

Levels and Human Health Risk Assessment of Persistent organics, metalloid and Heavy metals in Fish

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ABSTRACT

Concentrations of Persistent organics (Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), metalloid (As) and heavy metals (Fe, Zn, Mn, Cu, Ni, Cd, V, Cr, Pb, Hg) were measured in fish (*Clarias gariepinus*) samples collected from selected stations (S1, S2 and S3) along the stretch of Ovia River, Southern Nigeria, to assess the potential risks to humans consuming fish from the river. Acenaphthylene (AcPY), PCB 18 and iron (Fe) were the most dominant residues with mean concentrations ranging from 0.002 to 0.128, 0.001 to 0.003 and 175.97 to 255.52 mg/kg respectively. The most carcinogenic PAH, Benzo(a)pyrene (BaP) in S3, all the PCB congeners, cadmium (Cd), and lead (Pb) concentrations in the three stations were observed to be above EU recommended guideline values for food safety. Concentrations of dioxin-like PCB congeners, 77, 105, 114 and the sum of carcinogenic PAHs also contributed to the toxic burden of these contaminants in fish. The estimated cumulative THQ for the assessed metalloid and heavy metals indicates health risks from exposure to metalloid and Heavy metals through fish consumption.

Keywords: Fish, PAHs, PCBs, Metalloid, Heavy metals, Health Risk

INTRODUCTION

Human exposure to environmental contaminants including Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), metalloids and heavy metals occurs primarily from eating food contaminated with these chemicals (Copat *et al.*, 2012). These contaminants have been reported to occur in various foods including meat, fruits, vegetables, oils and fish (Tongo *et al.*, 2017).

Fish constitutes an important source of protein, minerals, and vitamins. It is highly sort after as an alternative to meat, and is a major constituent of most local diet. Catfish (*Clarias gariepinus*) in particular, is an important source of protein, vitamin D and omega-6 fatty acids. In Nigeria, catfish is common in many household diets. However, varying levels of contaminants have been reported in catfish (Cheung *et al.*, 2007; Tongo *et al.*, 2017). PAHs, PCBs, metalloids and Heavy metals are among such contaminants that have been reported in fish (Li *et al.*, 2008; Copat *et al.*, 2012; Tongo *et al.*, 2017). They represent a group of highly toxic compounds that are ubiquitous with mutagenic and carcinogenic potentials (Li *et al.*, 2008; Copat *et al.*, 2012; Tongo *et al.*, 2017). Consequently,

potential health risks to humans from dietary exposure to these contaminants, especially through fish consumption continue to raise concerns. Health risks resulting from dietary intake of PAHs, PCBs, and heavy metals are frequently assessed using human intake models (USEPA, 2000) and have proven useful in human health risk assessment studies (US EPA, 2000).

The Ovia River is one of the largest inland water bodies in Southern Nigeria composed of fresh and brackish environments that support a large variety of plant and animal species. Economically, the river provides water for fishing, irrigation, urban, domestic and industrial activities. Fishing is a local occupation of people living around this costal environment. Rapid urbanization and agricultural activities around the Ovia River, has caused anthropogenic vulnerability as it receives considerable pollutants from land-based sources (Imoobe and Adeyinka, 2009). Such activities expose fish from this ecological zone to contaminants hence posing a potential health risk to the local population

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This study aim to assess the contamination levels of PAHs, PCBs, metalloid and heavy metals in *Clarias gariepinus* species of fish from Ovia River, Southern Nigeria and to quantify the daily dietary intake of PAHs, PCBs, metalloid and heavy metals from fish consumption and to assess the possible health risk associated with fish consumption.

MATERIALS AND METHODS

Chemicals, Reagents and Equipment

All solvents used for this study were of analytical grade and were purchased from Sigma-Aldrich Co. USA. A Standard PAH mixture (17 compounds specified on EPA Method 610) containing, naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthrene, benzo(a)pyrene, benzo(b)fluoranthrene, indeno(1,2,3) perylene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene was also purchased from Sigma-Aldrich Co.USA. Dichloromethane and hexane were supplied by Fisher Chemicals (USA). The GC-FID system consist of a Hewlett-Packard HP-5890 Series gas chromatography (GC) equipped with a flame ionization detector (FID).

Study area

Ovia River is an ecologically and an economically important inland water body in Southern, Nigeria. The river drains into the Benin River and empties into the Atlantic Ocean (Imoobe and Adeyinka, 2009). Three sampling stations, S1 (6° 33' 3.62" N and 5° 31' 12.05" E), S2 (6° 29' 4.30" N and 5° 27' 51.05" E), and S3 (6° 10' 57.62" N and 5° 21' 43.63" E) were chosen along the stretch of the river. The sampling stations were selected to incorporate sites with fishing activities, anthropogenic impacts, and accessibility. Locations of the sampling stations are shown in **Figure 1**.

