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PESTICIDE RESIDUES IN FISHES FROM RANGPUR

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Abstract: Pesticide residues, specially the persistent organic pollutant (POP) were analyzed from some fish species of Rangpur floodplain, Bangladesh. Fish samples were extracted with ethyl acetate, cleaned by sulphuric acid and analyzed by gas chromatograph and gas chromatograph-mass spectrometer. Presence of endrin was detected in Taki fish (*Channa punctatus*) samples. Traces of other pesticides were also evident. This confirms the use of banned pesticide in the northwestern Bangladesh. We discussed some consequences of public health issues if these contaminantspasses through in the higher food chain from the wetland ecosystem.

***Key words**:* Pesticide residue, POPs, Fish, Rangpur

INTRODUCTION

Rangpur district in north-western Bangladesh is improtant for agriculture production, where Ghaghot River supports vast water for irrigation and contents fish resources. Great concern has arisen regarding pesticide application in agricultural land in recent years in Bangladesh as the past several decades, the increasing usage of pesticide has led to serious threat to people and environment. Bangladesh has promoted the use of pesticides to expand agricultural product. The use of pesticide has been more than doubled since 1992, rising from 7,350 to 16,200 metric tons in 2001 (Meisner 2004). Pesticide suppliers in rural Bangladesh continue to sell 12 controversial pesticides in particular, known by activists campaigning worldwide as the “dirty dozen” or POPs (Meisner 2004). Many of the pesticides in this group are no longer used for agricultural purposes but a few of them continue to be used in developing countries. Organochlorine pesticides were of particular concern due to their broad-spectrum positions for their persistency, toxicity and ability to be bio-accumulated in aquatic ecosystems (EPA 2014). Fish are one of the most important and largest groups of vertebrates in the aquatic system. Pollutants can be accumulated via both food chain and water in fish. Fish are considered good indicators for organochlorine pesticide pollution because they occupy different tropic levels. Meanwhile fish are widely consumed animal protein in Bangladesh and polluted fish might cause health hazard to human.

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The objective of the present study was to investigate the presence of 12 organochlorine pesticides in fresh water fishes of Rangpur. Further, the potential health risks posed to consumers from the exposure to these compounds through the ingestion of these fishes.

MATERIAL AND METHODS

A survey was conducted on the floodplain areas of Rangpur district. The district (25°44′N 89°15′E) is located by the bank of Teesta River. Fish samples were collected from four sampling sites of Rangpur floodplain including Mulatol Beel, Nilkunja Beel, Chikli Beel and Ghaghot River. The analytical study was conducted from January, 2007 to November, 2008 in Analytical Research Lab, BCSIR laboratories, Dhaka, Bangladesh.

Fishes were selected by their size, feeding habit and availability in water body round the year in the river system. Selected fish samples were planktivore: Mola (*Amblypharyngodon mola*), Dhela (*Rasbora daniconius*), Puti (*Puntius ticto*), Sarputi (*Puntius sarana*), Tengra (*Mystus tengra*), canivore and omnivore: Shingi (*Heteropneustes fossilis*), Kholisha (*Colisa fasciatus*), Shol (*Channa barca*), Taki (*Channa punctatus*), Chanda (*Chanda nama*), Guchi Baim (*Mastacembelus pancalus*), Bheda (*Nandus nandus*). Identification was made after Rahman (2005) and Shafi and Quddus (1982).

Fishes having similar size (length and weight) were chosen for each species. The edible muscle portion was only considered for the determination of pesticide analysis. Each fish was measured in cm, placed on ice and later stored in laboratory refrigerator until analysis being done.

