnenschein, 2010. OCPs are persistent and highly stable under different environmental conditions. These are fat soluble, thus leading to its bioaccumulation through food chain. It can be taken up by crops from the contaminated soil Kacalkova & Tlustos, 2011; Zohair *et al*., 2006 or the polluted air Yang *et al*., 2007 and transferred into different tissues of the plants. For oil crops, OCPs may accumulate into the oil consequently exist in the oils because of their lipophilicity. Many studies reported the OCPs contamination in edible oils Bajpal *et al*., 2007, Adenugba *et al*., 2008; Skrbic & Predojevic, 2008; Qin *et al*., 2011. As a necessity in daily life, edible vegetable oils occupy a large part in daily diet, particularly for Asian people. The consumption of edible oils in Bangladesh is about 3.1 million tons in 2021fiscal year with an annual per capita consumption 9.9 kg, which is costing about 1644 million US$ BIDA, 2022. So, the determination and monitoring of OCPs in edible vegetable oils is noteworthy for the dietary safety.

As a member of the Codex Alimentarius Commission (CAC), Bangladesh has neither listed or proposed its own national maximum residues limits (MRLs), nor adopted the codex MRLs for the monitoring of persistent organic pollutants (POPs) residues in food and feeds Rahman, 2008. The use of OCPs in Bangladesh has been started at the early 1950s for the purposes of controlling vector of malaria disease (mosquitos) and other pest of interior walls and furniture and it was banned in the late 1993 Matin *et al*., 1998.

Human exposure to OCPs is attributed mainly through the food chain. Edible oils are one of the important routes of pesticide exposure of human. The contamination of edible oils by OCPs is a worldwide phenomenon. How OCPs get accumulated to the edible oils are not clearly known. But residues of OCPs are found in edible oils in India (Gupta, 2012) and England (George, 2005). Hence, continued monitoring and regulation of OCPs in edible oils have a great importance to ensure good health and food security for human beings. Very little or limited information is however available on the levels of OCPs residues in edible oils in Bangladesh. Since most of the Bangladeshi people use oils in cooking, it is necessary to determine the levels of OCPs residues in edible oils, and assess their suitability for consumption. Therefore, the present investigation was planned to determine the level of contamination of OCPs residues in edible oils which might indicate the probable human health risk.

Materials and Methods

The experimental works were carried out in the pesticide and environmental toxicology laboratory of Bangabandhu Sheikh Mujibur Rahman Agricultural University (BSMRAU). The oil samples were collected from selected local markets of Bogura and Gazipur districts in Bangladesh.

Sampling

The selected ten samples of edible oils were mustard, soybean, sesame, sunflower, rice bran, coconut, ground nut, olive, palm, black cumin oil of different brands available in the local markets. All the brand (as much as possible) of oils were tried to collect from markets. Samples were kept in room temperature during their transportation to the laboratory where they were kept at room temperature until analysis.

Chemicals and reagents

All solvents *viz.*, acetone, acetonitrile, anhydrous sodium sulfate, sodium chloride, dichloromethane and n-hexane of pesticide residue grade were purchased from chemical importers of Bangladesh.

Pesticide Standards

The OCPs pesticide standards mixture including 22 organochlorine compounds were obtained from Sigma-Aldrich, Germany.

Methodologies

i. Sample preparation, extraction and cleanup

OCPs will be extracted from each individual sample following the modified version of the AOAC official method 2009.01. The extracted samples will be cleaned up using primary secondary amine (PSA), $MgSO_4$ (anhydrite) and Graphitized carbon black.

Procedure

a) Two and half (2.5) ml oil was transferred into 125 ml separatory funnel and hexane was added so that total volume was about 15 ml.

b) Exactly 30 ml acetonitrile was saturated with hexane and vigorously shaken by vortexed mixture for 1 minute. The layers were allowed to separate. Then acetonitrile was drained into first 1L separatory funnel containing 650 ml water, 20 ml saturated sodium chloride solution, and 100 ml 15% dichloromethane in hexane.

c) Hexane solution was extracted in 125 ml separatory funnel with three additional 20 ml portions of acetonitrile saturated with hexane by hand shaking vigorously 1 minute each time, and then all acetonitrile extracts was combined in first 1L separatory funnel. Then hexane was discarded.

d) The first 1L separatory funnel (containing sodium chloride solution and organic solvent as mentioned above) was held in horizontal position and mixed thoroughly for 30-45 sec. The layer was let to be separated and drained out aqueous layer into the second 1L separatory funnel.

e) One hundred (100) ml 15% dichloromethane was added in hexane to second 1L separatory funnel, shaken vigorously for 15 secs, and let the layers to be separated. The aqueous layer for further extraction was collected and preserved in screw caped vials.

f) The organic layer was combined in first 1L separatory funnel, and washed with two 100 ml portion of water.

g) The washings were discarded and drained out the organic layer through the bed of anhydrous sodium sulphate. The dried extract was concentrated to almost dryness and final volume was made up to 5 ml with 10% acetone in hexane by removing traces of dichloromethane (DCM).

h) The aqueous layer left in second 1L separatory funnel was further extracted with 2×100 ml dichloromethane. Combined organic layer was drained through the bed of anhydrous sodium sulphate.

i) The dried extract was concentrated to almost dryness with gentle stream of nitrogen and final volume was made up to 5 mL with 10% acetone in hexane.

j) The concentrated organic layer was dissolved in suspension mixture of primary secondary amine (PSA) + $MgSO_4$ + Graphitized carbon black (GCB) to clean up the sample.

k) Sample extract solution was transferred and drained out the organic layer through the bed of anhydrous sodium sulphate and rinse walls of chromatographic tube with additional small portions of hexane.

l) The sample was made into the volume to 2.5 ml with n-hexane for analysis with Gas Chromatograph (GC) equipped with ECD.

ii. Instrumental analysis

The OCPs detection and analyses was performed in either gas chromatography (GC) with electron capture detector (ECD). The pesticide detection and analyses were performed in GC-17A (Gas Chromatograph, origin Shimadzu Co. Ltd, Japan) with ECD. The details GC condition is showed in (Table 1).

