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Research Article

Polycyclic Aromatic Hydrocarbon Levels and Risk Assessment in Water, Sediment and Fish Samples from Alau Dam, Borno State, Nigeria

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Abstract

Background and Objective: Polycyclic aromatic hydrocarbon (PAHs) are of special interest because of their carcinogenicity, mutagenicity and teratogenicity. Their significant importance the awareness about their biochemical and toxicological roles in humans and animals. The objectives are to determine the distribution of PAHs in water, sediment and fish samples and to conduct risk assessment of PAHs levels . **Methodology:** Water, Sediments and fish samples were from Alau Dam for the determination of 17 PAHs. Extraction and cleanup of the samples were carried out using standard analytical procedures. The levels of the studied PAHs were determined using Agilent 7890A GC/MS. **Results:** Sources analysis indicated levels of PAHs as originated mainly from pyrogenic. Results from m-ERM-q in the sediments indicated 11% probability of toxicity which classified the sediments as low priority sites. The PAHs levels in the water samples were below the maximum allowable concentrations (MACs) of 0.005-3.0 mg L^{-1}. The PAHs were observed to be higher in *Heterotis niloticus* dominated in terms of accumulation of PAHs as compared to other fish samples. The average daily dose (ADD) value in the fish studied were less than the tolerable daily dose limit from the daily per capital fish consumption of 0.07 kg for Nigeria. The cumulative probability distributions of calculated incremental life expectancy cancer risk (ILECR) revealed that 3 out of 10,000,000 population are likely to suffer cancer-related illness in their lifetime due to consumption of fish from the study Dam. **Conclusion:** Results from risk assessment of PAHs in the water and sediment, suggested that the detected concentrations were not high enough to cause adverse effects in the aquatic ecosystem.

Key words: PAHs, water, sediments, fish, risk assessment, Alau Dam

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

The Polycyclic Aromatic Hydrocarbons (PAHs or polyaromatic hydrocarbons) have been extensively studied to understand their distribution, fate and effects in the environment[1,2]. The PAHs are of special interest because of their carcinogenicity, mutagenicity and teratogenicity; their significant importance lies on the awareness about their biochemical and toxicological roles in humans and animals[3]. Because of their sources, they are wide spread in the environment. Depending on their volatility, PAHs may be transported far from their original source, ending up in various environmental compartments, although their main environmental sink is the organic fraction of soils and sediments[3-5]. The present of PAHs in Nigeria, particularly Alau Dam would have adverse effect of the end users that used the Dam for domestic, agricultural and fishing activities. With the levels of PAHs in the study area, the risk of developing cancer related illness is high, since based on the available evidence both[6,7] classified a number of PAHs as carcinogenic to animal. The PAHs are potentially toxic and mutagenic to many living organisms, such as marine plants and animals[8]. The lower molecular weight PAHs (LMW PAHs) are acutely toxic but non-carcinogenic to many aquatic organisms, whereas, the high molecular weight PAHs (HMW PAHs) are strongly carcinogenic and mutagenic[9].

Alau Dam is located in Maiduguri, Borno State, Nigeria. The Dam is 9 m high with a square reservoir area of about 50 km^2. The maximum storage capacity is 112 m^3. Alau Dam received water from River Yedseram and River Gombole which meet at a confluent at Sambisa and flow as River Ngada into Alau Dam. Sambisa forest is a forest in Borno State, North east Nigeria. It is the southwest part of Chad Basin National Park about 60 km Southeast of Maiduguri, the capital of Borno State. Alau Dam is also use for commercial fishing activities. The Dam level rises during the rainy season (June-September). Socio-economic activities within the Dam include small and large scale agriculture, grazing, fishing and other activities, which are directly dependent on the Dam. The Dam is the main source of fish and vegetables to the state and neighboring states within and outside the study area. The domestic water supply within Maiduguri metropolis also come from this Dam. Alau Dam received a wide variety of waste from agricultural land and from activities of insurgency within the Sambisa forest. Industrial effluents, farming activities, wastewater discharge from residential sources, pollution from vehicle exhaust and sewages contain organic and inorganic contaminants. These are directly dumped into the waterways by humans or during run-off by rainfall, also the solid waste discharged as a results of insurgency activities within the sambisa forest flows directly into the Dam. This waste generated might contaminates Alau Dam with a variety of PAH acting as point sources. However, domestic usage and agricultural activities are carried out in the Dam without due regard to the chemistry of the water. Thus, the accumulation of PAHs by fish and the contamination of the aquatic environment by PAHs is viewed with serious concern; as it might ultimately, adversely affect humans and other species that depend on Dam as a means of survival. No information is available on the distribution and levels of PAHs in the Dam.