Fish Selection, Collection, and treatment

Catfish (*C. gariepinus*) were caught using hand fishing net from three locations (S1, S2 and S3) along the stretch of the river for a period of six (6) months. Samples were collected each month in triplicates from each of the stations. All fishes were weighed (g) and washed to remove dirt, then wrapped in aluminum foil and transported to the laboratory in polythene bags, where they were refrigerated at 4 °C until extraction.

Analytical procedures

Analytical procedures for PAHs, PCBs and heavy metals used in this study have been described previously (US EPA, 1986, Llobet *et al.*, 2003; Copat *et al.*, 2012). Organics present in fish samples were extracted according to method of Miglioranza *et al.* (2003). Prior to extraction, twenty-five grams of whole body tissues were homogenized with anhydrous sodium sulfate and Soxhlet extracted with dichloromethane and n-hexane (1:1 v/v) for 8 h. Lipid content was gravimetrically determined while the contaminants fraction was further purified with a silica gel column following the detailed procedure described by Connell *et al.* (2003). Each fraction was reduced to 100 mL. Quantitative PCBs analysis was done using a Hewlett-Packard (hp) 5890 Series II GC equipped with 63 Ni electron capture detector (ECD) and nitrogen as the carrier gas following an adapted procedure of EPA Method 8081a. The GC column employed was a low polar HP-column of 30m length with 0.25 mm film thickness.

The oven was programmed from 150 °C (5 mins hold) to 300 °C (4 °C/min). Nitrogen was used as a carrier gas in constant flow mode (1 mL/min).The injector port temperature was programmed at 250°C while the ECD temperature was 300°C. Quantification was performed using an external standard calibration mixture containing the selected congeners.

For PAH analysis, fish sample analysis was performed using gas chromatography (GC, Hewlett-Packard HP-5890 Series II with flame ionization detection (GC-FID)). The operations conditions were as follows: initial temperature of 60°C for 2 min and ramped at 25°C/min to 300°C for 5 min and allowed to stay for 15 min giving a total of run time of 22 min. The florasil SPE method was used to clean up the extracts. A fused silica DB-5MS capillary column (30 m × 0.32 mm i.d., 0.25-µm film thickness) was used. A standard mixture of 17 priority PAHs (naphthalene, 2-methylnaphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthrene, benzo(a)pyrene, benzo(b)fluoranthrene, indeno(1,2,3) perylene, dibenzo(a,h)anthracene, and benzo(g,h,i)perylene) was obtained and used for the analysis. Compounds were identified by comparing the retention time of

standards with that obtained from the extracts, and individual analysis of PAHs was used for quantitation. Individual PAHs were subjected to recommended quality control methods. An analytical blank and spiked sample containing all reagents was run with every 10 samples to assess interference and cross-contamination. The method detection limit (MDL) for all

the analyzed PAHs ranged from 0.0001 to 0.003 µg/L (water), 0.001– 0.003 µg/kg dw (sediment), and 0.001– 0.003 µg/kg ww (fish). The overall efficiency of the analytical method was determined by recovery of internal standard, and the average recoveries ranged from 78 to 102%.

