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Distribution and Health Risk Assessment of Selected Endocrine Disrupting Chemicals in Two Fish Species Obtained from Choba River in Rivers State, Nigeria

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Abstract The concentration of selected endocrine disrupting chemicals in tissues of *Chrysichthys nigrodigitatus* (catfish) and *Liza falcipinnis* (mullet) obtained from Choba river in Rivers State, Nigeria was analyzed to determine their levels and possible hazard for human consumption. Pesticides and polychlorinated biphenyls were assessed using gas chromatography coupled with electron capture detector. Heavy metals analysis was carried out using atomic absorption spectrophotometer. The concentration of pesticides ranged from 0.0013±0.0002 to 0.0130±0.0002 µg/l and 0.0077±0.0000 to 0.0390±0.0001µg/g in water and sediments, respectively. Similarly, pesticides concentration ranged from 0.0001±0.0000 to 0.0171±0.0002µg/g and 0.0002±0.0001 to 0.0385±0.0002µg/g respectively. The concentration of PCBs in analyzed fish ranged from 0.2439±0.0001 to 0.2683±0.0003µg/g in the muscle and liver, respectively. Heavy metal concentration ranged from 0.004±0.001 to 0.460±0.002µg/g for cadmium and mercury, respectively. Risk hazard estimates of dichlorodiphenyltrichloroethanes, Chlordanes, hexachlorobenzene, and heavy metals (Cd, Cr) in the studied fishes showed no potential adverse effect to human consumption at the observed concentrations. Mercury was high in all fish analyzed with a quotient value greater than unity indicating potential mercury poisoning. The cancer risk was also evaluated according to USEPA, (2005) and was within acceptable risk range of 10^{-4}. Thus exposed populations are not at cancer risk through consumption of fish.

Keywords Endocrine Disrupting Chemicals, Polychlorinated Biphenyls, Pesticides, Risk Hazard Estimates, Cancer Risk

1. Introduction

The environment, both aquatic and terrestrial are at risk due to several harmful materials and chemicals of natural and anthropogenic origin. Routine assessment of the environment is important to determine the presence as well as the effect of hazardous materials on human health and other organisms [1,2]. Bioaccumulation is an important means by which these chemicals and materials interfere with living organisms. This is a process by which these chemicals and materials are taken up by organisms either directly from exposure to a polluted medium or by ingestion of food containing the chemical material [2]. Since not all types of chemical contaminants can be bio-available in equal amounts and various contaminants can bioaccumulate in some organisms to a greater extent than in others, there is the necessity to assess the amounts of these contaminants in organisms to ascertain the risk resulting from the exposure to such pollutants in the environment [3,4]. Therefore analyses of the tissues of aquatic biotas such as fishes are employed as an established model in studies assessing the pollution of the aquatic environment, thereby providing a timely assessment of the levels of pollutants with biological significance [3].

Endocrine disrupting chemicals (EDC) are some of the pollutants found in the aquatic environment that are of public health concerns. Endocrine disrupting chemicals are exogenous chemicals or mixture of chemicals, which affect any aspect of hormonal action [5]. They also interfere with the production, release, transport, action or elimination of natural hormones necessary for homeostasis and regulation of developmental processes [6]. These chemicals even at low concentrations can cause severe damage including reproductive and birth defects, cancerous tumours, neurological and immune responses in living organisms [7]. EDCs include a wide range of industrial and agricultural chemicals with some occurring naturally [8]. Some of these chemicals include Polychlorinated Biphenyls (PCBs), Bisphenol A (BPA), Dioxins, Organochlorinated Pesticides (OCPs), Phthalates (DEHP), Cadmium, Mercury and Lead [9]. They are released into the environment through human activities such as industrial incinerator emissions, industrial effluents discharge, chlorine treatment in drinking water plants, municipal solid waste disposal, paper pulp and plastic production [9]. The discharge of these effluents and other environmental pollutants into the aquatic environment tends to increase the bioaccumulation of these disruptors in aquatic biota.