This study has three main objectives: First, to determine the spatial distribution of PAHs in sediments and water samples of Alau Dam, secondly, to assess the levels of PAHs in fish samples and thirdly, to conduct risk assessment, by evaluating the human health risk induced by PAHs.

MATERIALS AND METHODS

Sample and sampling: This study was conducted in 2017. The water and sediment samples were collected twelve times a month from each of the sampling points for a period of 5 months, beginning from July-November, 2017. A total of 36 samples were collected monthly, given a total of 180 samples each of water and sediments. Similarly, the study fish samples were collected thrice a month for a duration of 5 months beginning from July-November, 2017. In each of the month, a total of 30 samples were collected, given a total of 90 for each of the study fish. A total of 450 fish samples were collected for PAHs analysis.

Water samples: Water samples were collected from 3 sampling point designated S_1-S_3. Point S1 is located at the point of flow of water into the Dam. Point S2 to S3 was located 100 m from each other. The water samples was collected using plastic containers by dipping 1-5 cm below the top layer of the water and placed in an amber glass. The collected water samples were preserved in an ice box. The samples were transported to the Chemistry Laboratory, University of Maiduguri and stored in a refrigerator at 4°C for further analysis.

Sediment samples: Sediment samples were collected within Alua Dam using a plastic hand trowel sampler by scooping 1-5 cm of the top layer sediment. One kilogram of sediment samples were collected at each point and placed in an amber glass bottles, the labeled samples were stored in an ice-pack cooler. The samples were transported to the Chemistry Laboratory, University of Maiduguri and stored in a refrigerator at 4°C for further analysis.

Fish samples: Fish samples (*Tilapia zilli*, *Clarias anguillaris* and *Oreochronmis niloticus*) were caught using gill nets from Alau Dam, Konduga Local Government Area, Borno State, Nigeria. Fish samples of uniform size were collected in order to avoid the possible error due to size differences. The fish were labelled with an identification number. The samples of fish were transported to the laboratory on the same day, identified by an expert in the Department of Fisheries, University of Maiduguri and preserved in a refrigerator, pending extraction and analysis.

Extraction and clean-up of PAHs in water samples: Sample extraction were effected by liquid-liquid extraction in a separatory funnel using dimethyl chloride (DCM) as solvent. The sample extract were subsequently filtered through glass wool containing anhydrous sodium sulphate in a glass funnel. This were followed by clean-up using about 2 g of silica gel. The sample extract were allowed to stand for about 30 min and then decanted and concentrated to 1 mL.

Extraction of PAHs in sediment samples: Ten grams of the sample were dried using anhydrous sodium sulphate and 1 mL of 60 µg mL^{-1} o-Terphenyl surrogate standard was added and mixed thoroughly with the sample. About 30 mL of methylene chloride were added and the sample extracted. The sample extract were subsequently filtered through glass wool containing anhydrous sodium sulphate in a glass funnel. Two grams of silica gel were added and allowed to stand for a while. The extract were decanted and allowed to concentrate at room temperature to 1 mL volume.

Extraction of PAHs in fish samples

Preservation and processing: The original samples, until the commencement of the study were preserved by refrigeration at -15°C. The samples were smashed and ground for homogeneity using a mortar and pestle and was weighed and dried using anhydrous sodium sulphate prior to analysis.