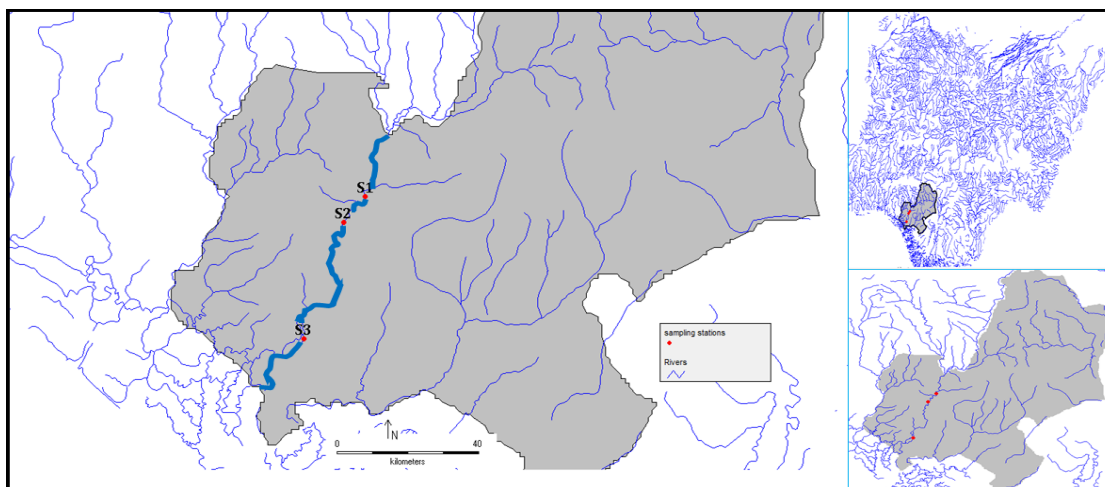


Figure 1: Map of Ovia River showing sampling stations

For metalloid and heavy metal analysis, fish samples were digested according to standard procedures (Novozamsky *et al.*, 1983). Prior to digestion, samples were dried for three days in an oven at 65°C to obtain a constant dry weight of 1.0g. The sample (1.0g) was digested using a mixture of H₂O₂ and HNO₃ in a 1:3 ratio at 150°C for 20 min and allowed to cool at room temperature. After digestion, the residues were diluted to a total of 50ml with HNO₃. The digest was finally filtered through 0.45 µm micropore membrane filter paper for analysis. Determination and quantification of the heavy metals was done in triplicates using Atomic Absorption Spectrophotometer (AAS).

Human Health Risk Assessment

Human health risk assessment was carried out to estimate the nature and probability of adverse health effects in humans as a result of exposure to PAHs, PCBs, and heavy metals through consumption of contaminated fish. All calculations were done based on USEPA standards (USEPA, 1996). Assessment was carried out for adults (70kg) for both non-carcinogenic and carcinogenic health risk. The description and

values of the parameters used for the various calculations are presented in Table 1.

Estimated daily intake (EDI)-The estimated daily intake (EDI) (mg/kg/day) of PAHs, PCBs, and heavy metals were calculated with Equation 1.

$$\text{Estimated Daily Intake (EDI)} = \frac{Cf \times IFR}{BW} \quad (1)$$

Assessment of non-carcinogenic health risks

Assessment of non-carcinogenic health risks was achieved by estimating the hazard quotient (HQ). For non-carcinogenic risks from exposure to PCBs and PAHs, the HQ was calculated as the quotient between the EDI and the reference dose (RfD) (Equation 2), while for heavy metals, the Target Hazard quotient was estimated using Equation 3.

$$\text{Hazard Quotient (HQ Non-carcinogenic)} = \frac{EDI}{RfD} \quad (2)$$

$$\text{Target Hazard Quotient (THQ)} = \frac{EF \times ED \times IFR \times Cf}{RfD \times BW \times ATn} \quad (3)$$

Table 1: Parameters used for estimating exposure assessment through Fish Consumption

Parameters	Unit	Value	Reference
Mean concentration of PAHs in Fish	mg/kg	Table 2	Table 2
Reference Dose (<i>RfD</i>)	mg/kg/day	USEPA, 1993	USEPA, 1993
Fish ingestion rate (<i>IFR</i>)	Kg/capita/day	0.0548	FAO, 2014
Exposure Duration (<i>ED</i>)	years	70	Qu <i>et al.</i> , 2015
Exposure Frequency (<i>EF</i>)	Days/year	365	Qu <i>et al.</i> , 2015
Adult body weight (<i>BW</i>)	kg	70	Tongo <i>et al.</i> , 2017
Average life span (<i>ATn</i>)	days	25550	Papadakis <i>et al.</i> , 2015
Oral Slope Factor (<i>SF</i>)	mg/kg/day	US EPA 2005	US EPA, 2005
Maximum acceptable risk level (RL)	dimensionless	10 ⁻⁵	US EPA, 2000
Toxicity equivalence factor (<i>TEFi</i>)	No Unit	Nisbet and LaGoy, 1992; EU, 2006	Nisbet and LaGoy, 1992; EU, 2006

Assessment of Carcinogenic health risks

HQ values for carcinogenic risks for PAHs and PCBs were estimated using Equation 4 (USEPA 2005). For heavy metals, HQ values for carcinogenic risks were estimated using equation 5. The CDI (chronic daily intake) was estimated using equation 6. Carcinogenic risks could only be computed for Arsenic (since As was the only assessed metal with available Slope factor (USEPA, 1993)).

$$\text{Hazard Quotient (HQ Carcinogenic)} = EDI \times SF \quad (4)$$

$$\text{Hazard Quotient (HQ Carcinogenic)} = CDI \times SF \quad (5)$$

$$\text{Chronic daily intake (CDI)} = \frac{EDI \times EF \times ED}{ATn} \quad (6)$$