Fish which is a source of important nutrients including proteins, minerals, vitamins and essential fatty acids (omega-3 fatty acids) for human nutrition are at risk because of the adverse effect of these disrupting chemicals in their natural habitat. Fishes tend to bioaccumulate these chemicals, and are consumed by humans which are higher up in the food chain [10]. The increasing discharge of industrial waste, domestic waste, run-off water from agricultural farmlands into the aquatic environments and the increase in chemical production has impacted negatively on aquatic organisms and invariably the human population [11]. Humans depend on the aquatic environment as water source for domestic, industrial, agricultural and fishing activities. Pollution of the aquatic environment by persistent organic pollutants, among which several EDCs belong, may lead to their bioaccumulation in fish tissues thereby posing a serious public health risk [12].

Due to increased public health concerns about EDCs and their effect on the endocrine systems of both humans and fish [13], it is therefore highly imperative to evaluate the levels of some of these chemicals in the water and selected fish species obtained from Choba fishing community in Rivers State, Nigeria and their health risk to exposed populations.

2. Methodology

Sample Collection

Water samples were obtained from the Choba River in Choba community of Rivers State, Nigeria following US-EPA procedure. Samples were taken from surface parts of the water body using composite sampling techniques at three different positions in a particular location using a stainless steel Kemmerer bottle and transferred to pre-cleaned aluminum jars, acidified with 0.1N hydrochloric acid, clearly labeled and stored in the dark at temperature between 0 and 4^{o}C. Sediments were collected using a teflon coated spoon and immediately transferred into an aluminum foil and stored [15]. Three samples each of catfish and mullet were bought from local fishermen, immediately stored in an ice-chest at 4^{o}C and taken for analysis in the laboratory.

3. Extraction and Analysis

Extraction and cleanup of water, sediments and fish parts were done according to [16]. They were analyzed for pesticides (glyphosate, γ-Chlordane, t-Nonachlor, α-Hexachlorocyclohexane, Hexachlorobenzene, Dichlorodiphenyltrichloroethane, Dichlorodiphenyldichloroethane, Dichlorodiphenyldichloroethylene) and polychlorinated biphenyls (mono, di and trichlorinated biphenyls). Results were obtained using gas chromatograph (GC) Buck 530 equipped with an on-column automatic injector, Electron Capture Detector, HP88 capillary column (100m x 0.25μm film thickness) CA, USA, powered by Peak simple software to identify and quantify compounds. The GC operating conditions were set as: Detector and injector temperatures were 250^{o}C and 22^{o}C respectively; Integrator chart speed was set at 2cm/min, oven temperature was set at 180^{o}C. The column temperature was programmed as follow: held at 70^{o}C for 5min; 70-220^{o}C at 15^{o}C/min; 220^{o}C maintained for 2min; 220-280 at 15^{o}C/min. The carrier gas used was Helium. When the equipment is ready, the "NOT READY" light will turn off, and then 1μl of the samples are then injected onto the column.

Heavy metal analysis was conducted according to [17].

Statistical Analysis

Analysis of variance (ANOVA) was carried out using IBM SPSS statistical software version 21.

Health Risk Estimation

In assessing the risk of endocrine disruptors through fish consumption, the guidelines drawn up by the USEPA were used. The oral reference dose (RfD) of each contaminant as provided by the USEPA was also used [18]. The estimated daily intake (EDI and hazard quotients (HQ) were calculated at the 50th and 95th percentile to evaluate the non-cancer risks of contaminants exposure. Cancer risk was calculated to estimate the likelihood of an individual developing cancer in his entire life as a result of exposure to these contaminants [19].

For this study, fish consumption rate per day at 50th percentile was set at 4g/day and 31.9g/day at the 95th percentile. This range covers the FAO [20] per capita fish consumption rate (9kg) for Nigeria which was 24.7g/day, while body weight was set at 70kg.