Saponification: The homogenized samples were fortified with a surrogate standard solution and saponified with methanolic KOH. After repeated extraction in hexane, further cleanup were carried out with silica gel.

Instrumental analysis of PAHs using GCMS for water samples: The extract were transferred into the vials and analyzed using Agilent 7890A/5975C GC/MS previously calibrated with PAH standards under specific temperature programmed inlet, oven and detector conditions. The equipment was turned out the concentration of the PAHs as the sample details were supplied for water samples.

Instrumental analysis of PAHs using GCMS for sediment and fish samples: The extract were thereafter analyzed using Agilent 7890A GC/MS previously calibrated with PAHs standards.

Carcinogenic risk assessment of PAHs in water samples: Carcinogenic risk (CR) values of polycyclic aromatic hydrocarbons in water via ingestion pathway was predicted from their chronic daily intake (CDI) obtained from the Eq. 1 predicted by Caylak[10] and USEPA[11]:

$$CR = CDI \times SF \tag{1}$$

Where:

CR = Cancer risk
SF = Slope factor
CDI = Chronic daily Intake ingestion pathway

Chronic daily intake via ingestion were calculated by Eq. 2:

$$CDI = \frac{C \times IR \times EF \times ED}{Bw \times AT} \tag{2}$$

Identification of PAHs sources in sediment samples: Diagnostic ratios was used to distinguish the possible sources of PAHs in the sediment. The following ratios was used as source indicators: Ant/Ant+Phe, BaA/BaA+Chr and LMW-PAH to HMW-PAH.

Ecological risk assessment of PAHs in sediment samples: The mean ERM quotient approach was used to evaluate the possible ecotoxicity of PAHs in the sediment. The mean ERM quotient values was calculated according to the method formular suggested by Long *et al.*[12]:

$$m-ERM-q = \sum\left(\frac{Ci}{ERMi}\right)/n$$

Dietary exposed to PAHs in fish: Estimation of human dietary PAHs exposure dosed 9 mg kg^{-1} b.wt./day occurring over a lifetime was determined. The daily BaP equivalent dose of mixture of carcinogenic PAHs compound was calculated for carcinogenicity using the following equation:

$$ADD = \frac{TEQ \times IR \times CF}{Bw}$$

These exposure assumption was made to be consistent with EPA guidance on assumption on reasonable maximum exposure[11]. Where, IR is the ingestion or intake rate of carcinogenic PAHs based on average fish consumption rate set at 68.5 g/day per person from the annual per capital fish consumption of 25 kg for Nigeria[13], CF is the conversion factor (0.000001 mg μg^{-1}) and BW represents body weight which is set at 70 kg.

Carcinogenic risk calculation for fish samples: The total risk due to exposure to mixture of carcinogenic PAHs is the product of the dietary carcinogen exposure dose (mg kg^{-1} b.wt./day) and benzo(a)pyrene's slope factor value.

$$\text{Risk (carcinogenic)} = \text{Average daily dose} \times \text{slope factor}$$

Data analysis: Data obtained were presented as exponential and one way analysis of variance (ANOVA) and used to assess whether PAHs varied significantly between samples. Probabilities less than 0.05 ($p<0.05$) were considered statistically significant.

RESULTS

Concentrations of PAHs in water and sediment samples: The mean concentrations of some polycyclic aromatic hydrocarbon in water and sediment samples from points S1 to S3 of Alau Dam, Borno State, Nigeria are as presented in Table 1. Among the PAHs studied in the water sample, dibenz(a.h)anthracene was observed to have the highest concentration at point S1 with a value of 5.40E-04 µg L^{-1}, while benzo(k)fluoranthene 40E-04 µg L^{-1} benzo(a)pyrene recoded the second highest concentrations of 40E-04 and 3.40E-04 µg L^{-1}, respectively. The highest total concentration of 2.37E-03 µg L^{-1} was observed at point S1, while point S2 shows the lowest value of 1.13E-03 µg L^{-1}. Table 2 show the mean concentrations of some polycyclic aromatic hydrocarbon in sediment samples from points S1 to S3 of Alau Dam, Borno State, Nigeria. The concentration of naphthalene ranged from 1.20E-01 to 1.60E-01 mg kg^{-1}; 1.40E-01 to 1.60E-01 mg kg^{-1} 2-methylnaphthalene; 1.20E-01 to 2.20E-01 mg kg^{-1} acenaphthylene; For sediment samples, benzo(a)pyrene shows the highest concentration ranging from 8.30E-01 to 9.70E-01 across the sampling points.