The hazard index, which estimates the total risk from multiple contaminant pathways, was obtained by summing the HQ of each contaminant pathway (Equation 7). Risk was evaluated for both non-carcinogenic and carcinogenic risks. Values of HQ and HI of contaminants less than one (1) are considered as safe.

$$HI = \sum_{i=1}^n HQ_i \quad (7)$$

The potency of PAHs and PCBs to cause carcinogenic health risk was further evaluated using Carcinogenic Toxic Equivalents (TEQs). This was determined as the sum of the product of the concentrations of individual PAH congeners or $\sum PCBs$ and their toxicity equivalency factor (TEF) (Equation 8).

$$\begin{aligned} \text{Carcinogenic toxic equivalents (TEQs)} &= \sum PAH_i \text{ or } \sum PCB_i \times TEF_i \quad (8) \\ &= \sum B(A)P_{teq} \text{ or } (\sum PCB_i \times TEF_i) \end{aligned}$$

Screening Value Determination

The screening value (SV) is the threshold concentration of contaminants in edible tissue that is of potential public health concern (Cheung *et al.*, 2007; Wu *et al.*, 2012). The screening values calculated were used to identify potential chemical compounds of concern. The US EPA document (US EPA, 1995) was used in developing the contaminant screening values for both non-carcinogenic and carcinogenic risks. SV values were calculated using Equation 9 and 10.

$$\text{Screening Value (SV Non-carcinogenic)} = \frac{RfD \times BW}{IFR} \quad (9)$$

$$\text{Screening Value (SV Carcinogenic)} = \frac{((RL/SF) \times BW)}{IFR} \quad (10)$$

Statistical analysis

Data analysis was performed using Microsoft Excel 7.0 programme and Statistical version 8.0. Individual PAHs. The Total PAHs concentrations were summarized separately for each sample station using descriptive statistics (means, range, standard deviation, standard error). Statistical differences in PAH concentrations between stations, individual PAHs and total PAHs were performed using Analysis of variance (ANOVA) at 0.05 level of significance.

RESULTS AND DISCUSSION

Concentrations of PAHs in fish (*Clarias gariepinus*) from Ovia River

Quantitative results of fish tissue analysis for PAHs, PCBs, metalloid and heavy metals residues are presented in Table 2. The total mean PAH

concentrations in fish ranged from 0.01 mg/kg at S1 to 0.92 mg/kg at S3, the downstream station of the river (Table 2). The total mean for carcinogenic PAHs (sum of BaA, Chr, BkFL, BaP, BbFL, Ind, DBA, BP) in the fish samples ranged from 0.0002 mg/kg at S1 to 0.06 mg/kg at S2 and S3 stations (Table 2). The Total PCB levels in fish samples varied from 0.002 to 0.026 mg/kg (Table 2). PCB concentrations in fish samples (0.026 mg/kg) caught from S3, the downstream portion of the river and site of the highest anthropogenic impact, were significantly higher ($P < 0.05$, $F = 19.0$) than S1 (0.002 mg/kg) and S2 (0.021 mg/kg) (Table 2). Mean concentrations of metalloid and heavy metal residues in the fish samples from the different stations are shown in Tables 2.

With increasingly intense urbanization around the Ovia River, the amount of PAHs, PCBs, metalloid and heavy metals detected is likely related to anthropogenic activities around the river. These stations sampled receive effluents from domestic, municipal and industrial activities which were observed during sampling. These sources of pollution connected to anthropogenic activities around river catchments are generally known to be sources of PAHs, PCBs, metalloids and heavy metals (Jaward *et al.*, 2012).

The highest levels of benzo(a)pyrene were found in S3 and the mean BaP concentrations exceeded the EU recommended safe limit of 0.002 mg/kg ww for human fish consumption (EU, 2006), PCB concentrations in the fish samples were above the EU's recommended safe limit of 0.000008mg/kg wet weight for the Sum of dioxins and dioxin-like PCBs in muscle meat of fish (EU, 2006) while mean Pb and Cd fish concentrations in all the stations sampled were above the maximum allowable limits of 0.30 and 0.05 mg/kg respectively which calls for serious health concerns.

Human health Risk Assessment

Human exposure to PCBs is principally through diet, especially via fish from contaminated waters (Tard *et al.*, 2007). Food consumption has been the major source of PCBs body burden in humans (ATSDR, 2000). The estimated daily intake of PAHs, PCBs, and heavy metals in fish samples from the different stations are shown in Table 3.