$$\text{EDI} = \frac{\text{Concentration of contaminant } (\text{mg}/\text{kg}) \text{ X Daily Intake Rate } (\text{g}/\text{day})}{\text{Body weight } (\text{kg})} \quad [15,21]$$

$$\text{Hazard Quotient} = \frac{\text{Average Daily Intake } (\text{mg}/\text{kg}/\text{day})}{\text{Oral Reference Dose} (\text{mg}/\text{kg}/\text{day})} \quad [15,21]$$

$$\text{Cancer Risk} = \frac{\text{Intake }(\text{mg/kg/day})}{\text{cancer slope factor }(\text{mg/kg/day})} \quad [19]$$

$$\text{Intake} = \frac{\text{C x IR x EF x ED x CF}}{\text{BW x AT}}$$

I= Intake – the level of chemical at exchange region ($mg^{-1}kg^{-1}$body weight/day)
C = Chemical level in contact over the period expose ($mgkg^{-1}{}_{fish}$)
IR = Ingestion Rate in $gday^{-1}$
EF = Exposure Frequency- (days/year).
ED = Exposure Duration - (year).
CF = Conversion Factor (kgg^{-1}).
AT = Averaging Time – (days).
BW= Body Weight.

4. Results

Table 1. PCBs in liver and muscle of catfish and mullet from the study area

PCBs (µgg^{-1})	Catfish (Liver)	Catfish (Muscle)	Mullet (Liver)	Mullet (Muscle)
Biphenyl	0.0855±0.0002^{a}	0.0890±0.0002^{b}	0.0513±0.0002^{ab}	0.0475±0.0002^{ac}
2-Chlorobiphenyl	0.0189±0.0001^{a}	BDL^{b}	0.0470±0.0001^{ab}	0.0360±0.0001^{ac}
3-Chlorobiphenyl	0.0300±0.0002^{a}	0.0529±0.0002^{b}	BDL^{ab}	BDL^{ab}
4-Chlorobiphenyl	0.0540±0.0002^{a}	0.0540±0.0004^{a}	0.0578±0.0001^{ab}	0.0460±0.0002^{ac}
2-2'-Dichlorobiphenyl	0.0200±0.0002^{a}	0.0200±0.0001^{a}	0.0187±0.0001^{ab}	0.0184±0.0002^{ab}
2-3'-Dichlorobiphenyl	0.0210±0.0002^{a}	0.0239±0.0008^{b}	0.0061±0.0001^{ab}	0.0055±0.0002^{ab}
2-4'-Dichlorobiphenyl	BDL	BDL	0.0334±0.0002^{ab}	0.0334±0.0002^{ab}
2-2'-4-Trichlorobiphenyl	0.0280±0.0002^{a}	0.0210±0.0002^{b}	0.0575±0.0002^{ab}	0.0732±0.0002^{ac}
3-3'-Dichlorobiphenyl	BDL ^{a}	BDL^{a}	BDL^{ab}	BDL^{ab}
3-4-Dichlorobiphenyl	0.0330±0.0001^{a}	0.0323±0.0001^{a}	BDL^{ab}	BDL^{ab}
3-5-Dichlorobiphenyl	0.0160±0.0002^{a}	0.0132±0.0001^{b}	0.0237±0.0001^{ab}	0.0158±0.0001^{ac}
4-4'-Dicholorobiphenyl	0.0220±0.0002^{a}	0.0210±0.0001^{a}	BDL^{ab}	BDL^{ab}
2-2'-3-Trichlorobiphenyl	0.0360±0.0003^{a}	0.0253±0.0002^{b}	0.0305±0.0002^{ab}	0.0231±0.0002^{ac}
Total	**0.3644±0.0000^{a}**	**0.3516±0.0018^{b}**	**0.3260±0.0008^{ab}**	**0.2989±0.0002^{ac}**

Values are represented as mean± standard error of mean (SEM) of three replicates, (n=3). Values with different superscript in the same row are significant at p≤0.05 while values with same superscript are not statistically significant. BDL implies below detection limit.

Concentrations of PCBs in tissues (liver and muscle) of the selected fish species are shown in **Table 1** with catfish (liver) recording the highest amount of total mean PCB of 0.3644±0.0000 with the least amount of 0.2989±0.0000 recorded for mullet (muscle). The level f total PCBs in the liver was also significantly higher in catfish as compared to the levels in muscles at the sampling station. Similar pattern was observed for tissue sample of mullet analyzed.