Extraction of fish samples was carried out according to EMP manual (Akerblom 1995). About 100 g of fish sample was taken from deep freeze and put to laboratory temperature until thawing. Each sample was chopped into small pieces and mixed thoroughly. Ten g sample was ground in a mortar with 10 g sand and 30 g sodium sulphate and more sodium sulphate was added to make the sample float freely. The ground sample was taken in a quick-fit conical flask. Then it was extracted with 50 ml ethyl acetate by shaking for 3 minutes. This extraction was repeated three times with 20 ml ethyl acetate. The extract was combined and then filtered through the glass wool. The filtrate was evaporated to 2 ml by rotary vacuum evaporator at temperature not exceeding 40ºC. The solvent was exchanged from ethyl acetate to cyclohexane by evaporation and the volume of the solution was re-adjusted to 2 ml.

Acid solution was prepared by mixing cyclohexane and concentrated sulphuric acid. The two chemicals were mixed in a column at 1 : 4 ratios, upper organic part was withdrawn and discarded. The 2 ml extract and 1 ml acid solution were taken into a fresh screw cap test tube and was inverted 20 times (about 40 second). Then the mixed solvent was centrifuged for 3 minutes to separate two layers. The upper organic layer was taken into a fresh vial and used for pesticide residue analysis by GC and GC-MS.

The gas chromatograph GC-14B (Shimadzu) equipped with ECD (Electron Captured Detector) mode and having fused silica capillary column (SPB-5) was used for analysis. Column was of 60 m length and 0.25 mm internal diameter (ID). Column oven initial temperature 80°C and final 300°C, carrier gas-helium (purity 99.997%), gas flow 1.5 mL/min, column pressure 100 (kilo pascal), injection volume 0.4 μl, injection temperature 280°C and interface temperature 300°C.

The gas chromatograph mass spectrometer GC-17A and GCMS-QP5050A (Shimadzu, Japan) equipped with electron ionization (EI) mass detector and 30 m length and 0.252 mm internal diameter (ID) fused silica capillary column (DB-1) was used for mass analysis under the following analytical conditions: temperature ranged from 150 to 250°C speed 3°C/min, carrier gas-helium (purity 99.998%), gas flow 50 ml/min, column pressure 100 (kilo pascal), injection volume 0.4 μl, injection temperature 230°C and interface temperature 250°C. The recovery of organochlorine ranged within 75 - 90%.

RESULTS AND DISCUSSION

Fish samples were analyzed by GC and GC-MS and the results obtained from the screening of fishes by GCMS library search (Figs 1 & 2). Twelve species of fish were analyzed to detect POP residues. Three types of fishes were selected on different trophic levels with different sizes and ages. Planktivore fishes usually consume planktons, omnivore takes crustaceans, planktons and small fishes, but carnivore mainly stays at lower part of water body and takes all food including small fish, larvae, sediments, etc. Among these tested fish samples POPs; Endrin were detected in Taki fishes at 0.023 ppm level (Table 1 and Fig. 2). Minimum Residue Limits (MRLs) of Endrin is 0.01 (JFCRF 2013). Thus the presence of Endrin in Taki fishes poses threats to human health. GCMS detected some other organic compounds which are fatty acids, cholesterols and some harmful contaminants (Table 2). A dangerous POP : Endrin contamination was found in all Taki fish samples. Detectable POPs range found in fish samples considered a serious threat to human health (Table 1). Among 12 POPs endrin, dieldrin and aldrin are classified by WHO as highly hazardous on the basis of their acute toxicity to experimental animals (Stober 2015). Endrin can cause convulsions and lead to death within a few minutes or hours. Less serious exposure to endrin can result in headaches, dizziness, confusion, nervousness, nausea, or vomiting (Toxipedia 2016).