Estimated intake of PAHs, PCBs, Metalloid and Heavy metals through fish consumption-

The estimated daily intake of PAHs, PCBs, metalloid and heavy metals in fish samples from the different stations are shown in Table 3. The average intake (mg/kg body weight/day) of PAHs through fish consumption was estimated to be 0 to 1.4E-06, 3.9E-07 to 3.8E-05 and 1.3E-07 to 1.3E-04 for S1, S2 and S3 respectively (Table 3). Estimated EDI (mg/kg body weight/day) for PCBs ranged from 0 to 7.8E-07 in S1, 1.2E-06 to 3.1E-06 in S2 and 5.9E-07 to 3.6E-06 in S3. EDI (mg/kg body weight/day) values for the metalloid and heavy metals in S1, S2 and S3 ranged from 0 to 0.155, 0 to 0.200, 0 to 0.138 respectively. Fish species caught downstream (S3) contributed to the highest intake of total PAHs and PCBs while fish species caught in S2 has the highest EDI values for heavy metals. Carcinogenic PAHs accounted for 10.7% of the estimated daily intake of PAHs in the fish species. Varying estimates for daily intake of PAHs, PCBs, and heavy metals from fish consumption have been reported in other countries (PCBs- Spain (92 g/kg/d, Llobet *et al.*, 2003), China (1.62 ng/kg/d, Li *et al.*, (2008)), PAHs- India (1.77 -10.7 mg/kg/d, Dhananjayan and Muralidharan, 2012), Korea (13.8–16.7 ng/kg body weight/d, Moon *et al.*, 2010), Heavy metals - Sicily (0.007 -0.503 $\mu\text{g/kg/d}$, Copat *et al.*, 2012). Variations in results seem to be associated with the consumption rate of fish, body weight and accumulation level of the contaminants in the fish.

The estimated daily intake of PAHs, PCBs, and heavy metals were however observed to be lower than the reference dose (RfD) indicating low risk through fish consumption.

Non-carcinogenic health risks assessment

The averages HQ for PAHs, PCBs, and THQ for Heavy metals in fish samples for non-carcinogenic health risk are shown in Tables 4-6. Estimated HIs for PAHs, PCBs and heavy metals were 0.008, 0.63 and 1.60 respectively (Tables 4-6). Estimated HQ and HI values for PAHs and PCBs were below 1, indicating that exposure to either individual PAHs or complex PAH and PCB mixtures through fish consumption would have no potential negative health effect on consumers.

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Table 2: Mean Concentrations (mg/kg) of PAHs, PCBs, Metalloid and Heavy metals residues in Fish from Ovia River

PAHs (mg/kg)	PCBs			Heavy Metals							
	S1	S2	S3	S1	S2	S3	S1	S2	S3		
NaP	0.00±0.00	0.03±0.05	0.13±0.29	PCB7	0.00±0.00	0.00±0.00	0.00±0.00	Fe	198.60±39.49	255.52±71.12	175.97±27.00
2-MNaP	0.00±0.00	0.03±0.05	0.02±0.03	PCB18	0.00±0.00	0.00±0.01	0.00±0.00	Zn	78.65±24.39	109.38±32.34	79.39±14.87
AcPY	0.00±0.00	0.05±0.08	0.15±0.24	PCB28	0.00±0.00	0.00±0.00	0.00±0.00	Mn	13.31±4.64	17.37±8.29	9.61±3.39
AcP	0.00±0.00	0.01±0.00	0.16±0.35	PCB52	0.00±0.00	0.00±0.00	0.00±0.00	Cu	8.73±3.35	9.92±6.94	5.55±3.12
Flu	0.00±0.00	0.01±0.01	0.10±0.14	PCB43	0.00±0.00	0.00±0.00	0.00±0.00	Ni	12.45±1.37	13.50±3.61	8.40±0.90
Phe	0.00±0.00	0.00±0.00	0.01±0.01	PCB60	0.00±0.00	0.00±0.00	0.00±0.00	Cd	0.89±0.51	0.85±1.00	0.38±0.52
Ant	0.00±0.00	0.01±0.01	0.09±0.20	PCB77	0.00±0.00	0.00±0.00	0.00±0.00	V	2.42±0.65	2.00±0.65	2.63±1.47
FL	0.00±0.00	0.01±0.01	0.17±0.28	PCB101	0.00±0.00	0.00±0.00	0.00±0.00	Cr	0.82±0.16	0.89±0.39	0.52±0.10
Pyr	0.00±0.00	0.01±0.03	0.03±0.06	PCB105	0.00±0.00	0.00±0.00	0.01±0.01	Pb	1.42±0.56	1.36±1.17	0.51±0.66
BaA	0.00±0.00	0.00±0.00	0.02±0.03	PCB114	0.00±0.00	0.00±0.00	0.00±0.00	Hg	0.00±0.00	0.00±0.00	0.00±0.00
Chr	0.00±0.00	0.03±0.06	0.01±0.01	PCB153	0.00±0.00	0.00±0.00	0.00±0.00	As	0.00±0.00	0.00±0.00	0.00±0.00
BkFL	0.00±0.00	0.03±0.07	0.03±0.07	∑PCB	0.00±0.01	0.02±0.01	0.03±0.02	∑HM	317.29±66.84	410.79±117.81	282.95±52.03
BaP	0.00±0.00	0.00±0.00	0.00±0.01								
BbFL	0.00±0.00	0.00±0.00	0.00±0.00								
Ind	0.00±0.00	0.00±0.00	0.00±0.00								
DBA	0.00±0.00	0.00±0.00	0.00±0.00								
BP	0.00±0.00	0.00±0.00	0.00±0.00								
∑PAH	0.01±0.01	0.21±0.17	0.92±0.52								
∑CPAH	0.00±0.00	0.06±0.08	0.06±0.08								