Table 1. Details of gas chromatographic conditions equipped with ECD

Parameter	Condition			
Column	Column name: Rtx-CL pesticide (Sl# 726625) Column length: 30 mtr Inner diameter: 0.32 mm Film thickness: 0.50µm Column max temp: 340 °C			
Column temperature program	Rate °C/min	Temperature (°C)	Hold time (min)	Total Program
	---	160	1.0	24 min
	10	200	7.0	
	10	240	8.0	
Oven temperature	300 ºC			
Injector temperature	280 ºC			
Detector temperature	240 ºC			
Gas flow rate	Nitrogen as carrier, 30 ml.min^{-1}			
Injection volume	1 µl			

Calculation

The residue level in the test solution was quantified using the following formula (Sharma, 2013):

$$\text{Residue level (mg.kg}^{-1}\text{ or ppm)} = \frac{\text{Area of the sample peak}}{\text{Area of the standard}} \times \frac{\text{µg of the standard injected}}{\text{µl of the sample injected}} \times \frac{\text{Final volume of the sample solution (ml)}}{\text{Weight of the sample (kg)}}$$

Method validation

Linearity, precision, accuracy, limit of detection (LOD), limit of quantitation (LOQ), and recovery parameters were determined for validation of method for OCPs. The instrumental linearity, determined by the injection of the standard solutions at five different concentration levels ranging from 0.002 to 0.2 mg.kg-1 in triplicate, and found regression coefficients higher than 0.97 for all analytes. The accuracy and precision of the method were evaluated by fortifying known amounts of the 16 OCPs in two blank edible oils (sesame and soybean oil) at two concentration levels, 0.01 and 0.04 mg.kg-1.

Tolerable daily intake

Tolerable daily intake (TDI) is an estimate of the amount of a chemical substance in air, food or drinking water that can be taken in daily over a lifetime without appreciable health risk (Mudgal *et al*., 2010). Daily intake of OCPs by an adult was calculated based on the assumption that the average oil consumption of a 48-kg adult is 20 g.day-^{1} (Kriti, 2015). The mean values of daily intake of organochlorines were estimated by using Eq. (1):

$$\text{Daily intake (DI)} = \frac{\text{Coil} \times 20\text{ g} \times \text{Clipid}}{\text{W}} \quad \text{.....Eq (1)}$$

Where,

DI = Daily intake (µg.kg^{-1} body wt./day)

C_{lipid} = Concentration of the chemical in oil (µg.g^{-1})

C_{lipid} = Lipid content in oil (%)

W = Body weight of adult (48 Kg).

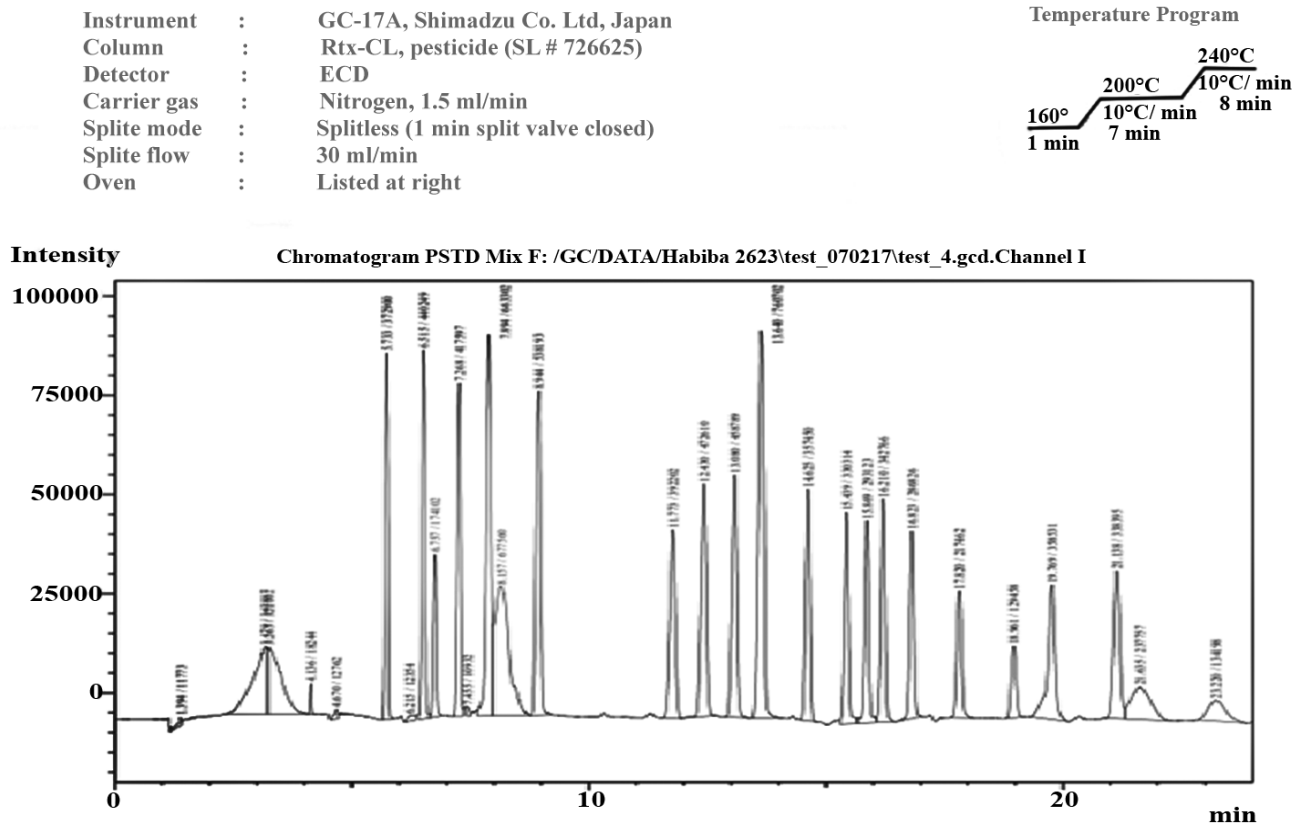


Fig. 1. Chromatogram organochlorine pesticides standard mixture (1 mg.kg^{-1})

Results and Discussion

The recovery (%), LOD, and LOQ data of the fortified (0.01 mg.kg^{-1} and 0.04 mg.kg^{-1}) sesame and soybean oils are presented in the Table 2. These data ensured the validation of method as well as ensured standardization of Gas Chromatograph machine.