Table 2. PCBs in water and sediment from the study area

PCBs	Water (µgml^{-1})	Sediment (µgg^{-1})
Biphenyl	BDLa	0.0175±0.0001b
2-Chlorobiphenyl	0.0437±0.0001a	0.0329±0.0003b
3-Chlorobiphenyl	BDLa	BDLa
4-Chlorobiphenyl	0.0200±0.0002a	0.0136±0.0002b
2-2'-Dichlorobiphenyl	BDLa	0.0390±0.0001b
2-3'-Dichlorobiphenyl	0.0046±0.0003a	0.0077±0.0000b
2-4-Dichlorobiphenyl	0.0265±0.0001a	BDLb
2-2'-4-Trichlorobiphenyl	0.0359±0.0001a	0.0277±0.0003b
3-3'-Dichlorobiphenyl	BDLa	BDLa
3-4-Dichlorobiphenyl	0.0187±0.0002a	BDLb
3-5-Dichlorobiphenyl	BDLa	BDLa
4-4'-Dicholorobiphenyl	BDLa	0.0228±0.0001b
2-2'-3-Trichlorobiphenyl	BDLa	BDLa
Total	**0.1494±0.0005a**	**0.1701±0.0007b**

Values are represented as mean± standard error of mean (SEM) of three replicates, (n=3). Values with different superscript in the same row are significant at p≤0.05 while values with same superscript are not statistically significant. BDL implies below detection limit.

Result in **Table 2** shows that PCB 2- dichlorobiphenyl had the highest average mean concentration of 0.0437±0.0001 with the least value of 0.0046±0.0003 recorded for 2-3'-dichlorobiphenyl in the river water analyzed. The sediment recorded the highest and lowest concentrations of 0.0390±0.0001 and 0.0077±0.0000 for 2-2'-dichlorobiphenyl and 2-3'-dichlorobiphenyl respectively.

Table 3. Pesticides in liver and muscle of catfish and mullet from the study area

Pesticides $(\mu gg)^{-1}$	Catfish (Liver)	Catfish (Muscle)	Mullet (Liver)	Mullet (Muscle)	FDA/WHO
Glyphosate	BDL^{a}	BDL^{a}	0.0037±0.0001^{ab}	0.0034±0.0001^{ab}	0.3
γ-Chlordane	0.0017±0.0001^{a}	0.0017±0.0001^{a}	0.0018±0.0002^{ab}	0.0019±0.0002^{ab}	0.3
t-Nonachlor	0.0013±0.0002^{a}	0.0012±0.0001^{a}	0.0037±0.0001^{ab}	0.0039±0.0002^{ab}	0.3
α-HCH	BDL^{a}	BDL^{a}	0.0031±0.0001^{ab}	0.0002±0.0001^{ac}	-
γ-HCH	0.0001±0.0000^{a}	0.0001±0.0000^{a}	0.0003±0.0001^{ab}	0.0003±0.0001^{ab}	-
HCB	0.0122±0.0002^{a}	0.0119±0.0002^{a}	BDL^{ab}	BDL^{ab}	
DDE	0.0011±0.0001^{a}	0.0010±0.0001^{a}	0.0029±0.0002^{ab}	0.0020±0.0002^{ab}	5.0
DDT	0.0171±0.0002^{a}	0.0166±0.0002^{a}	0.0385±0.0002^{ab}	0.0344±0.0002^{ac}	5.0
DDD	BDL^{a}	BDL^{a}	BDL^{ab}	BDL^{ab}	5.0
Total	**0.0335±0.0007^{a}**	**0.0325±0.0004^{a}**	**0.0540±0.0002^{ab}**	**0.0461±0.0001^{ac}**	

Values are represented as mean± standard error of mean (SEM) of three replicates, (n=3). Values with different superscript in the same row are significant at p≤0.05 while values with same superscript are not statistically significant. BDL implies below detection limit.

Result in **Table 3** showed that DDT was the predominantly pesticide which contributed significantly to the amount of total organochlorine pesticides in fish tissues investigated in this study. The mean concentration of 0.0171±0.0000 and 0.0166±0.0001 µg/g was recorded for DDT in the liver and muscle respectively of catfish collected from the study site.