NaP-,Naphthalene, 2-MNaP-2-Methylnaphthalene, AcPY-Acenaphthylene, AcP-Acenaphthene, Flu-Fluorene, Phe-Phenanthrene, Ant-Anthracene, FL-Fluoranthene, Pyr-Pyrene, BaA-Benzo(a)anthracene, Chr-Chrysene, BkFL-Benzo(k)fluoranthrene, BaP-Benzo(a)pyrene, BbFL-Benzo(b)fluoranthrene, Ind-Indeno(1,2,3)pyrene, DBA-Dibenzo(a,h)anthracene, BP-Benzo(g,h,i)perylene, ∑PAH-Sum of Total PAH, ∑PAH-Sum of Total Carcinogenic PAH.

PCB7-2,4-Dichlorobiphenyl,PCB18, 2,2',5-Trichlorobiphenyl,PCB28-2,4,4'-Trichlorobiphenyl,PCB52-2,2',5,5'-Tetrachlorobiphenyl,PCB43-2,2',3,5-Tetrachlorobiphenyl,PCB60-2,3,4,4'-Tetrachlorobiphenyl,PCB77-3,3',4,4'-Tetrachlorobiphenyl,PCB101-2,2',4,5,5'-Pentachlorobiphenyl,PCB105-2,3,3',4,4'-Pentachlorobiphenyl,PCB114-2,3,4,4',5-Pentachlorobiphenyl,PCB153-2,2',4,4',5,5'-Hexachlorobiphenyl,∑PCB-Total PCBs.

Fe-Iron, Zn-Zinc, Mn-manganese, Cu-Copper, Ni-Nickel, Cd-Cadmium, V-Vanadium, Cr-Chromium, Pb-Lead, Hg-Mercury, As-Arsenic, ∑HM-Total Heavy Metals.

Table 3: Estimated daily intake(mg/kg body weight/day) of PAHs, PCBs, Metalloid and Heavy metals for adult (70-kg body weight) through consumption of fish from Ovia River

