DISTRIBUTION, BIOACCUMULATION AND RISK CONSIDERATION OF PAHS IN WATER, SEDIMENT, FISH AND PRAWN FROM BONNY RIVER, RIVER STATE, NIGERIA

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Abstract: The levels of 16 polycyclic aromatic hydrocarbons (PAHs) were determined in surface water, sediment, fish (*Mugil cephalus*) and prawn (*Penaeus monodon*) from fishing areas affected by oil and gas exploration activities, along Bonny River, Southern Nigeria. Samples were collected for a period of four months (July to October) and analyzed using Gas chromatography coupled to flame ionization detector (GC/FID). Biota-sediment accumulation factor (BSAF) and Bioaccumulation factor (BAF) were assessed using the accumulated levels of PAHs in the biota. Benzo(a)anthracene was the most dominant congener in the surface water, sediment, fish, and shrimp samples comprising about 75, 52, 50 and 17%, respectively, of the sixteen PAHs detected. Total PAH concentrations ranged from 0.07 to 3.67 mg/L in water, 0.09 to 0.16 mg/kg in sediments, 0.06 to 0.13 mg/kg in fish and 0.02 to 0.11 mg/kg in prawn. The sources of contamination of PAHs in Bonny River were of both petrogenic and pyrolytic origin, however, a strong pyrolytic source fingerprint was observed to be dominant at almost all the stations investigated. BSAF values of total PAHs in fish was higher than prawn indicating higher accumulation in fish. Assuming prawn as the main prey of the fish (*Mugil cephalus)*, bioaccumulation factor of PAHs in fish ranged from 0 to 1.36, suggesting tissue bioaccumulation. Estimated daily intake (EDI) of PAHs through consumption of fish and prawn were observed to be lower than the reference dose (RfD) indicating low risk from consumption. Results of the estimated excess cancer risk (ECR) for Benzo (a) anthracene in fish, however, suggests that lifetime exposure to Benzo(a)anthracene through fish consumption could result in cancer risk which calls for public health and safety concerns.

Keywords: Bioaccumulation, Bonny River, *Mugil cephalus*, *Penaeus monodon*

Introduction

PAHs are ubiquitous environmental pollutants that occur naturally in fossil fuel products, or are among the effluents of combustion processes. Significant accumulation of PAHs in the aquatic ecosystem, especially, Nigerian coastal waters have been caused by anthropogenic inputs principally associated with gas flaring, ground pipeline leakage, oil waste dumping, sabotage and oil spills (Nwaichi and Ntorgbo, 2016). The Bonny River is one of such rivers affected by these anthropogenic inputs (Awajiusuk, 2015), as the river is flanked by several oil companies (Exxon Mobil, Nigeria Liquefied Natural Gas company (NLNG), and SHELL Nigeria) and also marred by incessant spills from illegal bunkering and refining of crude oil in the area.

PAHs are of great concern on global and regional scales, with 16 PAHs listed as priority pollutants by the US EPA (Hiu *et al.*, 2012). Recently, high concentrations of PAHs are found in the coastal environment (Hiu *et al.*, 2012). PAHs in the aquatic environment may endanger aquatic organisms as fish and their prey can accumulate PAHs at relatively higher levels in impacted aquatic compartments, such as streams, rivers and lakes, which can in turn lead to the deterioration of the aquatic ecosystem (Zhang *et al.*, 2015). PAHs in the aquatic environment binds with particles and thus bottom sediments have become the primary reservoir of these contaminants to aquatic biota, especially for organisms living in the water–sediment interfaces (Latimer and Zheng, 2003).

Several studies on the levels of PAHs in different environmental matrices has been reported by several authors (Zhang *et al.* 2004; Anyakora *et al.* 2005; Chen and Liao, 2006; Shi *et al.* 2007; Kafilzadeh *et al*,. 2011) but very little studies exists in Nigeria on the Bonny River. Bioavailability studies of PAHs in aquatic biota from water and sediments, especially through the examination of bioaccumulation factor (BAF) and biota-sediment accumulation factors (BSAF), are also scarce. Little information is known about the ecological human health risks posed by individual PAHs and PAH mixtures in the Bonny River. Bioaccumulation and Ecological risk assessment (ERA) studies are important scientific evaluators of PAHs used to quantify the likelihood and magnitude of the adverse ecological effects that might occur as a result of exposure to one or more stressors (Hiu *et al.*, 2012; Amot and Gobas, 2003).It is therefore necessary to assess the PAHs in the biota as well as the surrounding media (water and sediment) as bioaccumulation patterns could serve as a good indication of pollution and greatly enhance our understanding of the environmental behavior of PAHs which is essential for the monitoring and management.

Therefore, the main aim of the present study is to provide an overview of exposure levels, geographic distributions and bioaccumulation patterns of PAHs in surface water, sediment, fish (*Mugil cephalus*) and prawn (*Penaeus monodon*) from fishing areas affected by oil and gas exploration activities, along Bonny River, Southern Nigeria with a view to ascertaining the ecological and human health risks from exposure to PAHs.

Materials and Methods

Study area

Satellite images of the study area indicates that Bonny River is an arm of Niger River Delta in Rivers state, Southern Nigeria on the Bight of Bonny (Fig. 1). It covers a total area of about 645.60 km^2 with geographical co-ordinates of 4° 26′ 0″ N and 7° 10′ 0″ E (Awajiusuk, 2015). Bonny River is a terminal for crude oil export and along its coast are three oil and gas exploration companies, which have been in existence for over two decades. They are: Shell Nigeria, Mobil producing and Nigeria Liquefied Natural Gas (NLNG). There is also an awareness of illegal bunkering activities by militants.