Three replicates were carried out at each spiking level to determine the mean recovery and RSD, and the results were summarized in Table 2. The mean recoveries were in the range of 72.6 to 97.3% at 0.01 mg.kg^{-1} and 71.3 to 99.8% at 0.04 mg.kg^{-1} (Table 2). RSD values ranged from 1.3% to 11.5% in both levels for the analytes, except for o,p'-DDT and p,p'-DDT with a little higher RSD values of 9.2 to 19.5% at both levels of the analytes in all the oils, which might be caused by matrix effect.

The limits of detection (LODs) and limits of quantification (LOQs) were in the range from 0.03 to 0.54 ng/g and 0.11 to 1.35 ng/g for the 16 OCPs (Table 2), based on the signal-to-noise ratio (S/N) of 3 and 10, respectively. The S/N was measured with the spiked sample at level of 0.01 mg.kg-^{1} for each analyte. Compared with other reported methods (Patel *et al*., 2005; Yague *et al*., 2005, Kodba & Voncina, 2007; Deme *et al*., 2014) for determination of OCPs in edible oils, the present method had similar recoveries by using lesser quantity of organic solvents.

(i) Contamination of OCPs in edible oils

Among 22 OCP standard mixture, only 16 OCP compounds *viz*., Alpha BHC, Beta BHC, Gama BHC, Delta BHC, Heptachlor, Heptachlor Epoxide, Alpha Chlordane, Gama Chlordane, Alpha Endosulfan, Aldrin, Dieldrin, Endrin, p,p´- DDD, p,p´- DDE, o,p´-

Table 2. Recovery (n = 3), LOD and LOQ of OCPs analyzed in sesame and soybean oils by the developed method.

Organochlorine pesticides	Recovery (%) (mean ± RSD)				LOD	LOQ
	Sesame oil		Soybean oil			
	0.01 mg.kg^{-1}	0.04 mg.kg^{-1}	0.01 mg.kg^{-1}	0.04 mg.kg^{-1}	ng.g^{-1}	ng.g^{-1}
1. Alpha BHC	85.6±3.2	83.4±4.2	85.1±3.7	86. ±3.2	0.04	0.15
2. Beta BHC	83.2±4.1	77.5±4.1	86.3±4.5	83.4±2.6	0.03	0.14
3. Gamma BHC	87.2±4.7	81.6±4.5	87.3±3.8	84.2±7.2	0.04	0.13
4. Delta BHC	79.6±4.4	77.5±4.3	83.4±3.7	80.1±5.4	0.06	0.16
5. Heptachlor	72.6±7.8	78.2±4.5	80.9±9.6	71.3±8.5	0.28	1.27
6. Heptachlor Epoxide	75.8±2.4	76.4±4.3	81.2±4.6	72.3±5.1	0.32	1.25
7. Alpha Chlordane	85.0±3.2	88.2±4.5	90.1±2.5	80.4±8.2	0.06	0.17
8. Gama Chlordane	91.4±3.6	89.3±4.9	97.3±2.4	87.5±9.3	0.07	0.19
9. Alpha Endosulfan	78.2±4.9	76.3±5.1	85.5±3.5	81.2±9.2	0.09	0.18
10. Aldrin	82.3±4.7	77.5±3.2	84.6±2.9	82.7±8.2	0.07	0.16
11. Dieldrin	85.1±2.7	79.5±5.2	88.6±3.4	81.3±4.9	0.06	0.15
12. Endrin	83.2±3.2	74.0±3.8	85.2±6.2	80.6±11.5	0.05	0.11
13. p,p´- DDD	89.5±1.3	87.5±4.2	92.3±1.8	87.7±7.4	0.11	0.35
14. p,p´- DDE	89.3±3.2	88.7±6.3	89.5±2.9	83.4±11.5	0.12	0.38
15. o,p´- DDT	72.8±11.5	86.4±15.6	90.5±10.5	85.2±19.5	0.16	0.45
16. p,p´- DDT	73.7±9.2	99.8±11.5	92.4±17.7	94.8±14.2	0.54	1.35

DDT, and p,p´- DDT were detected (Table 3).

On an average 26.87% of the oil samples were found contaminated with at least one OC residues. The majority of the OCPs contamination observed in oils of mustard, soybean, rice bran, olive and black cumin. All the residues concentration were found below the MRL recommended by (FAO)/WHO, 2006) except p,p´-DDE in rice bran(0.05 ppm) and heptachlor epoxide in olive oil (0.01 ppm) The maximum number of samples were found to be contaminated by alpha- chlordane (60%) followed by beta BHC (50%). Endrin was not found in any of the oil sample tested.

(ii) Occurrence and level of OCPs

The results of the present study revealed the presence some organochlorine pesticides in the edible oils at varying concentration (Table 4). The occurrence and level of residues of organochlorine pesticides in different oils are discussed below (separately):

Benzene hexachloride (BHC)

The present study investigated the occurrence and level of all these isomers of BHC in ten edible oils (Fig. 2). Alpha BHC observed in soybean (0.027 mg.kg^{-1}), olive (0.022 mg.kg^{-1}), and black cumin 0.006 (mg.kg^{-1}) oils. Beta BHC was observed in mustard (0.008 mg.kg^{-1}), soybean (0.052 (mg.kg^{-1}), sesame (0.011 mg.kg^{-1}), rice bran (0.017 mg.kg^{-1}) and olive (0.077 mg.kg^{-1}) oils. Gamma BHC observed in rice bran (0.004 mg.kg^{-1}) and olive (0.019 mg.kg^{-1}). Delta BHC observed in mustard (0.023 mg.kg^{-1}), soybean (0.041 mg.kg^{-1}) and black cumin (0.009 mg.kg^{-1}) oils. All the residues concentration was found below the recommended MRL set by WHO (2006).