Concentrations of PAHs in fish samples: The mean concentrations of some polycyclic aromatic hydrocarbon in *Tilapia* zilli, *Clarias anguillaris* and *Hetrotius niloticus* from Alau Dam are as presented in Table 3. The highest total

Table 1: Concentrations of polycyclic aromatic hydrocarbon (µg L^{-1}) in water sample from different locations of Alau Dam

PAHs	MACs	S1	S2	S3
Naphthalene	3	4.00E-05	2.00E-05	1.00E-05
2-methyl Naphthalene	3	5.00E-05	3.00E-05	2.00E-05
Acenaphthylene	3	2.00E-05	5.00E-05	5.00E-05
Acenaphthene	3	2.00E-05	5.00E-05	4.00E-05
Fluorene	3	3.00E-05	1.00E-05	1.00E-05
Phenanthrene	3	5.00E-05	1.00E-05	2.00E-05
Anthracene	3	2.00E-05	3.00E-05	2.00E-05
Fluoranthene	3	4.00E-05	3.00E-05	3.00E-05
Pyrene	3	3.00E-05	5.00E-05	4.00E-05
Benz(a)anthracene	0.005	9.00E-05	8.00E-05	7.00E-05
Chrysene	-	7.00E-05	9.00E-05	8.00E-05
Benz(b)fluoranthene	0.005	1.50E-04	7.00E-05	9.00E-05
Benz(k)fluoranthene	-	4.30E-04	8.00E-05	1.60E-04
Benz(a)pyrene	0.005	3.40E-04	1.30E-04	2.30E-04
Dibenz(a,h)anthracene	0.005	5.40E-04	1.10E-04	1.80E-04
Benzo(g,h,i)perylene	3	1.70E-04	1.30E-04	1.40E-04
Indinol(1,2,3-cd)pyrene	0.005	2.80E-04	1.60E-04	2.80E-04
Σ of 17 PAHs		2.37E-03	1.13E-03	1.47E-03

MACs: Maximum allowable concentrations (ATSDR[15])

Table 2: Concentrations of polycyclic aromatic hydrocarbon (mg kg^{-1}) in sediment sample from different locations of Alau Dam

PAHs	MACs	S1	S2	S3
Naphthalene	1	1.20E-01	2.10E-01	1.60E-01
2-methyl Naphthalene	1	1.40E-01	1.60E-01	1.40E-01
Acenaphthylene	3	1.20E-01	1.70E-01	2.20E-01
Acenaphthene	3	1.30E-01	2.20E-01	3.20E-01
Fluorene	3	1.50E-01	3.20E-01	1.70E-01
Phenanthrene	3	2.30E-01	2.60E-01	2.10E-01
Anthracene	3	3.20E-01	1.80E-01	2.40E-01
Fluoranthene	3	1.80E-01	3.40E-01	2.80E-01
Pyrene	3	1.60E-01	2.70E-01	3.30E-01
Benz(a)anthracene	0.15	5.40E-01	5.60E-01	6.70E-01
Chrysene	-	7.40E-01	6.50E-01	7.20E-01
Benz(b)fluoranthene	0.3	8.30E-01	5.70E-01	9.10E-01
Benz(k)fluoranthene	-	8.20E-01	7.80E-01	6.30E-01
Benz(a)pyrene	0.3	9.10E-01	9.70E-01	8.30E-01
Dibenz(a,h)anthracene	0.3	7.40E-01	6.80E-01	5.50E-01
Benzo(g,h,i)perylene	3	6.70E-01	7.80E-01	4.90E-01
Indinol(1,2,3-cd)pyrene	-	5.60E-01	6.40E-01	8.70E-01
Σ of 17 PAHs		7.36E+00	7.76E+00	7.74E+00

concentration of 6.00E-01 mg kg^{-1} was observed in *hetrotius niloticus*, while *Tilapia zilli* shows the lowest total value of 3.09E-01 mg kg^{-1}.