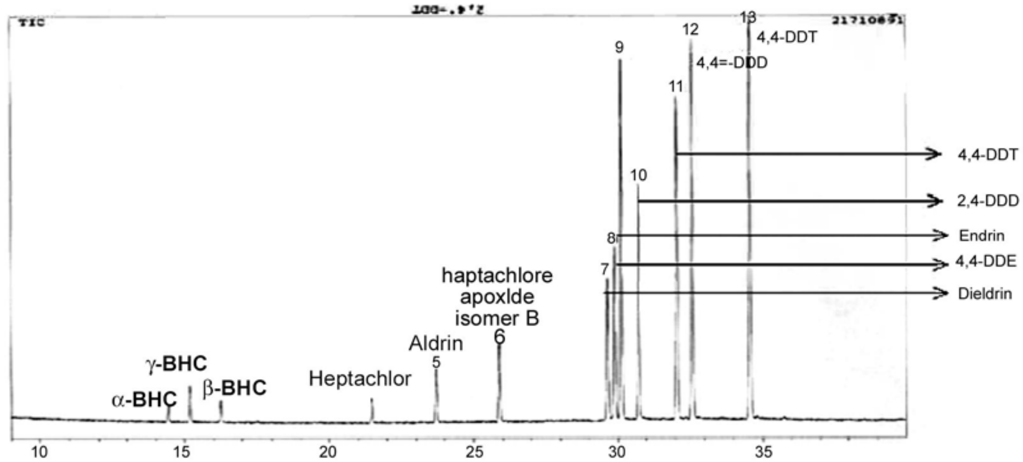


Fig.1. Mixed standard of 13 organochlorine pesticides (POPs).

Table 1. Moisture, fat and POPs levels in sample fishes (BDL - below detection level)

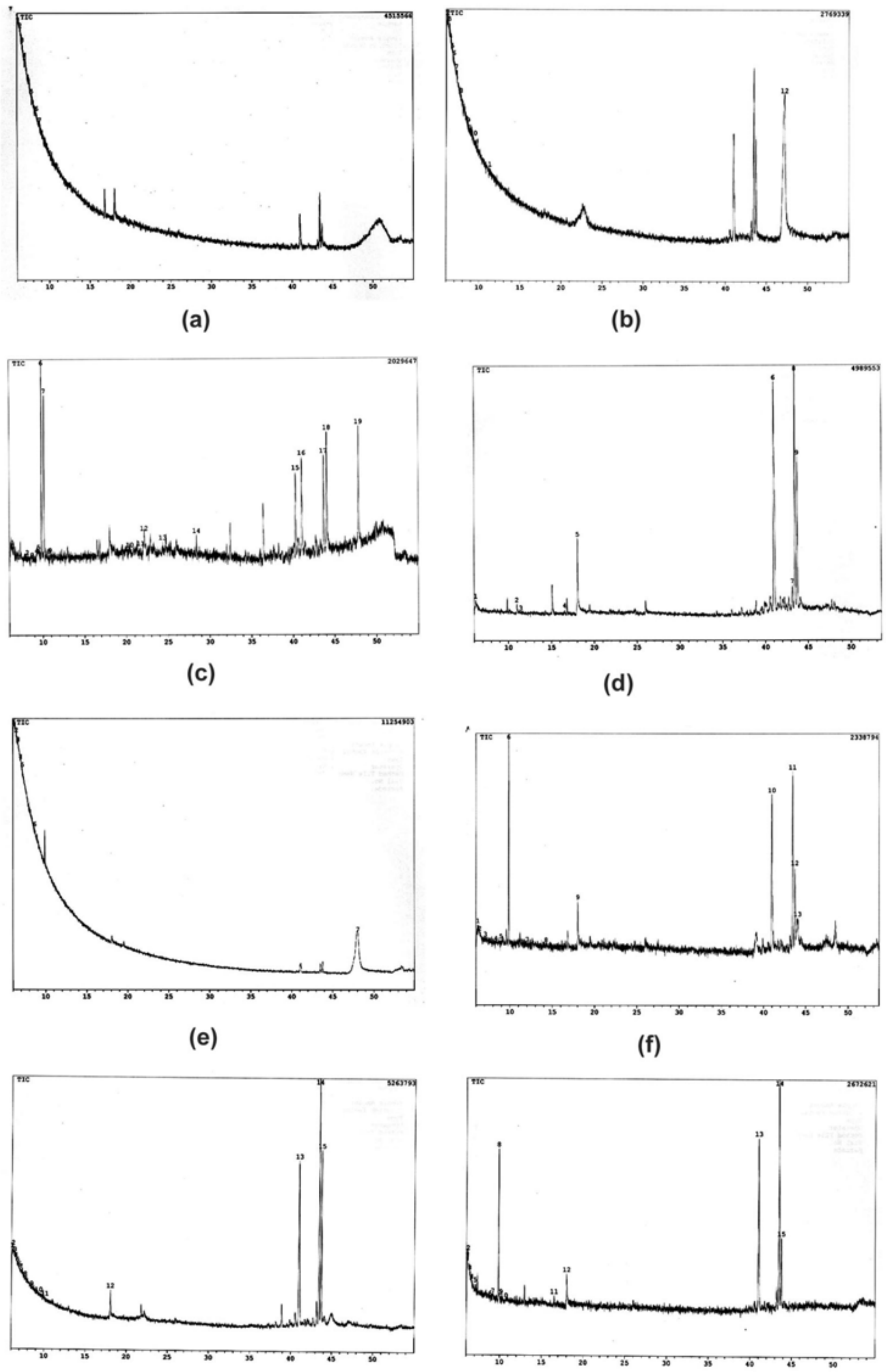
Sl. no.	Fishes	Moisture content (%)	Fat content (%)	POPs (Endrin) (ppm)	GCMS library search (%)
1	Mola	77.32	5.78	BDL	-
2	Dhela	76.43	4.38	"	-
3	Puti	78.71	2.90	"	-
4	Sarputi	69.16	9.38	"	-
5	Tengra	81.01	1.18	"	-
6	Shingi	78.62	1.67	"	-
7	Kholisha	75.53	2.54	"	-
8	Shol	76.62	1.63	"	-
9	Taki	78.99	2.21	0.043	89
10	Chanda	73.87	2.91	BDL	-
11	Bheda	81.64	2.15	"	-
12	Guchi Baim	80.21	2.61	"	-