Table 3. Descriptive statistics of sixteen organochlorine residues detected from 10 edible oils collected from two districts

Parameter	Organochlorine pesticides															
	Alpha BHC	Beta BHC	Gama BHC	Delta BHC	Heptachlor	Heptachlor Epoxide	Alpha Chlordane	Gama Chlordane	Alpha Endosulfan	Aldrin	Dieldrin	Endrin	p,p´- DDD	p,p´- DDE	O,p´- DDT	p,p´- DDT
Total number of samples	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
No. of samples contaminated	3	5	2	3	4	4	6	2	3	3	1	0	1	3	2	1
% of samples contaminated	30.00	50.00	20.00	30.00	40.00	40.00	60.00	20.00	30.00	30.00	10.00	0.00	10.00	30.00	20.00	10.00
Max. amount ($mg.kg^{-1}$)	0.027	0.077	0.019	0.041	0.021	0.100	0.020	0.020	0.025	0.022	0.005	0.000	0.036	0.012	0.049	0.011
Min. amount ($mg.kg^{-1}$)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Total amount ($mg.kg^{-1}$)	0.055	0.164	0.023	0.072	0.053	0.151	0.075	0.028	0.048	0.047	0.005	0.000	0.036	0.029	0.061	0.011
Mean amount ($mg.kg^{-1}$)	0.005	0.016	0.002	0.007	0.005	0.015	0.008	0.003	0.005	0.005	0.000	0.000	0.004	0.003	0.006	0.001
Standard deviation (SD)	0.010	0.027	0.006	0.014	0.008	0.032	0.008	0.007	0.009	0.007	0.002	0.000	0.011	0.005	0.016	0.003

Note : *BDL = below detection limit (the level at which residues are detected by GC)*

Table 4. Occurrence and level of sixteen organochlorine residues in ten edible oils

Edible oils	Organochlorine pesticides residues (mg.kg^{-1})															
	Alpha BHC	Beta BHC	Gama BHC	Delta BHC	Heptachlor	Heptachlor Epoxide	Alpha Chlordane	Gama Chlordane	Alpha Endosulfan	Aldrin	Dieldrin	Endrin	p,p´- DDD	p,p´- DDE	O,p´- DDT	p,p´- DDT
Mustard oil	0	0.008	0	0.023	0.008	0.006	0.016	0.009	0.007	0	0.005	0	0	0.011	0.012	0.011
Soybean oil	0.027	0.052	0	0.041	0.021	0.036	0.020	0.020	0	0.013	0	0	0.036	0	0.049	0
Sesame oil	0	0.011	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sunflower oil	0	0	0	0	0	0.008	0.004	0	0.015	0	0	0	0	0	0	0
Rice bran oil	0	0.017	0.004	0	0.010	0	0.012	0	0	0.006	0	0	0	0.012	0	0
Coconut oil	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Groundnut oil	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Olive oil	0.022	0.077	0.019	0	0.015	0.100	0.016	0	0	0.022	0	0	0	0	0	0
Palm oil	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Black cumin oil	0.006	0	0	0.009	0	0	0.007	0	0.025	0.006	0	0	0	0.006	0	0
*MRLs	0.20	0.20	0.20	0.20	0.02	0.02	0.02	0.02	0.50	0.06	0.06	0.01	0.05	0.05	0.05	0.05

* The Japan Food Chemical Research Foundation, 2016; “0” indicates no residues detected or below detection level (JFCRF, 2016).

Benzene hexachlorides are the stereoisomers formed by the light-induced addition of chlorine to benzene. The spectrum of insecticidal action of BHC is very wide that includes almost all insects of sucking and chewing types. It is active both contact and stomach poison owing to its volatility as a fumigant. For humans and warm-blooded animal technical BHC is weaker but its isomers are stronger poison than DDT (Matolcsy *et al.*, 1989). Technical BHC and the alpha, beta, gamma and delta isomers of BHC are carcinogenic for the liver and developed carcinomas and hyperplastic nodules of the liver as early as 24 weeks (Reuber, 1980).

Heptachlor and Heptachlor epoxide

Heptachlor and heptachlor epoxide were found in 40% of the edible oils. The concentration of Heptachlor ranged from 0.008 to 0.021 mg.kg-^{1} with an average of 0.005 mg.kg-^{1} and that of Heptachlor epoxide 0.008 to 0.100 ppm with an average 0.015 mg.kg-^{1} (Fig. 3). Heptachlor was observed in oils of mustard (0.008 mg.kg-^{1}), soybean (0.021 mg.kg-^{1}), rice bran (0.010 mg.kg-^{1}) and olive (0.015 mg.kg-^{1}) oil. Whereas the heptachlor epoxide observed in mustard (0.006 mg.kg-^{1}), soybean (0.036 mg.kg-^{1}), sunflower (0.008 mg.kg-^{1}) and olive (0.100 mg.kg-^{1}). The residues concentration of heptachlor in soybean oil was found slightly higher than the recommended MRL (0.02 mg.kg-^{1}) set by WHO (2006). But the residues concentration of heptachlor epoxide in olive oil (0.100 mg.kg-^{1}) was found much higher than the recommended MRL. However, the detected residues in other oil were observed below this critical limit.

Heptachlor epoxide was observed in maximum concentration (0.10 mg.kg^{-1}) in olive oil but the mother compound heptachlor was detected only 0.021 mg.kg^{-1}. It might be due the rapid transformation of heptachlor to the heptachlor epoxide in oil medium. Heptachlor and Heptachlor epoxide are probable human carcinogen (B2) and can pass directly from mother's blood to an unborn baby through the placenta. It is related to liver tumors (LDWG, 2007).

Alpha Chlordane and Gamma Chlordane

Analysis of edible oils extract by gas chromatography showed the residues of alpha and gamma chlordane.