Table 4. Pesticides in water and sediment from the study area

Pesticides	Water (μgml^{-1})	Sediment (μgmg^{-1})	FDA(μgml^{-1})
Glyphosate	0.0082±0.0001^{a}	BDL^{b}	0.7
γ-Chlordane	0.0013±0.0002^{a}	0.0062±0.0002^{b}	0.002
t-Nonachlor	0.0020±0.0001^{a}	0.0024±0.0002^{a}	-
α-HCH	0.0022±0.0001^{a}	0.0057±0.0001^{b}	0.0002
γ-HCH	BDL^{a}	0.0022±0.000^{b}	0.0002
HCB	0.0069±0.0002^{a}	0.0083±0.0002^{a}	0.002
DDE	0.0010±0.0000^{a}	0.0015±0.0003^{a}	
DDT	0.0130±0.0002^{a}	0.0149±0.0002^{b}	0.00036
DDD	BDL^{a}	BDL^{a}	
Total	**0.0346±0.0004^{a}**	**0.0412±0.0004^{b}**	

Values are represented as mean± standard error of mean (SEM) of three replicates, (n=3). Values with different superscript in the same row are significant at p≤0.05 while values with same superscript are not statistically significant. BDL implies below detection limit.

Result in **Table 4** shows that DDT had the highest values of 0.0130±0.0002 and 0.0149±0.0002 µg/g for water and sediment respectively. DDD was not detected in either the water or sediment sample as it was below detection limit.

Table 5. Heavy metals in catfish and mullet from the study area

Heavy metals (μgg^{-1})	Catfish	Mullet	WHO/FAO Standard (μgg^{-1})
Cadmium	0.004±0.001^{a}	0.014±0.002^{a}	0.05-0.20
Lead	BDL^{a}	BDL^{a}	0.01-0.20
Mercury	0.460±0.002^{a}	0.114±0.001^{a}	0.06
Chromium	0.006±0.001^{a}	BDL^{a}	

Values are represented as mean± standard error of mean (SEM) of three replicates, (n=3). Values with different superscript in the same row are significant at p≤0.05 while values with same superscript are not statistically significant. BDL implies below detection limit.

The mean concentration of heavy metals in the two species of fish from the study site as presented in **Table 5** showed that Catfish had the highest mercury concentration (0.460±0.002 µg/g) while mullet had the least concentration (0.114±0.001 µg/g). Lead (Pb) was found to be the least (BDL) in all heavy metals analyzed as it was never detected in any of the fish analyzed. Cadmium concentration was found to be 0.004±0.001 and 0.014±0.002 µg/g for catfish *and* mullet respectively.

Table 6. Heavy metals in water and sediment from the study area

Heavy metals	Choba Water(ppm)	Choba Sediment($\mu g g^{-1}$)
Cadmium	0.057±0.003a	0.006±0.001b
Lead	BDLa	BDLa
Mercury	0.238±0.005a	0.018±0.002b
Chromium	0.008±0.001a	BDLb

Values are represented as mean± standard error of mean (SEM) of three replicates, (n=3). Values with different superscript in the same row are significant at p≤0.05 while values with same superscript are not statistically significant. BDL implies below detection limit.

Results in **Table 6** showed that mercury had the highest concentration (0.238±0.005 µg/ml) in water as compared to 0.018±0.002 µg/ml recorded for the sediment. Lead (Pb) was never detected in all sediment and water samples analyzed at both sites. Cadmium level was found to be highest (0.057±0.003µg/ml) in water as compared to 0.006±0.001µg/g recorded for sediments.

Table 7. Estimated daily intake and hazard quotient of contaminants in catfish and mullet from the study site

Contaminants	**Oral RfD ($mg^{-1}kg^{-1}day^{-1}$)**	**50th (95th) Estimated daily intake ($mg^{-1}kg^{-1}day^{-1}$) (10^{-4})**		**50th (95th) hazard quotient**		
		Catfish	mullet	catfish	mullet	**ADI ($mg^{-1}kg^{-1}day^{-1}$)**
∑PCBs	0.00002	0.2(1.6)	0.17(1.36)	1.0(8.0)	0.85(6.8)	0.00005
∑DDTs	0.0005	0.01(0.08)	0.02(0.16)	0.002(0.02)	0.004(0.032)	0.02
∑CHLs	0.00006	0.0009(008)	0.003(0.03)	0.0015(0.01)	0.005(0.05)	0.0005
HCB	0.0008	0.007(0.05)	BDL	0.00089(0.006)	BDL	0.0002
∑HCH	0.0003	0.00006 (0.0005)	0.0003 (0.002)	0.00002(0.0002)	$1x10^{-7}$(0.0008)	0.003
Glyphosate	0.1	BDL	0.002(0.02)	BDL	$2x10^{-6}$(0.0002)	0.3
Mercury	0.0001	0.26(2.0)	0.07(0.52)	0.26(2.1)	0.07(0.5)	0.00002
Cadmium	0.001	0.002(0.02)	0.0008(0.006)	0.0002(0.002)	0.0008(0.006)	0.0001
Chromium	0.003	0.003(0.03)	BDL	0.0001(0.001)	BDL	0.3