BDL= below detection level

Phenol is a toxic and corrosive compound. Some phenolic compounds are believed to be cancer chemopreventives, compounds that may decrease your risk of developing cancer (Livestrong 2016). Di-n-octylphthalate used as a plasticizer for many resins and pesticides (Toxipedia 2016). Pyrine, napthalene, furan, tolune, benzoyl chloride, propionic acid are toxic chemical compounds which can be used in pesticide industry, dyes and other chemical manufacturing companies. Pyridine used as precursor to agrochemicals, bactericide and herbicide (Wikipedia 2016). Toluene exposure may cause liver and kidney damage (Wikipedia 2016). Cyclohexane and Butenal are residue of extracted solvents (Zaman *et al.* 2012). Aflatoxin indicates the contamination and Arsine indicates possibility of Arsenic pollutions. These chemicals are present in the fish samples in a little amount which could indicate the presence of pollutants in the river system.

Table 2. Harmful organic compounds are detected in fish muscle

Type of fishes		Planktivore					Carnivore and omnivore						
Fishes	Molecular weight	Mola	Dhela	Puti	Sarputi	Tengra	Shingi	Kholisha	Shol	Taki	Chanda	Bheda	Guchi baim
POPs													
Endrin	$C_{12}H_8Cl_6O$									*			
Other hazardous chemicals													
Phenol	$C_{17}H_2O$		*					*	*			*	
Pyridine	$C_{12}H_{14}ClN$								*	*			*
Napthalene	$C_{20}H_{34}O_2$	*	*								*	*	*
Furan	C_5H_8O	*		*					*			*	
Cyclohexane	C_6H_{12}	*	*	*	*	*	*	*	*	*	*	*	*
Butenal	$C_4H_8Cl_3O$	*		*		*		*		*		*	
Histidine	$C_6H_{13}NO_4S$		*	*	*	*	*		*				
Arsine	$C_{12}H_{27}As$		*		*		*				*		
Aflatoxin	$C_{16}H_{14}O_5$		*		*								
Tolune	C_7H_8			*	*			*	*	*			*
Dibutyltin dibromide	$C_8H_{18}Br_2Sn$	*		*						*			
Di-n-octyl phthalate	$C_{24}H_{38}O_4$			*									*
Benzoyl chloride	C_8H_7ClO	*	*	*	*								
Propionic acid	$C_{25}H_{44}O_8$		*										



(Fig. 2 contd.)