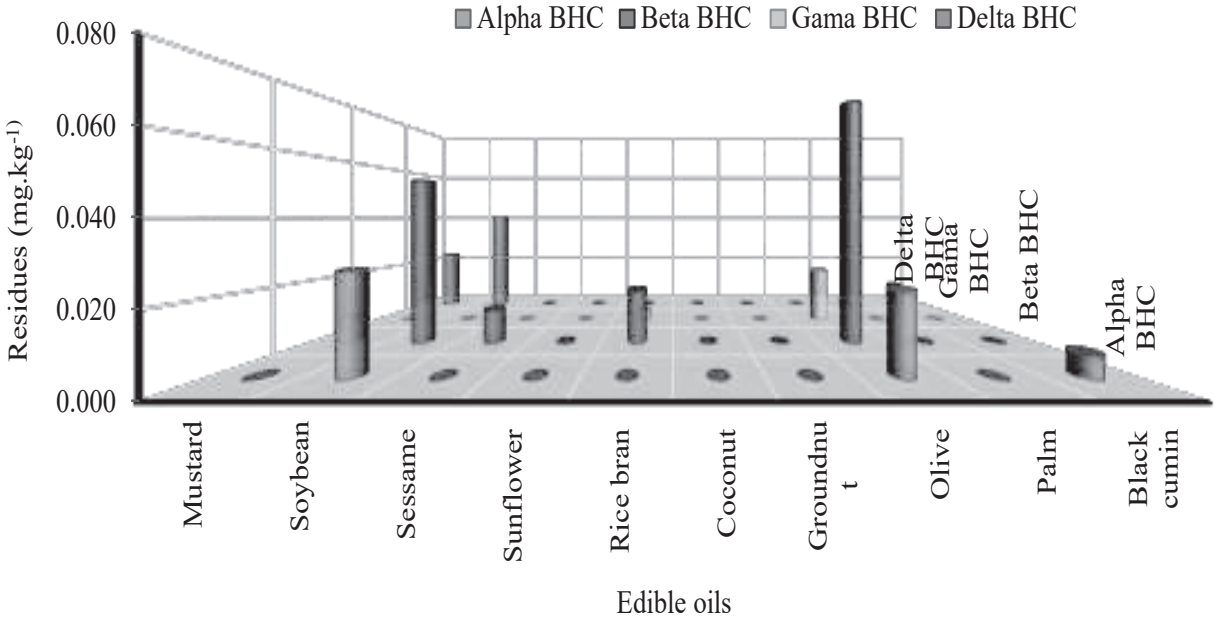


Fig. 2. Residues of three different isomers of BHC in ten edible oil samples.

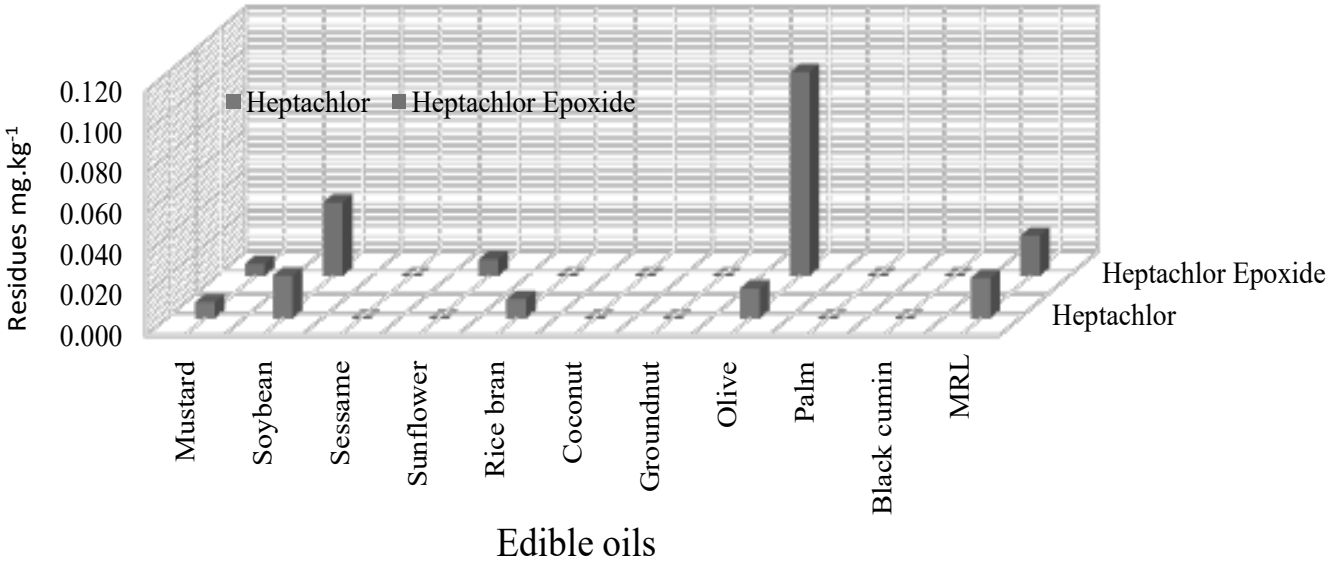


Fig. 3. Residues of heptachlor and heptachlor epoxide in edible oils.

Alpha chlordane detected in mustard (0.016 mg.kg-^{1}), soybean (0.020 mg.kg-^{1}), sunflower (0.004 mg.kg-^{1}), rice bran (0.012 mg.kg-^{1}), olive (0.016 mg.kg-^{1}) and black cumin (0.007 mg.kg-^{1}) oils. Gamma chlordane was detected only in mustard (0.009 mg.kg-^{1}) and soybean (0.020 mg.kg-^{1}) oils (Fig. 4. In soybean oil the concentration of residues both alpha and gamma chlordane were found equal to the recommended limit (0.020 mg.kg^{-1}) set by WHO(2006).

Alpha Endosulfan

Results indicated that α-endosulfan found in mustard (0.007 mg.kg-^{1}), sunflower (0.015 mg.kg^{-1}), and black cumin (0.025 mg.kg^{-1}) oils were widely variable (Fig. 5). However, the values of residues were found below the recommended MRL (0.50 mg.kg^{-1}). The result envisaged that α-endosulfan is used in cultivation of oil crops in Bangladesh. Although it does not exceed the limit but presence of this off-patent genotoxic chemical is really alarming.

Endosulfan is a derivative of hexachlorocyclopentadiene, and is chemically similar to aldrin, chlordane, and heptachlor (Vivekanandhan and Duraisamy, 2012). Technical endosulfan is a 7:3 mixture of stereoisomers, designated α and β. α-endosulfan is the more thermodynamically stable of the two. α-eEndosulfan has been used in agriculture around the world to control insect pests including whiteflies, aphids, leafhoppers, Colorado beetles and cabbage worms (Simon, 2014). However, as it is not specific, it can negatively affect populations of beneficial insects, wild organism and human beings. It is considered as neurotoxic and endocrine disruptor to both insects and mammals (Silva and Gammon, 2009). Moreover, edible oil might be a major route for bioaccumulation in human. This why α-Endosulfan has been considered as a test chemical compound.

Aldrin, Dieldrin and Endrin

In the environment, aldrin gets converted to dieldrin, which is more stable. This two-products are specially used in controlling soil insects and their use are not frequent for soil treatment. In the present study, aldrin observed in soybean (0.013 mg.kg-^{1}), rice bran (0.006 mg.kg-^{1}), olive (0.022 mg.kg-^{1}) and black cumin oil (0.006 mg.kg-^{1}). Dieldrin found only in mustard oil (0.005 mg.kg-^{1}) only. But no endrin was detected in any edible oils (Fig. 6).