Sampling stations

Three sampling stations along the Bonny River were selected for the study. These sites are landing sites for fish catch and are also within area of sources of pollution (Fig. 1). The stations were:

Amariaria/Light house (4° 24′ 10″ N and 7° 8′ 12″ E): This station is located in Finima town of Bonny Local Government Area, on the East side of the Nigeria Liquefied Gas company export site. This station is a fishing settlement and a landing site for fish catch.

Coal beach (4^0 27' 24.104"N and 7^0 10' 35.935"E). This is the commercial nerve center of Bonny town hosting major economic activities. It is a landing site for fishermen who have ready buyers for their fish catch. It is North East of NLNG export site. In addition, there is an abattoir situated about 500m from the Coal beach jetty where waste is emptied directly into the Bonny River.

Kuruama (4^0 28' 42.488"N and 7^0 6' 50.416"E). This is a small Island and a fishing settlement in the Bonny Kingdom. It is a landing site for fisheries especially for prawn.

Fig. 1: Map of Bonny River, showing sampling stations

Collection of samples

Water, sediment, prawn (*Penaeus*. *monodon*) and fish *(Mugil*. *cephalus*) samples were collected from July to October 2016 from the three stations; Amariaria, Coal beach and Kuruama (Fig. 1), which are fishing areas affected by oil and gas exploration activities, along Bonny River, Southern Nigeria. The study period and sampling stations (July– October 2016) were chosen to reflect the hydrological status of the river incorporating areas with high anthropogenic impacts. Samples were collected in triplicates each month from each of the stations.

Water samples were collected at low tide and taken from 1 m below the water surface into pre-cleaned glass bottles using a hydrobios sampler as described by Ezemonye (2006). All foreign bodies were excluded through filtration and samples were homogenized. Sediment samples were collected from the top 20 cm bed sediment of the river at each station using a Van-Veen grab samples from spots with accumulated fine texture substrate (Ezemonye, 2006). Sediment samples were collected into a non-stick polythene bag and wrapped in aluminum foil, labeled and stored in ice-packed coolers before transportation to the laboratory for extraction and analysis. Biota samples, Tiger prawn (*Penaeus monodon*) and mullet fish *(Mugil cephalus*) were purchased from local fishermen at sampling locations. All samples were weighed (kg), washed then wrapped in aluminum foil and transported immediately to the laboratory in polythene bags. They were refrigerated at 4 °C until extraction (Ezemonye *et al.*, 2008).

Analytical methods

Analytical procedures for PAHs was carried out following EPA method 3510 (USEPA, 1993), APHA 6630 method and other published procedures (Zeng and Vista 1997; Ezemonye 2006; Ezemonye *et al.*, 2008; Witt, 1995).

Sample extraction and purification

Analytical procedures for PAHs used in this study are described in detail previously (US EPA, 1986). Water samples were thoroughly homogenized before extraction. Soxhlet extraction was done using a 20 ml mixture of N-hexane and dichloromethane (DCM) (3:1) with periodic venting to allow for complete separation of the organic-phase from the water-phase. Concentration of the extract was achieved using rotary evaporator and the extract was concentrated to 10 ml. Samples were purified using column chromatograph (activated silica gel) eluted with 40 ml n-hexane solvent. The extract was then evaporated again until 1 ml. For sediment samples, extraction of PAHs from sediment was performed using fifteen grams (15 g) of well-mixed and finely grounded sample weighed into a clean extraction bottle. A mixture of dichloromethane and n-hexane (2:3) was added and placed in a sonicator for about 5 h for shaking. Anhydrous sodium sulfate was then added to the sample till a transparent extract was achieved. Afterwards, the samples were precleaned with column chromatograph and concentrated with a rotary evaporator. 1-3 ml of the finial extract was pipetted into the vial bottle and corked for gas chromatographic analysis. For biota (fish and prawn), frozen whole-body tissue was inserted into a homogenizer cup and 100 ml of acetone was added. Samples were homogenized for 20 min at 100 rpm and mixed further with 5 g of anhydrous sodium sulphate. Extraction was done using soxlet extraction for approximately 5 h using dichloromethane and n-hexane mixture. The resulting solvent was eluted with 50 ml n-hexane solvent. The lipid content of fish/prawn samples was evaluated gravimetrically in replicates following solvent removal from a known portion of the crude soxhlet extract prepared for the PAH determination.

PAH Analysis

Determination of PAHs in the matrices (water, sediment and biota) was carried out following standard procedures (USEPA, 1986). Sample analysis was performed using Gas chromatography (GC, Hewlett-Packard HP-5890 Series II with flame ionization detection (*GC-FID*)). The GC was programmed as follows: Initial temperature of 60°C for 2 min

and ramped at 25ºC/min to 300ºC for 5 min and allowed to stay for 15 min. A 2 μL volume splitless injection mode was used and the injection port temperature was set at 250ºC, while 300ºC was maintained for the injection port of the FID detector. A standard mixture of 17 priority PAHs 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 were used for quantitation.

For quality assurance and quality control, individual PAHs were subjected to standard quality control methods. Spiked sample containing all reagents and an analytical blank were run with every 10 samples to assess interference and cross-contamination. The minimum detection limit (MDLs) for all the analyzed PAHs ranged from 0.001 – 0.003 µg/kg wet weight. The overall efficiency of the analytical method was determined by recovery of internal standard and the average recoveries ranged from 78–102%.

Bioaccumulation and Risk consideration of PAHs

Calculation of biota-sediment accumulation factor and Bioaccumulation factor

The biota sediment accumulation factor (BSAF) was carried out according to the method described by Amot and Gobas, 2003. The BSAF is the ratio of the tissue concentration of a particular chemical to its sediment concentration (Equation 1). BASF was evaluated to determine the tendency of PAH compounds to accumulate in tissue. Assuming the prawn (*Penaeus Monodon*) as the main prey of the fish (*Mugil cephalus)*, the bioaccumulation factor of PAHs in fish was estimated using Equation 2.