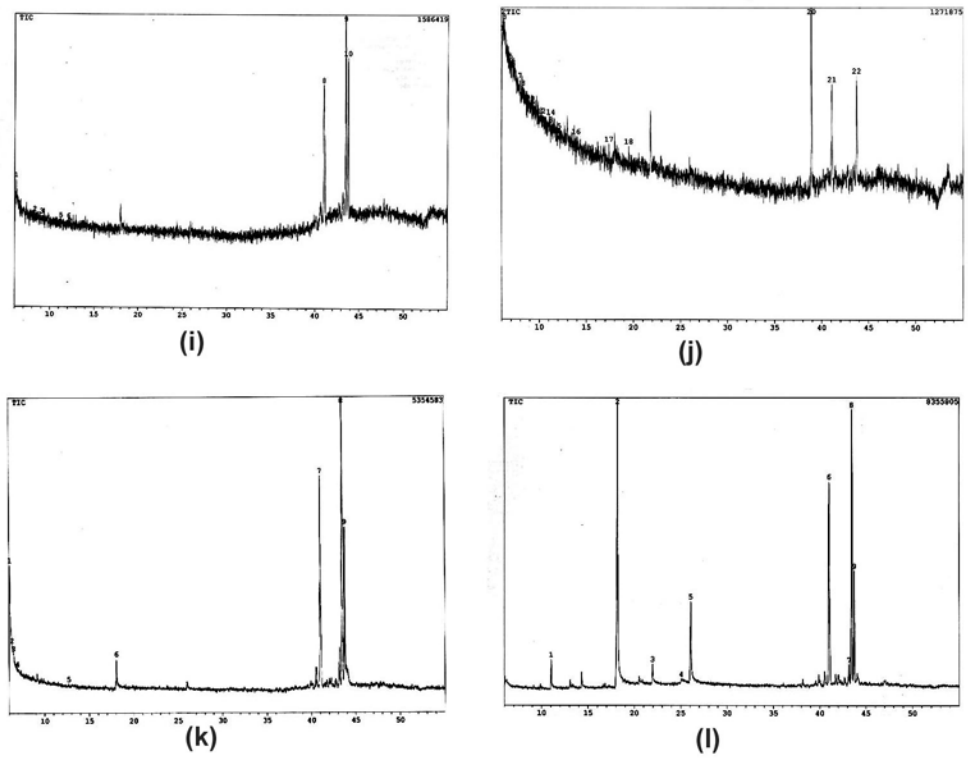


Fig. 2. GCMS chromatograms of (a) Guchi baim, (b) Bheda, (c) Dhela, (d) Gura chanda, (e) Mola, (f) Puti, (g) Khalisha (h) Sarputi (i) Shingi, (j) Shol, (k) Taki and (l) Tengra.

Pollutants are present in almost all herbivore, omnivore and carnivore fish samples. But carnivore and omnivore samples had more pollutants than herbivores. Organochlorine pesticides are never manufactured in Bangladesh and are imported from other countries. Dangerous pesticide and one of targeted POPs 'Endrin' was detected in Taki fish samples indicating the pesticide pollution in the study area (Fig. 2). POPs were also implicated in reduced immunity in infants and children and the concomitant increase in infection, also with developmental abnormalities, neuro-behavioural impairment and cancer and tumour induction or promotion (Stober 2015). Some POPs are also being investigated as a potentially important risk factor in the etiology of human breast cancer (Stober 2015, Thuy 2015). To prevent exposure to pesticide, it is necessary to reduce the illegal use in agriculture land and control the entry of such pesticides in northern Bangladesh.

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