The occurrence of aldrin was found much frequent than dieldrin, suggesting high persistency of chemical

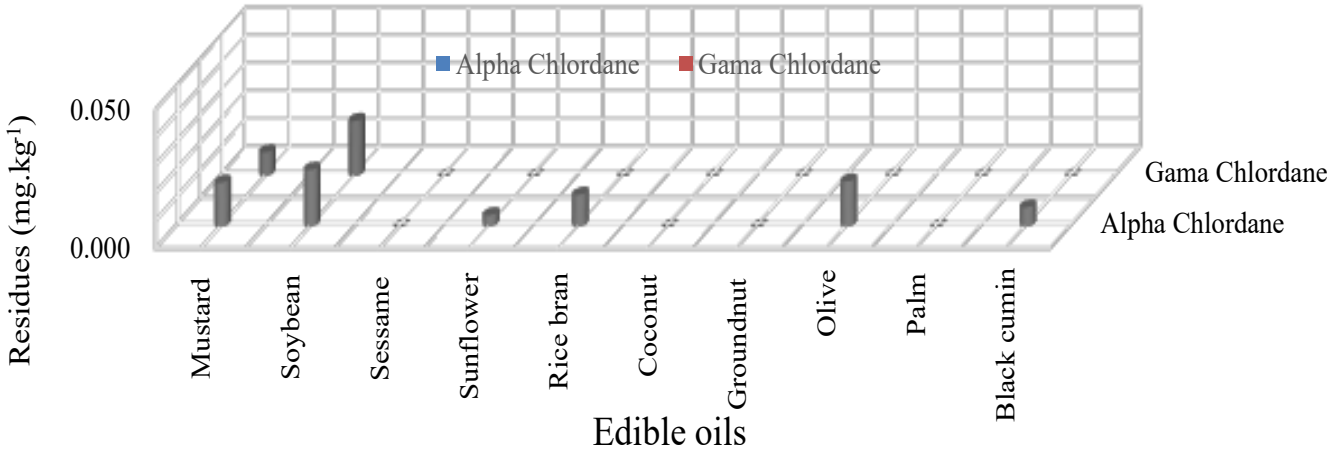


Fig. 4. Residues of alpha and gamma chlordane in edible oils.

and less conversion to dieldrin in the oil matrix. Since, aldrin was being used as an anti-termite agent against oilseeds, potato, corn and cotton crops earlier, that might be reasons of the frequent occurrence in oil products. But Aldrin is under complete ban in Bangladesh since September 1997 (Rahman et al., 2012).

p,p´-DDD (4,4 DDD) and p,p´-DDE (4,4 DDE)

Out of ten edible oils, DDD found only in soybean oil with mean concentration of 0.036 (mg.kg-1) which is below the recommended MRL. DDE observed in rice bran oil (0.012 mg.kg-1) and black cumin oil (0.006 (mg.kg-1) (Fig. 7). Both the cases, the residues concentration was found below MRL (0.05 mg.kg-1) set by FAO/WHO (2006). DDD and DDE are the break down product of DDT, which are more toxic compound than original source of DDT in Environment. DDD is in the "Group B2" classification, meaning that it is a probable human carcinogen and DDE is an endocrine disruptor and contributes to breast cancer (Guillette, 2006).

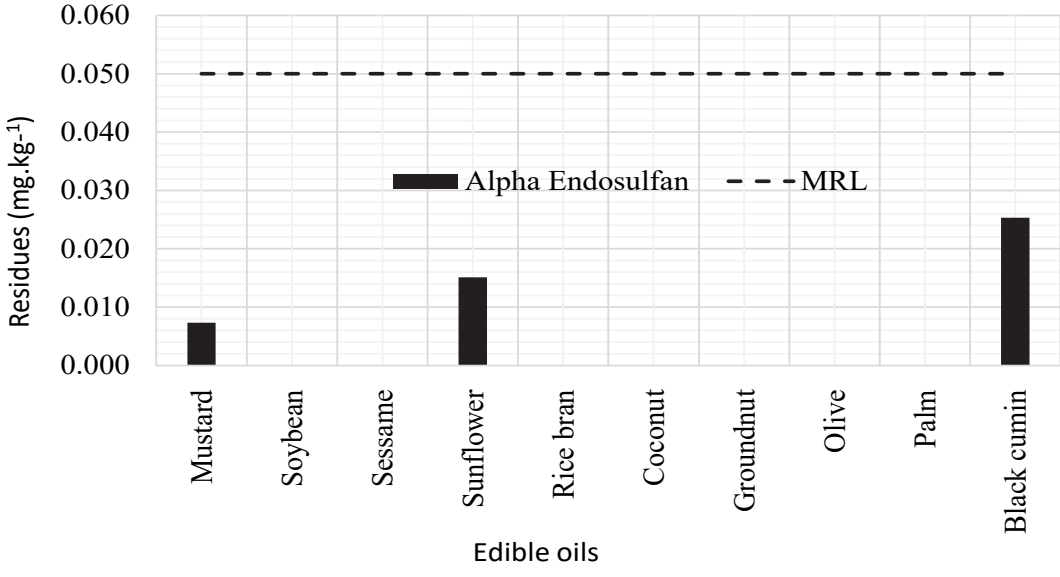


Fig. 5. Residues of alpha endosulfan in edible oils.

o,p´-DDT (2,4 DDT) and p,p´-DDT (4,4 DDT)

The residues of o,p´-DDT in this study was found in 20% of the tested oils. Only mustard and soybean oil showed residues at concentration 0.012 mg.kg-1 and 0.049 mg.kg-1, respectively (Fig. 7). The residues concentration of o,p´-DDT in soybean oil (0.049 mg.kg-1) is very close to codex MRL (0.05 mg.kg-1). The mean concentration of o,p´-DDT was found 0.006 mg.kg-1 which is also below the recommended MRL. p,p´-DDT detected with low level of concentration than recommended MRL in mustard oil (0.011 mg.kg-1) only.