PAH(mg/kg body weight/day)				PCB(mg/kg body weight/day)				Heavy metals(mg/kg body weight/day)			
	S1	S2	S3		S1	S2	S3		S1	S2	S3
NaP	1.20 X 10 ⁻⁶	2.20X 10 ⁻⁵	1.00X 10 ⁻⁴	PCB7	7.8X 10 ⁻⁷	1.50X 10 ⁻⁶	1.80X 10 ⁻⁶	Fe	0.155	0.200	0.138
2-MNaP	1.40X 10 ⁻⁶	2.10X 10 ⁻⁵	1.50X 10 ⁻⁵	PCB18	5.20X 10 ⁻⁷	3.10X 10 ⁻⁶	2.20X 10 ⁻⁶	Zn	0.062	0.086	0.062
AcPY	1.40X 10 ⁻⁶	3.80X 10 ⁻⁵	1.20X 10 ⁻⁴	PCB28	0.00	1.20X 10 ⁻⁶	2.30X 10 ⁻⁶	Mn	0.010	0.014	0.008
AcP	7.80X 10 ⁻⁷	4.40X 10 ⁻⁶	1.30X 10 ⁻⁴	PCB52	6.50X 10 ⁻⁸	1.60X 10 ⁻⁶	2.40X 10 ⁻⁶	Cu	0.007	0.008	0.004
Flu	1.30X 10 ⁻⁶	6.80X 10 ⁻⁶	7.70X 10 ⁻⁵	PCB43	0.00	1.80X 10 ⁻⁶	2.70X 10 ⁻⁶	Ni	0.010	0.011	0.007
Phe	1.00X 10 ⁻⁶	2.10X 10 ⁻⁶	7.70X 10 ⁻⁶	PCB60	0.00	1.60X 10 ⁻⁶	2.00X 10 ⁻⁶	Cd	0.001	0.001	0.000
Ant	2.60X 10 ⁻⁶	7.20 X 10 ⁻⁶	7.40X 10 ⁻⁵	PCB77	1.30X 10 ⁻⁷	1.40X 10 ⁻⁶	1.00X 10 ⁻⁶	V	0.002	0.002	0.002
FL	6.50X 10 ⁻⁷	6.00X 10 ⁻⁶	1.30X 10 ⁻⁴	PCB101	0.00	1.20X 10 ⁻⁶	5.90X 10 ⁻⁶	Cr	0.001	0.001	0.000
Pyr	1.30X 10 ⁻⁷	1.10X 10 ⁻⁵	2.40X 10 ⁻⁵	PCB105	0.00	1.20X 10 ⁻⁶	3.60X 10 ⁻⁶	Pb	0.001	0.001	0.000
BaA	0.00	2.00X 10 ⁻⁶	1.40X 10 ⁻⁵	PCB114	6.50X 10 ⁻⁸	1.20X 10 ⁻⁶	6.20X 10 ⁻⁷	Hg	0.000	0.000	0.000
Chr	1.30X 10 ⁻⁷	2.20X 10 ⁻⁵	5.60X 10 ⁻⁶	PCB153	6.50X 10 ⁻⁸	7.20X 10 ⁻⁷	7.80X 10 ⁻⁷	As	0.000	0.000	0.000
BkFL	0.00	2.20X 10 ⁻⁵	2.40X 10 ⁻⁵	ΣPCBs	1.60X 10 ⁻⁶	1.70X 10 ⁻⁵	2.00X 10 ⁻⁵	ΣHM	0.248	0.322	0.222
BaP	0.00	7.80X 10 ⁻⁷	2.10X 10 ⁻⁶								
BbFL	0.00	7.80X 10 ⁻⁷	1.20X 10 ⁻⁶								
Ind	0.00	5.20X 10 ⁻⁷	2.60X 10 ⁻⁷								
DBA	0.00	3.90X 10 ⁻⁷	2.60 X 10 ⁻⁷								
BP	0.00	5.20X 10 ⁻⁷	1.30X 10 ⁻⁷								
ΣPAH	8.4X 10 ⁻⁶	1.70X 10 ⁻⁴	7.20X 10 ⁻⁴								
ΣCPAH	1.3X 10 ⁻⁷	4.80X 10 ⁻⁵	4.70X 10 ⁻⁵								

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However, the estimated HI values for the assessed metals were above 1 (1.60) (Table 5), indicating possible health risk from heavy metal exposure through fish consumption. The mean concentrations of PAHs, PCBs, and heavy metals in all the analysed samples were observed to be lower than the estimated threshold screening values, indicating low risk from consumption of the fish species.

Assessment of Carcinogenic health risks

Estimated average HQ values for carcinogenic risks, for total PAHs, PCBs and metalloid (arsenic) are presented in Table 6. HQ values for PAHs ranged from 1.9×10^7 to 6.98×10^6 , PCBs- 1.04×10^6 to 3.87×10^6 while the HQ for Arsenic was 2.24×10^7 . The total risk from multiple contaminant pathways estimated using the HI was 1.43×10^5 , 2.54×10^5 and 2.24×10^7 for PAHs, PCBs and metalloid (arsenic) respectively. Estimated HQ and HI values for all the assessed contaminants were below 1 indicating minimal risks from exposure through the consumption of fish from Ovia River. In terms of Individual carcinogenic potencies for PAHs and PCBs, values varied among

the different compounds assessed. Among the PAH congeners, Benzo(k)fluoranthrene had the highest carcinogenic potency (mg/kg) in *C. gariepinus* (0.002) while for PCBs, PCB 105 had the highest carcinogenic potency (1.38×10^7) (Table 6).

The potency of PAHs and PCBs to cause carcinogenic health risk was further evaluated using Carcinogenic Toxic Equivalents (TEQs). TEQ values were 0.006 and 0.307 for PAHs and PCBs respectively. These values were however observed to be lower than the calculated SV (Table 6), which is the threshold concentration of the contaminants in the fish tissue that is of potential public health concern (Cheung *et al.*, 2007). Results of the calculated SVs indicate that the assessed contaminants in Ovia River were not of potential health concern, and the potential carcinogenic risks from exposure to individual PAHs and PCBs through fish consumption are low. Estimated HQ and HI values for all the assessed contaminants were below 1 indicating minimal risks from exposure through the consumption of fish from Ovia River.