Biota sediment accumulation factor (BSAF) = $\frac{\text{Tissue concentration}}{\text{Sediment concentration}}$ Equation 1

Bioaccumulation factor (BAF) = $\frac{\text{Fish Tissue concentration}}{\text{Prawn Tissue concentration}}$ Eqn 2

Assessment of human health risk

Assessment of human health risk was carried out to estimate the likelihood of adverse health effects in humans as a result of exposure to PAHs through consumption of contaminated fish and prawn from Bonny River. Human intake models as described by USEPA (1996) were applied. The assessment was carried out for adults (70 kg) 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.

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

Parameters	Unit	Value	Reference
Mean concentration of PAHs(Cf/Cp)	mg/kg-Fish/Prawn	Table 4.5	Table 4.5
Reference Dose (RfD)	mg/kg/day	USEPA (1993)	USEPA (1993)
Fish/Crustacean ingestion rate *(IFR)*	Kg/capita/day	0.85 (Marine Fish) 0.33 (Crustaceans)	FAO (2014)
Exposure Duration (*ED)*	years	70	Qu *et al.* (2015)
Exposure Frequency (*EF*)	Days/year	365	Qu *et al.* (2015)
Adult body weight (*BW*)	kg	70	Tongo *et al.* (2017)
Average life span *(ATn)*	days	25550	Papadakis *et al.* (2015)
Oral Slope Factor *(SF)*	mg/kg/day	US EPA 2005	US EPA (2005)
Toxicity equivalence factor (*TEFi*)	No Unit	Nisbet and LaGoy, 1992	Nisbet and LaGoy (1992)

Estimated daily intake (EDI)

The estimated daily intake (EDI) (mg/kg/day) of PAHs in fish and prawn samples were estimated using Equation 3.

Estimated Daily Intake (EDI) = $\frac{Cf/Cp\ X\ IFR}{BW}$ *Equation 3*

Assessment of non-carcinogenic and carcinogenic health risks

Non-carcinogenic and carcinogenic health risk assessments were evaluated by estimating the hazard quotient (HQ) and hazard index (HI), while further assessment of the carcinogenic health risk was estimated using the carcinogenic potency of individual PAHs and Excess Cancer Risk (ECR). The HQ for non-carcinogenic risks from exposure to PAHs was calculated by dividing the EDI by reference dose (RfD) (Equation 4), while the HQ for carcinogenic risks was estimated using Equation 5.

Hazard Quotient (HQ $_{\text{Non-carcinogenic}}$) = $\frac{EDI}{RfD}$ *Equation 4*

Hazard Quotient (HQ $_{\text{Carcinogenic}}$) = $EDI\ X\ SF$ *Equation 5*

The hazard index, which is the total risk from multiple contaminant pathways, was achieved by summing the HQ of the contaminant pathway (Equation 6). Risk was evaluated for both non-carcinogenic and carcinogenic risks. Values of HQ and HI of contaminants below one (1) are considered as safe (USEPA, 1986).

HI = $\sum_{i=1}^{n} HQi$ *Equation 6*

The carcinogenic potency of individual PAHs was determined as the product of the concentration of individual PAH congeners and their toxicity equivalency factor (TEF) (Equation 7) while Excess cancer risk from dietary exposure to PAHs through consumption of was estimated using Equation 8.

Carcinogenic potencies for PAHs (B(A)Pteq) = $PAHi\ X\ TEFi$ *Equ. 7*

Excess Cancer Risk (ECR) = $\frac{\sum Q\ X\ \text{B(A)Pteq X IFR X ED}}{BW\ X\ ATn}$ *Equ. 8*

Statistical analysis

Statistical significance of the data obtained was assessed using one-way analysis of variance (ANOVA) to compare PAHs levels between species across sampling stations while comparisons of PAHs levels between species within stations were made using student t-test, statistical package SPSS 16.0. Correlation analysis was done to determine any linear relationship ($p<0.05$) between BSAFs/BAFs for PAHs in biota and the octanol–water partition coefficients (Kow) of the corresponding organic compounds and also between the matrices.

Results and Discussion

PAHs concentrations in water, sediment, fish and prawn

Concentrations of PAHs in water samples

The concentrations of PAHs in water samples are shown in Table 2. The concentrations (mg/L) of total PAHs in water ranged from 0.071 at Coal Beach to 3.667 at Kuruma. Mean concentrations of total PAHs across the stations was in the order Coal Beach> Amamariah>Kuruma, however concentrations were not statistically significant ($p>0.05$, $F=1.34$). Benzo(a)anthracene was the most frequently

detected PAHs in water samples with mean concentrations ranging from 0.182 mg/L to 2.703 mg/L and accounting for 74.6% of total mean PAHs. The PAH concentrations of water samples were principally dominated by the 4-rings PAHs compounds which accounted for approximately 85.4% of the total PAHs in the water samples (Fig. 2). The total concentrations of potentially carcinogenic PAHs (BaA, Chr, BbFL, BaP, BbFL, Ind, DBA, BP) were quite high accounting for 75% of the total PAHs in the water samples. In general, PAH concentrations were highest in water sample than in the other matrices, but differences in concentrations were not statistically significant (p>0.05) (Fig. 2).