Collectively DDT and its metabolites usually called DDTs. DDTs residues were observed in mustard, soybean, rice bran and black cumin oils. The total DDTs (i.e ΣDDT=p,p´-DDD+p,p´-DDE+o,p´-DDT+p,p´-DDT) was found higher than the recommended MRL in soybean oil (0.085 mg.kg-1). Since the seeds of these oil products are proven in contamination with DDT observed by other researchers (Nath *et al.*, 2002; Uddin *et al.*, 2007) which might be the reason of DDTs presence in edible oils. DDT is highly stable under most environmental conditions which favors its bioaccumulation throughout the food chain (Morrison and Newell, 1999). DDT can be transferred from generation to generation through breast milk (Solomon and Weiss, 2001).

(iii) Variation of residue level

A comparative study was made with the detected residue level of OCPs in different edible oils (Table 5). Out of sixteen OCPs, the maximum number of residues were detected in mustard (11) and soybean (10) which was followed by olive oil (7), rice bran (06), and black cumin oil (6), sunflower oil (3), sesame oil (1), coconut, ground nut, and palm oil (0). Kaphalia *et*

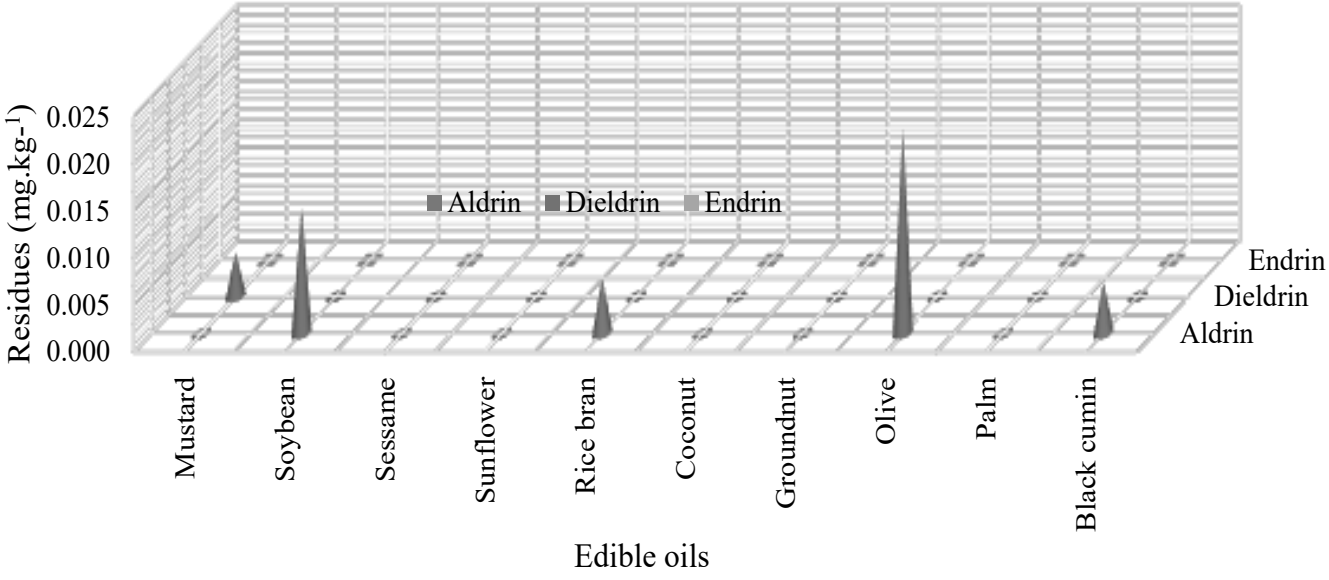
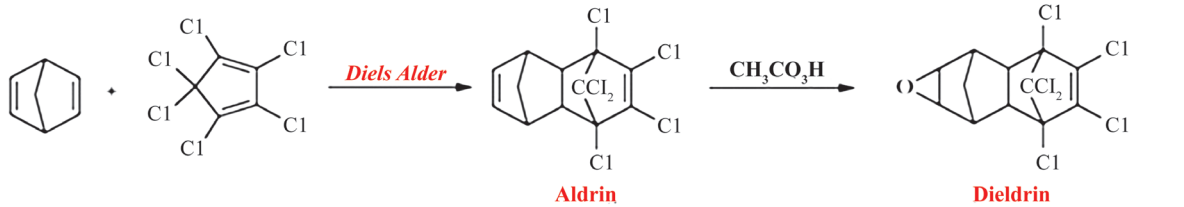


Fig. 6. Residues of aldrin, dieldrin and endrin in edible oils.



Conversion of aldrin to dieldrin **(Source: Gautam and Suresh, 2006)**

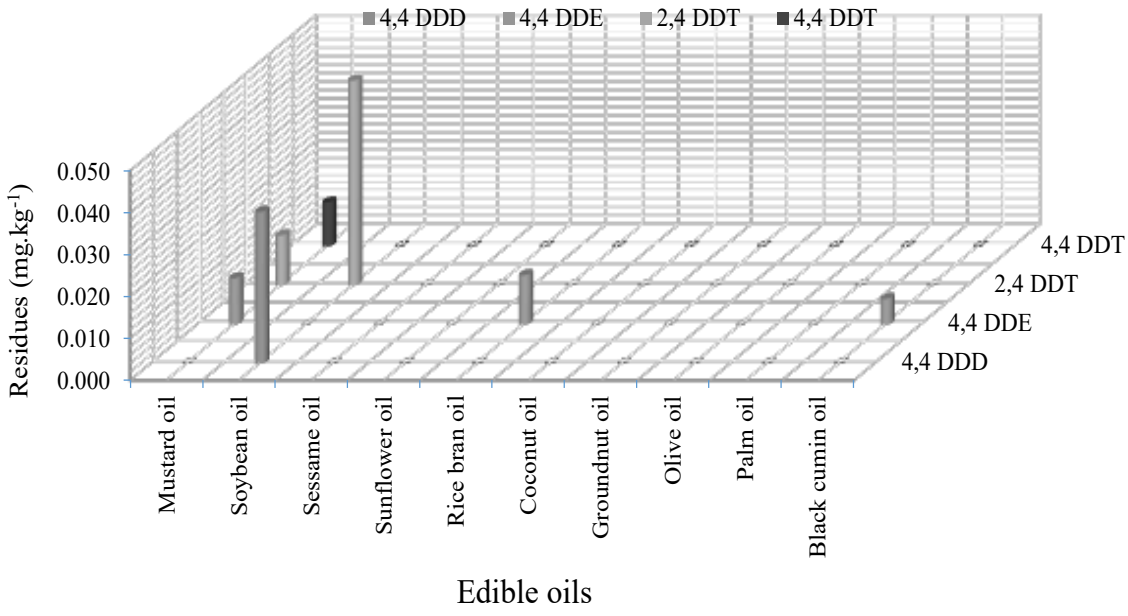


Fig. 7. Residues of DDT and its metabolites in edible oils.

al. (1989) found DDT metabolites and HCH isomers in mustard, groundnut and sunflower oils collected from different regions of India. They found DDT level ranged 0.2 ng g^{-1} to 222.0 ng g^{-1} and that of ΣHCH 8.0 ng g^{-1} to 1500 ng g^{-1} in mustard oil. But maximum *p*,*p*′-DDE was in groundnut oil.