Carcinogenic risk values of PAHs in water samples: The carcinogenic risk values of some PAHs in water samples from points S1 to S3 based on adult and children are as presented in Table 4. The value of benzo(a)anthracene ranged from 3.74E-07 to 5.91E-07; 3.27E-09 to 5.91E-09 chrysene. benzo(a)pyrene and dibenz(a.h)anthracene shows the highest cancer risk values of 6.08E-06 to 2.23E-05 and 5.14E-06 to 3.55E-05, respectively when compared to other PAHs. The highest value of all the PAHs was detected in the adult, while the lowest values were detected in children.

Table 3: Total concentrations of polycyclic aromatic hydrocarbon (mg kg^{-1}) in fish samples from Alau Dam

PAHs	*Tilapia zilli*	*Clarias anguillaris*	*Hetrotius niloticus*
Naphthalene	9.00E-03	8.00E-03	1.70E-02
2-methyl Naphthalene	1.10E-02	1.50E-02	2.60E-02
Acenaphthylene	1.10E-02	1.10E-02	2.20E-02
Acenaphthene	9.00E-03	1.30E-02	2.20E-02
Fluorene	1.00E-02	1.30E-02	2.30E-02
Phenanthrene	1.10E-02	7.00E-03	1.80E-02
Anthracene	7.00E-03	9.00E-03	1.60E-02
Fluoranthene	1.20E-02	1.30E-02	2.50E-02
Pyrene	7.00E-03	1.10E-02	1.80E-02
Benz(a)anthracene	2.30E-02	2.30E-02	4.60E-02
Chrysene	3.00E-02	3.70E-02	6.70E-02
Benz(b)fluoranthene	2.90E-02	4.00E-02	6.90E-02
Benz(k)fluoranthene	3.20E-02	2.40E-02	5.60E-02
Benz(a)pyrene	3.00E-02	2.60E-02	5.60E-02
Dibenz(a,h)anthracene	2.70E-02	2.10E-02	4.80E-02
Benzo(g,h,i)perylene	2.30E-02	2.70E-02	5.00E-02
Indinol(1,2,3-cd)pyrene	2.80E-02	2.60E-02	5.40E-02
Σ of 17 PAHs	3.09E-01	3.24E-01	6.33E-01

Diagnostic ratio of PAHs in sediment: Table 5 showed the diagnostic ratio of polycyclic aromatic hydrocarbon in sediment sample from points S1 to S3 from Alau Dam, Borno State, Nigeria. The ratio of BaA/BaA+Chr ranged from 0.42-0.48; 0.41-0.58 for Ant/Ant+Phe; 0.46-0.55 for Flua/Flua+Pyr and 0.19-0.24 for LMW/HMW.

Mean effect range medium (ERM) quotient of PAHs in sediment samples: Table 6 showed the mean effect range medium (ERM) quotient of polycyclic aromatic hydrocarbon in Sediment. Naphthalene was observed to show the lowest ERM value which ranged from 5.71E-05 to 1.00E-04, while dibenz(a.h)antracene shows the highest ERM values of 2.12E-03 to 2.85E-03. The highest ERM values were detected within the high molecular weight PAHs when compared to low molecular weight PAHs. Point S2 shows the highest total mean effect range medium (ERM) quotient with a value of 8.99E-03, while point S3 shows the lowest value of 7.84E-03.