Concentrations of PAHs in sediment samples

Concentration of individual PAHs in sediment samples is shown in Table 3. Mean concentration in sediment samples according to ring type, showed a considerable predominance of the 4-ring PAHs, similar to what was detected in water (Fig. 3). Total PAH concentration in sediment ranged from 0.089 mg/kg at Amamariah to 0.159 at Kuruma with a mean PAH concentration of 0.13 mg/kg. Total mean concentration in water was generally higher than concentrations in sediment but the difference was not statistically significant (p>0.05). Also PAH concentrations between the stations were also not statistically significant (p>0.05). The total concentrations of potentially carcinogenic PAHs were also quite high accounting for 56% of the total PAHs in the sediment samples. Also similar to what was observed in water, benzo(a)anthracene was the major PAH in sediment samples with mean concentrations ranging from 0.061 mg/kg to 0.083 mg/kg and accounting for 52.4% of total mean PAHs. Total mean concentration of the high molecular weight PAH (HPAH) (4-6 rings) was higher than the low molecular weight PAH (LPAH) (2-3 rings), however concentrations were not significantly different (p>0.05). A significant positive correlation was observed between mean PAH concentrations in sediment and water (p<0.05, r = 0.94).

Table 2: Concentrations of PAHs in water (mg/L) from Bonny River, Southern Nigeria

PAHs	Ring Type	Code	STATIONS					
			KURUMA		COAL BEACH		AMAMARIAH	
			Mean	SD	Mean	SD	Mean	SD
Naphthalene	2	NaP	0.000	0.000	0.000	0.000	0.006	0.011
Acenaphthylene	3	AcPY	0.000	0.001	0.000	0.001	0.001	0.002
Acenaphthene	3	AcP	0.114	0.226	0.001	0.002	0.007	0.010
Fluorene	3	Flu	0.006	0.011	0.000	0.001	0.004	0.007
Phenanthrene	3	Phe	0.000	0.000	0.000	0.000	0.005	0.007
Anthracene	3	Ant	0.427	0.848	0.003	0.006	0.004	0.005
Fluoranthene	4	FL	0.412	0.824	0.001	0.001	0.000	0.000
Pyrene	4	Pyr	0.000	0.000	0.001	0.001	0.001	0.002
Benzo(a)anthracene	4	BaA	2.703	5.345	0.064	0.087	0.182	0.321
Chrysene	4	Chr	0.005	0.010	0.002	0.004	0.005	0.010
Benzo(k)fluoranthrene	4	BkFL	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(a)pyrene	5	BaP	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(b)floranthrene	5	BbFL	0.000	0.000	0.000	0.000	0.000	0.000
Indeno(1,2,3)pyrene	5	Ind	0.000	0.000	0.000	0.000	0.000	0.000
Dibenzo(a,h)anthracene	5	DBA	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(g,h,i,)perylene	6	BP	0.000	0.000	0.000	0.000	0.000	0.000
TOTAL PAH (mg/L)		∑PAH	3.667	7.251	0.071	0.088	0.214	0.316
TOTAL CARCINOGENIC PAHs		∑CPAH	2.708	0.955	0.065	0.022	0.187	0.064

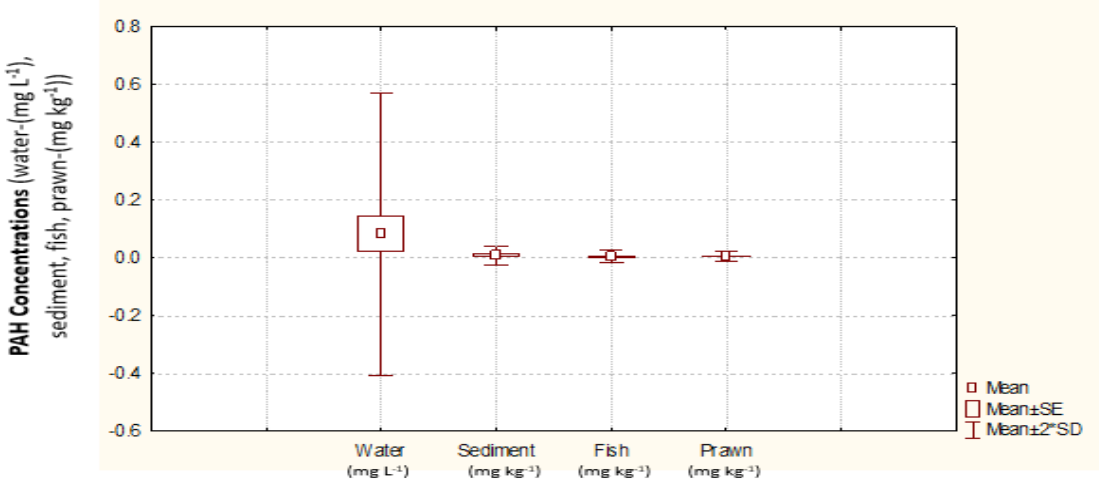

Fig. 2: Total mean concentrations of PAHs in environmental matrices from Bonny River, Southern Nigeria

Table 3: Concentrations of PAHs in sediment (mg/kg) from Bonny River, Southern Nigeria