Coconut, groundnut and palm oil did not show any OCPs residues. Hence these are safe for dietary use. Based on OCPs detection, the tested oils were in the following order:

The residues of heptachlor in soybean and heptachlor epoxide in olive oil exceeded the recommended MRL

Table 5. Comparison of the residues OCP level in different edible oils.

Edible oils	No. of tested OCP detected	Residue level above MRL	Highest OCP concentration	Total OCP Residues (mg.kg^{-1})
1. Mustard oil	11	nil	Delta BHC (0.023 mg.kg-^{1})	0.12
2. Soybean oil	10	Heptachlor	Beta BHC (0.052 mg.kg-^{1})	0.32
3. Sesame oil	01	nil	Beta BHC (0.011 mg.kg-^{1})	0.01
4. Sunflower oil	03	nil	Alpha endosulfan (0.011 mg.kg-^{1})	0.03
5. Rice bran oil	06	nil	Beta BHC (0.017 mg.kg-^{1})	0.06
6. Coconut oil	00	nil	nil	0.00
7. Groundnut oil	00	nil	nil	0.00
8. Olive oil	07	Heptachlor epoxide	Heptachlor epoxide (0.1 mg.kg-^{1})	0.27
9. Palm oil	00	nil	nil	0.00
10. Black cumin oil	06	nil	Alpha endosulfan (0.025 mg.kg-^{1})	0.06

Table 6. Estimated daily intake (µg.kg-^{1} body wt.day^{-1}) of OCPs by an adult from edible oils.

Edible oils	ΣBHC	ΣHeptachlor	ΣChlordane	ΣDDT	ΣOCPs
Mustard oil	0.013	0.006	0.010	0.014	0.050
Soybean oil	0.050	0.024	0.017	0.036	0.133
Sesame oil	0.004	0.000	0.000	0.000	0.004
Sunflower oil	0.000	0.003	0.002	0.000	0.013
Rice bran oil	0.009	0.004	0.005	0.005	0.025
Coconut oil	0.000	0.000	0.000	0.000	0.000
Groundnut oil	0.000	0.000	0.000	0.000	0.000
Olive oil	0.049	0.048	0.007	0.000	0.113
Palm oil	0.000	0.000	0.000	0.000	0.000
Black cumin oil	0.006	0.000	0.003	0.003	0.025
*TDIs	12.50	0.500	1.000	20.00	22.70

** Data were obtained from IPCS, 2017.*

set by WHO, 2006. Besides, all the residues remained below the MRL (Table 4). Olive oil showed the highest concentration (0.10 mg.kg-^{1}) among the tested oils followed by beta BHC in soybean (0.052 mg.kg-^{1}). The cumulative residues of OCPs were found maximum in soybean oil (0.32 mg.kg-^{1}) which was followed by olive oil (0.27 mg.kg-^{1}).

(iv) Impact assessment of OCP residues in human

OCPs are totally persistent toxic pesticides. Due to its carcinogenic, mutagenic and teratogenic effect the compound must be out of public contamination for their health security. But it was reported that OCPs are available everywhere in the environment due to persistency, volatility, long range transport (Shen *et al*., 2005). The present study revealed that the concentration of residues in different edible oils remained below the MRL. But 'no residue' of OCPs in edible oil is highly expected. Because, the OCPs gradually bioaccumulated in human body, especially in the adipose tissues. There are many ways to assess the impact of pesticide residues. Here only the tolerable daily intake (TDI) usually called 'acceptable daily intake (ADI)' of detected OCP residues were assessed, based on Oostdam *et al.* (1999) following Health Canada Guideline.

Tolerable daily intake

Daily intake of OCPs by an adult was calculated based on the assumption that the average oil consumption of a 48-kg adult is 20 g.day-^{1} (Kriti, 2015). The estimated daily intakes of total BHC, total heptachlor, total chlordane, total DDTs and total OCPs are given in Table 6.

It was recognized that the intake of all the OCPs by the people standard body weight was below the guideline proposed by Health Canada (IPCS, 2017). But intake by some OCPs compound was recorded close to or below this guideline. This fact may raise greater concerns on public health because human being is highly susceptible to the adverse effect of organochlorine pesticide.

Conclusion

A total of ten edible oils collected from two regions of Bangladesh were analyzed and sixteen organochlorine pesticides *viz*., Alpha BHC, Beta BHC, Gama BHC, Delta BHC, Heptachlor, Heptachlor Epoxide, Alpha Chlordane, Gama Chlordane, Alpha Endosulfan, Aldrin, Dieldrin, Endrin, p,p′- DDD, p,p′- DDE, O,p′- DDT, and p,p′- DDT were detected. On an average 26.87% of the oil samples were found contaminated with at least one of the OCP residues. No residues of OCPs were detected at all in coconut, groundnut and

palm oils. The majority of the OCPs contamination observed in mustard, soybean, rice bran, olive and black cumin oils. The residues of heptachlor epoxide in olive oil (0.10 mg.kg-1) was found higher than the recommended limit set by FAO. The cumulative residues of OCPs were found maximum in soybean oil (0.32 mg.kg-^{1}) followed by olive oil (0.27 mg.kg-^{1}). The present study measured tolerable daily intake of 48-kg body weight adult people following Health Canada Guideline for impact assessment of ΣBHC, ΣHeptachlor, ΣChlordane, ΣDDTs and ΣOCPs and found that that the intake of these OCPs by the people were below the limit. Therefore, the tested edible oils are safe for human consumption. But their presence is a threat to human health. However, periodical monitoring is suggested to ensure supply of safe edible oils to consumers.

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