Oral reference dose values were from the USEPA's Integrated Risk Information System [23]. Acceptable Daily Intake (ADI) values were obtained from USEPA [19]. ∑PCBs= summation of polychlorinated biphenyl; ∑DDTs = Summation of Dichlorodiphenyltrichloroethanes; ∑CHLs = Summation of chlordanes; ∑HCH= Summation of Hexachlorocyclohexane; BDL Implies below detection limit.

Results in **Table 7** shows that the hazard quotient for PCBs in catfish was greater than one (>1) at both the 50th and 95th percentile while for mullet it was greater than one (>1) at only the 95th percentile. HCH had the least hazard quotient and EDI values.

Table 8. Cancer Risk Estimates of contaminants in catfish and mullet from the study site.

Contaminants	Cancer Slope (mg/kg/day)	50th(90th) percentile Cancer Risk Estimates Catfish	50th (95th) percentile Cancer Risk Estimates Mullet
∑PCBs	2.0	1.7 x 10-6 (4.6 x 10-5)	1.5 x 10-6(3.9 x 10-5)
∑DDTs	0.34	5.1 x 10-7(1.3 x 10-5)	9.9 x 10-7(2.7 x 10-5)
∑CHLs	0.35	2.8 x 10-7(7.4 x 10-6)	9.5 x 10-7(2.5 x 10-5)
HCB	1.6	7.3 x 10-8(1.9 x 10-6)	NIL

Cancer slope factors were obtained from USEPA's Integrated Risk Information System [23].
∑PCBs= summation of polychlorinated biphenyl; ∑DDTs = Summation of Dichlorodiphenyltrichloroethanes; ∑CHLs = Summation of chlordanes; ∑HCH= Summation of Hexachlorocyclohexane; BDL Implies below detection limit.

The cancer risk as shown in **Table 8** shows that PCBs had the highest value while the least value was recorded for HCB.

5. Discussion

Choba community is in Obio-Akpor Local Government of Rivers State, Nigeria. It plays host to several industries such as petroleum service companies, food processing companies and several other commercial activities. The New Calabar River (NCR) passes through this community and is the major aquatic body in the community. The NCR is situated on the eastern side of the Niger Delta River System. The coordinates of the river is longitudes $4^o30^'$ and $5^o00^'$ N and latitudes $6^o30^'$ and $7^o00^'$E. The NCR takes its rise from Elele-Alimini where it is acidic, fresh and non-tidal [14]. It is among the important aquatic resources in the Niger Delta. However, it is also one of the most stressed rivers in the Niger Delta because of its strategic economic importance as a means of transporting industrial raw materials. Numerous crude oil facilities, food processing industries and agricultural farmlands are situated within the catchment area of this river. A large number of communities around this area depend on the river for their domestic, fishing, agricultural and recreational activities.

The liver accumulated significantly higher amounts of

PCBs as compared to the muscles at both sampling locations. Generally in this study, catfish accumulated more PCBs in their tissues as compared to mullet. This variation between the levels in the liver and muscle may be attributed to the fact that the liver is the primary tissue for bioaccumulation and as such has been widely studied in regards to the adverse effects of xenobiotics [22]. Hinton and Lauren [24] asserted that the liver is a vital detoxification organ as it is essential for both the metabolism and excretion of foreign substances in the body. Although similar PCB assemblages were observed in the different tissues of the fish species, their concentrations were different. Shaogang *et al.*[25] reported a total PCB level of 0.864µg/g for fish samples analyzed in China which was found to be higher than the concentration obtained in this study. Also, a total PCB concentration of 0.094 µg/g for fish sample (trout) caught in Luxembourg was reported by Cocco *et al.*[26].