PAHs	Ring Type	Code	STATIONS					
			KURUMA		COAL BEACH		AMAMARIAH	
			Mean	SD	Mean	SD	Mean	SD
Naphthalene	2	NaP	0.000	0.000	0.000	0.000	0.001	0.001
Acenaphthylene	3	AcPY	0.005	0.009	0.003	0.007	0.002	0.004
Acenaphthene	3	AcP	0.001	0.002	0.006	0.007	0.001	0.001
Fluorene	3	Flu	0.007	0.009	0.005	0.008	0.003	0.003
Phenanthrene	3	Phe	0.022	0.040	0.001	0.001	0.005	0.006
Anthracene	3	Ant	0.017	0.032	0.025	0.027	0.003	0.003
Fluoranthene	4	FL	0.008	0.010	0.014	0.018	0.007	0.006
Pyrene	4	Pyr	0.008	0.014	0.023	0.046	0.005	0.007
Benzo(a)anthracene	4	BaA	0.083	0.116	0.061	0.079	0.062	0.062
Chrysene	4	Chr	0.009	0.017	0.005	0.010	0.000	0.000
Benzo(k)fluoranthrene	4	BkFL	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(a)pyrene	5	BaP	0.000	0.000	0.002	0.004	0.000	0.000
Benzo(b)floranthrene	5	BbFL	0.000	0.000	0.002	0.004	0.000	0.000
Indeno(1,2,3)pyrene	5	Ind	0.000	0.000	0.000	0.000	0.000	0.000
Dibenzo(a,h)anthracene	5	DBA	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(g,h,i,)perylene	6	BP	0.000	0.000	0.000	0.000	0.000	0.000
TOTAL PAH (mg/kg)		∑PAH	0.159	0.196	0.146	0.204	0.089	0.072
TOTAL CARCINOGENIC PAHs		∑CPAH	0.091	0.029	0.070	0.021	0.062	0.022

Table 4: Concentrations of PAHs in fish (mg/kg) from Bonny River, Southern Nigeria

PAHs	Ring Type	Code	STATIONS					
			KURUMA		COAL BEACH		AMAMARIAH	
			Mean	SD	Mean	SD	Mean	SD
Naphthalene	2	NaP	0.000	0.001	0.000	0.000	0.000	0.000
Acenaphthylene	3	AcPY	0.005	0.011	0.013	0.016	0.000	0.000
Acenaphthene	3	AcP	0.010	0.013	0.027	0.035	0.001	0.002
Fluorene	3	Flu	0.002	0.003	0.005	0.006	0.000	0.000
Phenanthrene	3	Phe	0.009	0.011	0.013	0.015	0.003	0.006
Anthracene	3	Ant	0.006	0.012	0.006	0.010	0.004	0.008
Fluoranthene	4	FL	0.005	0.011	0.003	0.006	0.003	0.005
Pyrene	4	Pyr	0.001	0.002	0.000	0.000	0.000	0.000
Benzo(a)anthracene	4	BaA	0.017	0.021	0.060	0.060	0.049	0.048
Chrysene	4	Chr	0.002	0.004	0.000	0.000	0.002	0.004
Benzo(k)fluoranthrene	4	BkFL	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(a)pyrene	5	BaP	0.001	0.003	0.000	0.000	0.004	0.009
Benzo(b)floranthrene	5	BbFL	0.002	0.004	0.000	0.000	0.000	0.000
Indeno(1,2,3)pyrene	5	Ind	0.000	0.000	0.000	0.000	0.000	0.000
Dibenzo(a,h)anthracene	5	DBA	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(g,h,i,)perylene	6	BP	0.000	0.000	0.000	0.000	0.000	0.000
TOTAL PAH (mg/kg)		∑PAH	0.059	0.056	0.126	0.104	0.065	0.061
TOTAL CARCINOGENIC PAHs		∑CPAH	0.022	0.006	0.060	0.021	0.055	0.017

Table 5: Concentrations of PAHs in prawn (mg/kg) from Bonny River, Southern Nigeria

PAHs	Ring Type	Code	STATIONS					
			KURUMA		COAL BEACH		AMAMARIAH	
			Mean	SD	Mean	SD	Mean	SD
Naphthalene	2	NaP	0.000	0.000	0.006	0.011	0.000	0.000
Acenaphthylene	3	AcPY	0.002	0.004	0.029	0.057	0.004	0.007
Acenaphthene	3	AcP	0.006	0.012	0.000	0.000	0.022	0.042
Fluorene	3	Flu	0.001	0.001	0.000	0.000	0.008	0.015
Phenanthrene	3	Phe	0.015	0.024	0.008	0.017	0.017	0.033
Anthracene	3	Ant	0.005	0.011	0.001	0.002	0.005	0.006
Fluoranthene	4	FL	0.005	0.011	0.001	0.002	0.002	0.003
Pyrene	4	Pyr	0.001	0.003	0.009	0.019	0.001	0.001
Benzo(a)anthracene	4	BaA	0.015	0.014	0.033	0.030	0.047	0.042
Chrysene	4	Chr	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(k)fluoranthrene	4	BkFL	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(a)pyrene	5	BaP	0.011	0.021	0.004	0.008	0.002	0.003
Benzo(b)floranthrene	5	BbFL	0.004	0.007	0.000	0.000	0.000	0.000
Indeno(1,2,3)pyrene	5	Ind	0.000	0.000	0.000	0.000	0.000	0.000
Dibenzo(a,h)anthracene	5	DBA	0.000	0.000	0.000	0.000	0.000	0.000
Benzo(g,h,i,)perylene	6	BP	0.000	0.000	0.000	0.000	0.000	0.000
TOTAL PAH (mg/kg)		∑PAH	0.015	0.014	0.083	0.110	0.106	0.141
TOTAL CARCINOGENIC PAHs		∑CPAH	0.029	0.006	0.037	0.012	0.048	0.016

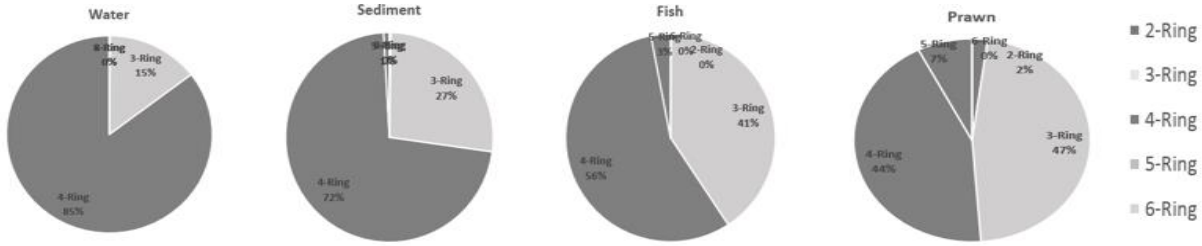

Fig. 3: Mean Percentage (%) Concentration of 2-ring, 3-ring, 4-ring, 5-ring and 6-ring PAHs in water, sediment, fish and prawn samples from Bonny River, Southern Nigeria