Table 4: Non-Carcinogenic and Carcinogenic Risk of PAHs for adult (70-kg body weight)

PAH	HQ		SV		B(A)Pteq
	Noncarcinogenic	Carcinogenic	Noncarcinogenic	Carcinogenic	
2-MNaP	2.00×10^{-3}	NA	25.55	NA	0.00
AcPY	3.00×10^{-3}	NA	5.11	NA	0.00
AcP	NA	NA	NA	NA	0.00
Flu	1.00×10^{-3}	NA	76.64	NA	0.00
Phe	1.00×10^{-3}	NA	51.10	NA	0.00
Ant	NA	NA	NA	NA	0.00
FL	0.00	NA	383.21	NA	0.00
Pyr	1.00×10^{-3}	NA	51.10	NA	0.00
BaA	0.00	NA	38.32	NA	0.00
Chr	NA	0.00	NA	0.02	1.00×10^{-3}
BkFL	NA	0.00	NA	1.75	0.00
BaP	NA	0.00	NA	0.18	2.00×10^{-3}
BbFL	NA	6.98×10^{-6}	NA	2.00×10^{-3}	1.00×10^{-3}
Ind	NA	4.76×10^{-7}	NA	0.01	0.00
DBA	NA	1.90×10^{-7}	NA	0.01	0.00
BP	NA	1.59×10^{-6}	NA	2.00×10^{-3}	2.00×10^{-3}
	NA	NA	NA	NA	NA
	HI = 8.00×10^{-3}	HI = 1.00×10^{-5}			$\sum B(A)Pteq = TEQ = 0.01$

HQ-Hazard Quotient, HI-Hazard Index, SV-Screening Value, B(A)Pteq-Carcinogenic potencies for PAHs, TEQ- Carcinogenic toxic equivalents, NA-Not available.

Table 5: Non-Carcinogenic and Carcinogenic Risk of Metalloid and Heavy metals for adult (70-kg body weight)

Heavy Metals	HQ Noncarcinogenic	HQ Carcinogenic	SV Noncarcinogenic	SV Carcinogenic
Fe	0.10	NA	894.16	NA
Zn	0.10	NA	383.21	NA
Mn	0.03	NA	178.83	NA
Cu	0.07	NA	51.10	NA
Ni	0.19	NA	25.55	NA
Cd	0.24	NA	1.28	NA
V	0.79	NA	1.28	NA
Cr	0.08	NA	3.83	NA
Pb	NA	NA	NA	NA
Hg	0.00	NA	0.38	NA
As	0.00	0.000	0.38	0.01
	HI = 1.60	HI = 2.24 X 10 ⁻⁷		

HQ- Hazard Quotient, HI- Hazard Index, SV-Screening Value, NA-Not available.

Table 6: Non-Carcinogenic and Carcinogenic Risk of PCBs for adult (70-kg body weight)

P CBs	HQ Noncarcinogenic	HQ Carcinogenic	SV Noncarcinogenic	SV Carcinogenic	Carcinogenic Toxic Potency
PCB7	0.07	0.000	0.03	0.01	NA
PCB18	0.10	0.000	0.03	0.01	NA
PCB28	0.06	0.000	0.03	0.01	NA
PCB52	0.07	0.000	0.03	0.01	NA
PCB43	0.07	0.000	0.03	0.01	NA
PCB60	0.06	0.000	0.03	0.01	NA
PCB77	0.04	0.000	0.03	0.01	1.33 X 10 ⁻⁷
PCB101	0.03	0.000	0.03	0.01	NA
PCB105	0.08	0.000	0.03	0.01	1.38 X 10 ⁻⁷
PCB114	0.03	0.000	0.03	0.01	2.38X 10 ⁻⁷
PCB153	0.03	0.000	0.03	0.01	NA
ΣPCB	0.63	0.000	0.03	0.01	NA
	HI = 0.63	HI = 3 X 10 ⁻⁵			TEQ = 0.31

HQ- Hazard Quotient, HI- Hazard Index, SV-Screening Value, TEQ- Carcinogenic toxic equivalents, NA-Not available.

CONCLUSION

Results of this study revealed that the land use activities in surrounding areas would have contributed to increasing levels of contaminants in fish from this Ovia River. The concentrations of PAHs (benzo(a)pyrene), PCBs and heavy metals (Pb and Cd) in the assessed fish species were above recommended safe levels for human consumption. The activities around the Ovia River especially downstream should, therefore, be kept under strict surveillance and monitoring of contaminants in fish for

human consumption should be done frequently to guarantee safety.

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