Table 4: Cancer risk of some carcinogenic polycyclic aromatic hydrocarbon in water samples

	S1		S2		S3	
PAHs	Adult	Children	Adult	Children	Adult	Children
Benz(a)anthracene	5.91E-07	4.21E-07	5.26E-07	3.74E-07	4.60E-07	3.27E-07
Chrysene	4.60E-09	3.27E-09	5.91E-09	4.21E-09	5.26E-09	3.74E-09
Benz(b)fluoranthene	9.86E-07	7.02E-07	4.60E-07	3.27E-07	5.91E-07	4.21E-07
Benz(k)fluoranthene	2.83E-06	2.01E-06	5.26E-07	3.74E-07	1.05E-06	7.48E-07
Benz(a)pyrene	2.23E-05	1.59E-05	8.54E-06	6.08E-06	1.51E-05	1.08E-05
Dibenz(a.h)anthracene	3.55E-05	2.53E-05	7.23E-06	5.14E-06	1.18E-05	8.42E-06
Indinol(1,2,3-cd)pyrene	1.84E-07	1.31E-07	1.05E-07	7.48E-08	1.84E-07	1.31E-07
Total	6.24E-05	4.44E-05	1.74E-05	1.24E-05	2.92E-05	2.09E-05

Table 5: Diagnostic ratio of polycyclic aromatic hydrocarbon in sediment samples

Points	BaA/BaA+Chr	Ant/Ant+Phe	Flua/Flua+Pyr	LMW/HMW
S1	0.42	0.58	0.52	0.19
S2	0.46	0.41	0.55	0.24
S3	0.48	0.53	0.46	0.23
Mean Ratio	0.36	0.52	0.53	0.66

Table 6: Mean effect range medium (ERM) quotient of polycyclic aromatic hydrocarbon in sediment samples

PAHs	ERM SSG	S1	S2	S3
Naphthalene	2100	5.71E-05	1.00E-04	7.62E-05
2-methyl Naphthalene	670	2.09E-04	2.39E-04	2.09E-04
Acenaphthylene	640	1.88E-04	2.66E-04	3.44E-04
Acenaphthene	500	2.60E-04	4.40E-04	6.40E-04
Fluorene	540	2.78E-04	5.93E-04	3.15E-04
Phenanthrene	1500	1.53E-04	1.73E-04	1.40E-04
Anthracene	1100	2.91E-04	1.64E-04	2.18E-04
Fluoranthene	5100	3.53E-05	6.67E-05	5.49E-05
Pyrene	2600	6.15E-05	1.04E-04	1.27E-04
Benz(a)anthracene	1600	3.38E-04	3.50E-04	4.19E-04
Chrysene	2800	2.64E-04	2.32E-04	2.57E-04
Benz(b)fluoranthene	-	-	-	-
Benz(k)fluoranthene	-	-	-	-
Benz(a)pyrene	1600	5.69E-04	6.06E-04	5.19E-04
Dibenz(a.h)anthracene	260	2.85E-03	2.62E-03	2.12E-03
Benzo(g.h.i)perylene	330	2.03E-03	2.36E-03	1.48E-03
Indinol(1,2,3-cd)pyrene	950	5.89E-04	6.74E-04	9.16E-04
	M-ERM-Q	8.17E-03	8.99E-03	7.84E-03

Table 7: Average daily dose (mg kg^{-1}/day) for polycyclic aromatic hydrocarbon in the three fish samples

PAHs	No. of rings	*Tilapia zilli*	*Clarias anguillaris*	*Hetrotius niloticus*
Naphthalene	2	8.81E-12	7.83E-12	1.66E-11
2-methyl Naphthalene	2	1.37E-10	1.47E-11	2.54E-11
Acenaphthylene	3	2.15E-10	1.08E-11	2.15E-11
Acenaphthene	3	3.13E-10	1.27E-11	2.15E-11
Fluorene	3	1.66E-10	1.27E-11	2.25E-11
Phenanthrene	3	2.06E-10	6.85E-12	1.76E-11
Anthracene	3	2.35E-09	8.81E-11	1.57E-10
Fluoranthene	4	2.74E-10	1.27E-11	2.45E-11
Pyrene	4	3.23E-10	1.08E-11	1.76E-11
Benz(a)anthracene	4	6.56E-08	2.25E-09	4.5E-09
Chrysene	4	7.05E-10	3.62E-11	6.56E-11
Benz(b)fluoranthene	5	8.91E-08	3.91E-09	6.75E-09
Benz(k)fluoranthene	5	6.17E-08	2.35E-09	5.48E-09
Benz(a)pyrene	5	8.12E-07	2.54E-08	5.48E-08
Dibenz(a,h)anthracene	5	5.38E-07	2.06E-08	4.7E-08
Benzo(g,h,i)perylene	6	4.80E-09	2.64E-10	4.89E-10
Indinol(1,2,3-cd)pyrene	6	8.51E-09	2.54E-10	5.28E-10
TDD		1.58E-06	5.52E-08	1.20E-07