Concentrations of PAHs in fish samples

Results of total residual levels of PAHs in fish (*Mugil cephalus)* indicated variations in total PAHs across the stations which ranged from 0.059 mg/kg to 0.126 mg/kg (Table 4). Total mean concentrations were lower in fish compared to water and sediment but concentrations were statistically not significant (p>0.05). Benzo(a)anthracene also had the highest proportion in all the stations accounting for 50.1% of total mean PAHs. However, no significant difference (p>0.05) in the distribution of PAHs between the stations were observed. The PAH concentrations of fish samples were also principally dominated by the 4-rings PAHs compounds accounting for approximately 56.3% of the total PAHs in the fish samples (Fig. 3). The total concentrations of potentially carcinogenic PAHs was 54.5% of the total PAHs in the fish samples. Significant linear relationships were also found between mean PAH concentrations in water and fish (p<0.05, r = 0.94), sediment and fish (p<0.05, r = 0.93) and fish and prawn (p<0.05, r = 0.95).

Concentrations of PAHs in prawn samples

For prawn, the 3 and 4-ring PAHs dominated prawn samples (*Penaeus monodon*) accounting for 56 and 60%, respectively (Fig. 3). Total mean concentrations ranged from 0.018 to 0.106 mg/kg with a mean of 0.068 mg/kg (Table 5). Again, benzo(a)anthracene was the most dominant PAH in prawn similar to results of the other matrices accounting for 46.5% of the total PAHs. Total mean concentrations were lowest in prawn compared to water, sediment and fish but concentrations were not statistically significant (p>0.05).

Total mean concentrations of potentially carcinogenic PAHs was 0.04 mg/kg accounting for 56% of the total PAHs in the prawn samples. Similar to what was observed in fish, significant positive linear relationships were also found between mean PAH concentrations in water and prawn (p<0.05, r = 0.85) and sediment and prawn (p<0.05, r = 0.87).

Identification of PAH sources

Identification PAHs sources were assessed by comparing the concentrations of ring type (Zhang *et al.*, 2004) and also by using ratios of certain individual PAHs concentrations in sediment samples (Doong and Lin, 2004). High ratio of low molecular weight (2 and 3-ring PAHs) to high molecular weight PAHs ($\frac{LPAH}{HPAH}$) (4, 5 and 6-ring PAHs)($\frac{LPAH}{HPAH}$<1) indicate the predominance of petrogenesis (Wise *et al.*, 1988) while ratios of$\frac{Phe}{Ant} < 10, \frac{FL}{Pyr} > 1, \frac{Chr}{BaA} < 1, \frac{FL}{FL+Pyr} > 0.5, \frac{Ant}{Ant+Phe} > 0.1, and\ \frac{BaA}{BaA+Chr} > 0.2$, indicate pyrolytic origin (Doong and Lin, 2004). Results are presented in Table 6.

Table 6: Source identification of PAHs in sediment samples from Bonny River, Southern Nigeria

PAH Ratios	Stations		
	Kuruma	Coal Beach	Amamariah
LPAH/HPAH	0.485	0.381	0.203
Phe/Ant	1.290	0.040	1.750
FL/Pyr	0.969	0.593	1.421
Chr/BaA	0.103	0.078	0.000
FL/FL + Pyr	0.492	0.372	0.587
Ant/Ant+Phe	0.437	0.962	0.364
BaA/BaA+Chr	0.907	0.928	1.000

Values of BSAFs/BAF for individual and ΣPAH in fish and prawn

The BSAFs for ΣPAHs varied between fish and prawn samples (Table 7), with a higher value recorded for fish samples (0.63) which was approximately 5 times more than concentrations in sediment. BSAFs values of individual PAHs were in the range of 0 to 4.51 for fish and 0 to 9.14 for prawn (Table 7), these values were however not statistically significant ($p>0.05$). Assuming the prawn (*Penaeus monodon*) as the main prey of the fish (*Mugil cephalus)*, the bioaccumulation factor (BAF) of PAHs in fish ranged from 0 to 1.36. Negative linear relationships were found between values of log Kow of individual PAH and the corresponding BSAFs for fish ($p>0.05$, $r= -0.301$) and prawn ($p>0.05$, $r = -0.287$). Also, a negative correlation was found between BAFs for individual PAH and corresponding log Kow in fish ($p>0.05$, $r = -0.401$).

Table 7: BSAFs for individual and Total (ΣPAH) in fish and prawn from Bonny River, Southern Nigeria

PAHs	K_{ow}	BSAF		BAF Fish
		Fish	Prawn	
Naphthalene	3.3	0.250	5.500	0.045
Acenaphthylene	3.93	1.895	3.632	0.522
Acenaphthene	3.92	4.515	3.333	1.355
Fluorene	4.18	0.431	0.604	0.714
Phenanthrene	4.46	0.860	1.386	0.620
Anthracene	4.45	0.346	0.254	1.363
Fluoranthene	5.16	0.391	0.295	1.325
Pyrene	4.88	0.028	0.310	0.091
Benzo(a)anthracene	5.76	0.608	0.460	1.322
Chrysene	5.73	0.264	0.000	0.000
Benzo(k)fluoranthrene	6.11	0.000	0.000	0.000
Benzo(a)pyrene	6.13	3.143	9.143	0.344
Benzo(b)floranthrene	5.78	1.143	2.000	0.571
Indeno(1,2,3)pyrene	6.7	0,000	0.000	0.000
Dibenzo(a,h)anthracene	6.5	0.000	0.000	0.000
Benzo(g,h,i,)perylene	6.63	0.000	0.000	0.000
TOTAL PAH (mg/L)		0.636	0.519	1.226