Water is the main media in which organic contaminants are dispersed into the environment. An estimated 99% of the total mass of PCBs in the universe is found in sediment, yet they are spread via waterways and most especially by the air [27]. Sediments are useful in the monitoring of aquatic environment as they are considered as the ultimate sink of most contaminants [28]. The level of PCBs in sediment sample at the study site had a significantly higher amount than the water sample. The results also showed that out of 12 PCBs analyzed; only 6 were detected in the water samples which may be attributed to the hydrophobic nature of PCBs [27]. This trend can be attributable to the assertion that marine sediments, especially those having elevated organic carbon content, may accumulate hydrophobic chemicals like PCBs to substantially higher amounts than those of the surrounding waters [29]. PCBs level in water as observed in this study was above the EPA's enforceable MCL (maximum contaminant level) for PCBs in municipal drinking-water system which is 0.0005 ppm [30].

Organochlorine and organophosphate pesticides are groups of several agrochemicals that have been used for decades. They have been used in agriculture as well as in termite, tsetse fly and mosquito control activities [31]. These pesticides have low polarity, low water solubility and high lipid solubility and as such, they have the capacity to bio-accumulate in food causing a serious threat to both human and aquatic lives [32]. According to [33], the amount of organochlorine pesticides in fresh water fishes of Punjab region in North India was measured and the result showed that DDT was the predominant pesticide while other organochlorine pesticides such as lindane, aldrin, chlordane, endosulfan, nonachlor and heptachlor were found at lower levels. The result in this present study generally agrees with their results. This finding is similar to [34], who reported higher amounts of pesticides in sediments as compared to water samples, indicating that pesticides are hydrophobic in nature. The presence of pesticides could either be as a result of direct uptake through bioconcentration from water through epithelial tissues or gills of fish or through the process of feeding leading to the eventual bioaccumulation and eventual biomagnifications in various organisms that occupy successive trophic levels [35]. Therefore, the presence of these chemicals in fish samples implies a clear prove of biomagnification of pesticides in this organism. The concentrations and presence of contaminants in fish samples seem to be determined their mode of feeding, age and fish mobility. Consequently, higher concentrations of pesticide residues observed in the fish species studied may be credited to their feeding mode [36]. Furthermore, Biego *et al* [37] stated that fishes that inhabit the level close to the sediment where they get their food have a greater likelihood of exposure to pesticides. This study also corroborates the findings of [38] who reported that the differences in the bio-accumulation of persistent organic pollutants in different fish species may be attributed to age, trophic position and lipid content. The concentration of pesticides observed in this study was lower than that reported by [39].

The concentration of pesticides in sediment was higher than the level in water as observed in this study. It was observed that concentration of pesticides in water as shown in was higher than the recommended value of 0.0001µg/ml in fresh water bodies as set by European Union and this corroborates the findings of Hamilton *et al.*[40]. Thus the water from this river is not suitable for human consumption.

Chromium level was found to be highest in catfish and was below detectable limit in mullet analyzed. Similar result for chromium was reported by [41]. The values obtained for mercury and cadmium in this study was lower than the values recorded by [42], where mercury level (0.549 mg/kg) was recorded for fresh *Clarias gariepinus*, with a mercury concentration as high as 1.733 mg/kg recorded for dried *C. gariepinus*. According to the same author, cadmium level (0.52 mg/kg) was also recorded. Lead (Pb) concentration obtained in this study was lower than the concentration recorded by [43], where the level of lead (Pb) (2.00±0.079 mg/kg) was recorded for tilapia, a value of 0.00 (below detection limit) was also recorded for copper in gills of tilapia.

The probable means where cadmium may enter surface water includes leaching from Nickel-cadmium batteries, surface run-offs from areas where phosphate fertilizers are in use for agricultural purposes and other wastes [44, 45]. Chromium was only detected in water from the study site and had a value of 0.008±0.001µg/ml. Generally, catfish may have accumulated more heavy metals than mullet in this study probably due to its high lipid content [46].