Table 8: Carcinogenic risk assessment (mg kg^{-1}/day) of some polycyclic aromatic hydrocarbon in fish samples

PAHs	No. of Rings	*Tilapia zilli*	*Clariasanguillaris*	*Hetrotiusniloticus*
Benz(a)anthracene	4	4.79E-08	1.64E-09	3.29E-09
Chrysene	4	5.14E-12	2.64E-13	4.79E-13
Benz(b)fluoranthene	5	6.50E-08	2.86E-09	4.93E-09
Benz(k)fluoranthene	5	4.50E-09	1.71E-10	4.00E-10
Benz(a)pyrene	5	5.93E-06	1.86E-07	4.00E-07
Dibenz(a,h)anthracene	5	3.93E-06	1.50E-07	3.43E-07
Indinol(1,2,3-cd)pyrene	6	6.21E-09	1.86E-10	3.86E-10
ILECR		9.98E-06	3.41E-07	7.52E-07

Average daily dose for PAHs in fish samples: Table 7 showed the daily dose of PAHs in *Tilapia zilli*, *Clarias anguillaris* and *Hetrotius niloticus*. The higher molecular weight PAHs showed the highest ADD values, when compared to lower molecular weight PAHs. The highest total daily dose of 1.58E-06 mg kg^{-1}/day was observed in *Tilapia zilli*, while *Hetrotius niloticus* shows the lowest total value of 5.52E-08 mg kg^{-1}/day.

Carcinogenic risk assessment of PAHs in fish samples: Table 8 showed the carcinogenic risk assessment of PAHs in the liver, gills, intestine and flesh of *Tilapia zilli*, *Clarias anguillaris* and *hetrotius niloticus*. Benzo(a)pyrene shows the total cancer risk value of 1.86E-07 and 5.93E-06 mg kg^{-1}/day across the fish samples, while chrysene shows the lowest cancer risk values of 2.64E-13 and 5.14E-12 mg kg^{-1}/day. *Tilapia zilli* showed the highest value of 9.98E-06 mg kg^{-1}/day, while intestine shows the lowest value of 3.41E-07 mg kg^{-1}/day.

DISCUSSION

The concentrations of all the studied PAHs in the water samples from the sampling points were below the standard of 0.7 µg L^{-1} as stipulated by institute of standard and industrial research of Iran and World health organisation[14]. The highest total concentration of the studied PAHs was detected at point S1 with a value of 2.37E-03 µg L^{-1}, while the lowest level was detected at point S1 with a value of 1.13E-03 µg L^{-1}. The levels of all the PAHs studied were lower than the maximum allowable concentrations as specify by ATSDR[15]. The value of C-PAHs in water samples from all the sample points were lower than the standard limit of 100ng L^{-1} (10^{-4} mg L^{-1}) and were below the standard limit of 0.7 µg L^{-1} as stipulated by ISRI[14], WHO[16], Srogi[17]. The CR values from the present study via ingestion of water for adult and children users from point S1 to S3 are within the safe levels 10^{-6} specified[18,19]. The application of diagnostic ratio and cancer risk assessment in sediment samples is paramount in order to predict the sources of PAHs and evaluate the cancer risk to benthic organisms. The diagnostic ratios used in the present study were BaA/BaA+Chr, Ant/Ant+Phe, Flue/Flue+Pyr and LMW/HMW ratio (Table 6). Ant/Ant+Phe ratio of >0.1 indicate dominance of heavy fuel composition, while <0.1 indicate petroleum source, BaA/BaA+Chr ratio of 0.2-0.35 indicate mixed petrogenic and pyrogenic origin and >0.35 indicate pyrogenic origin[20]. The ratios of BaA/BaA+Chrfrom the present study were between