Human health risks through fish and prawn consumption

The estimated average daily intake (EDI), the non-carcinogenic and carcinogenic risks are presented in Table 8. The EDI for the PAHs in fish ranged from 0 to 0.005 mg/kg/day while EDI values for PAHs in prawn ranged from 0 to 0.0001 mg/kg/day. EDI values for Carcinogenic PAHs accounted for 55% and 44% in fish and prawn respectively. Consumption of fish rather than prawn contributed to the highest intake of total PAHs with a mean value of 0.001 mg/kg/day. The average HQs and HIs for PAHs in fish and prawn samples for non-carcinogenic and carcinogenic health risk were below 1 (Table 8). Individual carcinogenic potencies for PAHs showed that benzo(a)anthracene had the highest carcinogenic potency (mg/kg) in fish (0.0042) and prawn (0.0032) samples (Table 8). Estimated excess cancer risk (ECR) for PAHs in fish ranged from 0 to1.014E-06 and 0 to 5.029E-07 in prawn (Table 8).

Distribution of PAHs in water, sediment, fish and prawn from fishing areas affected by oil and gas exploration activities, along Bonny River, Southern Nigeria

The distribution and levels of PAHs in the assessed environmental matrices (water, sediment, fish and prawn) varied among the matrices and between the stations. In general, the total PAH concentrations in water was higher than the other matrices (Fig. 3) and higher at Kuruma than the other stations, but concentrations were however not statically significant ($p<0.05$). Similar finding of higher PAH levels in surface water was also observed for Ekpan creek in the Niger Delta region as reported by Duke (2008). PAHs are known to have low solubility in water as a result of usually high octanol-water partition coefficient (K_{ow}) for majority of the PAHs,hence low availability in water (Rhea *et al.*, 2005). The presence of higher concentrations of PAH in water could therefore be an indication of recent or extensive industrial pollution (Duke, 2008; Li *et al.*, 2007). Mean concentrations of PAHs in water samples from Bonny were higher than data reported from other parts of Nigeria (Anyakora and Coker 2006; Adedayo *et al.*, 2012; Tongo *et al.*, 2017).

A larger presence of PAHs with high molecular weight was found in all samples in all sampling sites indicating the predominance of anthropogenic combustion or pyrolysis processes (Orecchio, 2010). Similar, results was observed for fish and invertebrates of Lagos Lagoon, Nigeria by Alani *et al.* (2012). The source identification of PAHs in this study also corroborates this fact as a strong pyrolytic source fingerprint was observed to be dominant at almost all the stations (Table 5). Correlation studies showed a significant positive correlation in PAHs concentrations between the matrices suggesting common source of pollution.

Benzo(a)anthracene was the most frequently detected PAH in all the matrices assessed. The pattern of benz(a)anthracene (BaA) release into air and water is quite general since it is a universal product of combustion of organic matter. When released into water it will rapidly become adsorbed to sediment or particulate matter in the water column, and bioaccumulate into aquatic organisms (Verbruggen and van Herwijnen, 2011) hence the observed high concentrations in sediment and biota. Benz(a)anthracene have been detected in surface water around heavily industrialized river basins (Ewing *et al.*, 1977; Verbruggen and van Herwijnen, 2011; Tongo *et al.*, 2017). Benz(a)anthracene has been reasonably anticipated to be a human carcinogen (IARC, 1973), therefore the observed concentrations in the matrices especially in fish and prawn calls for urgent concern. In terms of total PAH concentrations, the observed concentration in water (1.32 mg/L) was higher than the recommended level of 0.05 µg/L guideline value for PAHs in drinking water (WHO,1993). In addition, total mean concentration for benzo(a)pyrene (BaP) in prawn exceeded the EU recommended safe limit of 5 µg/kg ww for human prawn consumption, which also calls for serious concern.

Table 8: Estimated average daily intake (EDI), non-carcinogenic and carcinogenic risks are presented carcinogenic potencies