Health Risk Assessment of Contaminants in Biota

Catfish and mullet are among the commercial aquatic species consumed by humans at Choba community and other communities in Rivers State. Therefore, evaluating human health risk from the consumption of these fishes is a very vital part of public health safety [21]. The results in this study showed that the estimated daily intake (EDI) values of PCBs at the 95^{th} percentile was higher than the acceptable daily intake (ADI) values as stipulated by USEPA for both catfish and mullet respectively. Similarly, mercury (Hg) had an EDI value greater than the ADI set by USEPA for both catfish and mullet respectively at the 95^{th} percentile. Furthermore, the hazard quotient (HQ) for PCB in both fish samples at the 95^{th} percentile was greater than unity. This may be an indication of non-cancer adverse health effect on human consumption at the observed mean concentrations. The results from this study are in agreement with a health risk assessment conducted on mussel in China which indicated that the non-cancer risk quotients for DDTs and chlordanes were all below unity [47]. Glyphosate had a quotient value less than unity in both catfish and mullet at the study site. Similarly, HCHs and HCB had a quotient value less than unity at both the 50^{th} and 95^{th} percentile in both studied fish species. Consumption of contaminated fishes with high lipid content, may expose consumers to adverse health consequences as it has been established as one of the main route of human exposure to several contaminants [48].

All heavy metals analyzed had a quotient value below unity except for mercury which was observed to be high in all media analyzed, suggesting possible mercury poisoning from consumption of catfish and mullet from Choba community. Fish consumption is the principal source of exposure to methylmercury, which is bound to protein in the fish muscle [49]. Mercury can enter the environment from natural sources, but anthropogenic activities have increased mercury level in the environment by a factor of 2 to 4 [50]. Atmospheric mercury may be converted into organic methylmercury by bacteria, which is then taken up by planktonic organisms in water. It is then biomagnified and is thus found in higher concentrations in bigger fish at the top of the aquatic food chain that preys on other smaller fishes [50]. Mercury levels vary also with the feeding habit, age, size of fish, the season of capture and water body from which they arise (Toronto Public Health, 2008). Risk assessment results for DDTs, HCB, Chlordanes and HCH from this study is in contrast with studies by [51] who carried out studies on fruits from Kumasi market. Reports by [52] on the EDI and the resultant health hazard of contaminants present in fruits from Egypt are in contrast to those observed in this study. Fianko *et al.* [53] reported a higher level of pesticides in fishes from Ghana as compared to this study.

Cancer risk associated with fish consumption based on both the 50^{th} and 95^{th} percentile concentrations of total PCBs, DDTs, Chlordanes and HCB were all within the acceptable risk range of 10^{-4} as stipulated by USEPA [12]. The cancer risk obtained in our present study was low when compared to [12] where the cancer risk estimates ranged from $0.7x10^{-4}$ to 36×10^{-4} in *O. niloticus* and *C. gariepinus*. This suggests that fish consumption at the observed concentrations of these contaminants will not pose a cancer risk to exposed population.

6. Conclusions

The concentrations of Polychlorinated biphenyls (mono, di and trichlorobiphenyls), 9 pesticides residues (Glyphosate, γ-Chlordane, t-nonachlor, α-HCH, γ-HCH, HCB, DDE, DDD, and DDT) and heavy metals (cadmium, chromium, lead and mercury) in two fish species in Choba, Rivers State, Nigeria have been studied. The results obtained showed that the liver of the fish species studied had significantly elevated amounts of contaminants as compared to the muscles. Levels of pesticides, cadmium and chromium observed in both catfish and mullet were lower than the recommended acceptable daily intake (ADI) except, for PCBs and mercury at the 95^{th} percentile which was found to be above the recommended level. Risk assessment indicated that Hazard quotients for PCBs and mercury at the 95^{th} percentile were above unity. These results are an indication that human exposure to these contaminants through contaminated fish consumption could lead to adverse health effects. It also demonstrates that long term bio-accumulation of contaminants in the body via dietary fish intake is a source of health concern. Therefore strict regulations on pesticides use by farmers should be enforced and also regular monitoring of several environmental matrix particularly food should be encouraged to guard against adverse health outcomes on consumers.

Conflict of Interest

The authors declare no conflict of information regarding this manuscript.

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