	FISH					PRAWN				
PAHs	**EDI**	**HQ(Non-carcinogenic)**	**HQ (Carcinogenic)**	**Carcinogenic potencies of individual PAHs**	**ECR**	**EDI**	**HQ(Non-carcinogenic)**	**HQ (Carcinogenic)**	**Carcinogenic potencies of individual PAHs**	**ECR**
NaP	1.0E-06	5.06E-05	NA	8.33E-08	2.02E-11	8.64E-06	0.000	NA	1.83E-06	1.7E-10
AcPY	7.3E-05	0.018214	NA	0.000006	1.46E-09	5.42E-05	0.014	NA	1.15E-05	1.1E-09
AcP	1.5E-04	NA	NA	1.24E-05	3.02E-09	4.32E-05	NA	NA	9.17E-06	8.6E-10
Flu	2.5E-05	0.000422	NA	2.08E-06	5.06E-10	1.38E-05	0.000	NA	2.92E-06	2.8E-10
Phe	9.9E-05	0.002479	NA	8.17E-06	1.98E-09	6.21E-05	0.002	NA	1.32E-05	1.2E-09
Ant	6.3E-05	NA	NA	5.22E-05	1.27E-08	1.81E-05	NA	NA	3.83E-05	3.6E-09
FL	4.4E-05	0.000148	NA	3.65E-06	8.85E-10	1.30E-05	0.000	NA	2.75E-06	2.6E-10
Pyr	4.0E-06	0.000101	NA	3.33E-07	8.1E-11	1.73E-05	0.000	NA	3.67E-06	3.5E-10
BaA	5.1E-04	0.016904	NA	0.004176	1.01E-06	1.49E-04	0.005	NA	0.003158	3.0E-07
Chr	1.4E-05	NA	1.03E-05	1.17E-05	2.83E-09	0.00E+00	NA	0	0	0.0E+00
BkFL	0.0E+00	NA	0	0	0.0E+00	0.00E+00	NA	0	0	0.0E+00
BaP	2.2E-05	NA	1.63E-07	0.001833	4.45E-07	2.51E-05	NA	1.84E-07	0.005333	5.0E-07
BbFL	8.1E-06	NA	5.91E-06	6.67E-05	1.62E-08	5.50E-06	NA	4.02E-06	0.000117	1.1E-08
Ind	0.0E+00	NA	0	0	0.0E+00	0.00E+00	NA	0	0	0.0E+00
DBA	0.0E+00	NA	0	0	0.0E+00	0.00E+00	NA	0	0	0.0E+00
BP	0.0E+00	NA	0	0	0.0E+00	0.00E+00	NA	0	0	0.0E+00
		HI =0.0388	HI = 0.00002	∑B(A)Pteq =0.0062		HI = 0.0212		HI = 4.20E-06	∑B(A)Pteq =0.0087	

Bioaccumulation of PAHs in fish and prawn from Bonny River, Southern Nigeria

BSAF values for ΣPAHs were observed to be higher in the bottom-dwelling fish, (*Mugil cephalus*) than in the prawn (*Penaeus monodon*) (Table 6). The feeding habit of the fish as an omnivorous detritus feeder may contribute to the greater BSAF values observed in the mullet fish (Zhou *et al.*, 1998) since close proximity to bottom sediment increases the chances of greater accumulation of PAHs from bottom sediment (Zhou and Wong, 2000). Similar results of higher BSAFs of contaminants in organisms with close vicinity to bottom sediment have been reported (Leung *et al.*, 2010; Adeniyi *et al.*, 2008). Results therefore infer that sediment-feeding behavior of organism could generally affect the extent of PAH bioaccumulation in aquatic species. BSAFs for individual PAHs : Acenaphthylene, Acenaphthene, Fluorene, Benzo(a)pyrene and Benzo(b)floranthrene in fish and Naphthalene, Acenaphthylene, Acenaphthene, PhenanthreneFluorene, Benzo(a)pyrene and Benzo(b)floranthrene in prawn as BSAF values were above 1. BSAF values less than one indicate metabolism of the chemicals or the system not reaching a steady state (Thorsen, 2003). Observed BSAF values of these chemicals therefore suggests the tendency to accumulatein these species. Assuming the prawn (*Penaeus monodon*) as the main prey of the fish (*Mugil cephalus)*, the bioaccumulation factor (BAF) of ΣPAHs in fish showed evidence of bioaccumulation (1.23) of PAHs in fish from prawn consumption. Furthermore, the observed negative linear relationships between values of log Kow of individual PAH and the corresponding BSAFs/BAF for fish and prawn is expected as high molecular weight PAHs with high Kow values tend to bind more tightly with the sediments resulting in lower bioavailability and bioaccumulation in fish.

Risk consideration of PAHs in fish and prawn from Bonny River, Southern Nigeria

Daily dietary intake of PAHs (mg/kg body weight/day) through fish and prawn consumption for an adult weighing 70kg showed that consumption of fish from Bonny River contributed the highest intake of PAHs.

The estimated average daily intake (EDI), for individual and carcinogenic PAHs were observed to be lower than the recommended reference dose (RfD) indicating low risk from consumption of fish and prawn from Bonny River. HQs and HIs for PAHs in fish and prawn samples for non-carcinogenic and carcinogenic health risk also showed low potentials for negative health effect to consumers as values were below 1.

Results of the carcinogenic potency of PAHs in fish and prawn showed values for benzo(a)anthracene having the highest carcinogenic potency (mg/kg) in both species. Concentrations of benzo(a)pyrene in fish and prawn showed values exceeding the guideline screening value of 0.67 ng/g (0.00067 mg/kg) wet wt (USEPA, 2000), for human consumption indicating a high potential carcinogenic risk.In addition, results of the estimated excess cancer risk (ECR) from lifetime exposure to PAHs showed ECR value for benzo(a)anthracene in fish (Table 3) exceeding the threshold value of 1×10^{-6} set by USEPA (USEPA, 2000) indicating that lifetime exposure to benzo(a)anthracene through fish consumption would result in cancer risk.

Conflict of Interest

Authors declare there is no conflict of interest associated with the research.

Conclusion

The present results revealed varying levels of PAHs in surface water, sediment, fish (*Mugil cephalus*) and prawn (*Penaeus Monodon*) from fishing areas affected by oil and gas exploration activities, along Bonny River, Southern Nigeria with higher concentrations observed in water samples across sampling sites Higher BSAF levels for ΣPAHs was found for the bottom-dwelling mullet fish (*Mugil cephalus*) while BSAFs for some individual PAHs compounds suggestedtendency for accumulation in fish and prawn tissues. Evidence of bioaccumulation of PAHs in fish (*Mugil cephalus)* from consumption of the prawn (*Penaeus Monodon*) was also obvious from the results. Human risk assessment of PAHs in fish and prawn from Bonny River revealed the exceedance of recommended threshold values in water and for prawn consumption. In addition, results of human health risk assessment suggests possible cancer risk from exposure to benzo (a) anthracene through fish consumption which imperatively, calls for public health and safety concerns.

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