0.42 and 0.48 with mean of 0.45 suggestive pyrogenic origin. The Ant/Ant+Phe ratios were between 0.41 and 0.58 indicating pyrogenic sources of PAHs. Ratio of Flua/Flua+Pyris used to distinguish between different combustion origins such as burning of liquid fossil fuels or coal wood or grass[21]. The total ratio of Flua/Flua+Pyrconfirm the combustion of fuel and pyrogenic as the main sources of PAHs into the study Dam. The LMW/HMW ratios were lower than <1, this further indicate the pyrogenic source of PAHs to the study Dam.

The Mean ERM quotient (m-ERM-q) were calculated and compared with the screening values. According to Long *et al.*[12], m-ERM-q are categorised according to their possibility of toxicity. Values $\leq$0.1 indicates an 11% probability of toxicity, 0.1-0.5 indicates a 30% probability of toxicity and 0.5-1.5 indicates a 46% probability of toxicity and >1.5 indicates a 75% probability of toxicity[22]. The calculated ERMs of individual PAHs and the total ERM quotient of the studied PAHs were below 0.1 indicating an 11% probability of toxicity and are therefore classified as low priority sites (Table 7). The implication of the 11% probability of toxicity is that there would be minimal effect of PAH on sediment functions such as the capacity to act as substrate for aquatic life.

For all the fish samples study, *Heterotis niloticus* showed the highest PAHs concentrations with total value of 6.33E-01 mg kg^{-1}, while *Tilapia zilli* showed the lowest total value of 3.24E-01 mg kg^{-1}. *Heterotis niloticus* feed on detritus and most species have unusually muscular stomach and pharynx that help in digestion[23] and differences in feeding preferences and general behaviour, as well as the mode of feeding in these species[24]. Results from the present study showed that the high molecular weight PAHs (HMW-PAHs) was generally predominant compared to low molecular weight PAHs (LMW-PAHs). The above variation might be due to the fact that HMW-PAHs readily undergoes bio-degraded persist in the aqueous environment when compared to LMW-PAHs[25,26]. The estimated average daily dose (ADD) of polycyclic aromatic hydrocarbons (PAHs) through the consumption of fish in the study area was less than tolerable daily dose limit from the daily per capital fish consumption of 0.07 kg/day for Nigeria set by the FAO[13]. The cumulative probability distributions of calculated incremental life expectancy cancer risk (ILECR) for *Tilapia zilli*, *Clarias anguillaris* and *Hetrotius niloticus* with a total values of 3.41E-07 and 9.98E-06 mg kg^{-1}/day revealed that 3 out of 10,000,000 and 10 out of 1,000,000 of the population are likely to suffer cancer-related illness in their lifetime due to consumption of fish from the study Dam.

CONCLUSION

Results from the present study showed that the water and sediments of Alau Dam are contaminated by PAHs in all sampling points. The mean concentration of the total PAHs in the water, sediments and fish of the study area were lower than those of other rivers around the world. Among the PAHs study, HMW-PAHs had the highest mean concentrations in the study area. Furthermore, results from diagnostic ratios, showed that pyrogenic sources were found to be responsible in PAH release to the Alau Dam sediment. Generally, the major environmental concern and the ability of developing cancer related illness from Alau Dam in term of Water, sediments and fish contamination is low and not relatively serious. Hence, relevant agencies should be involve in the management of Alau Dam with respect to PAHs contamination.

SIGNIFICANCE STATEMENTS

The present study have showed marked levels of PAHs in the studied rice, and the results would help to educate Nigerian on the levels of PAHs in locally produced rice and the possible harmful effect of PAHs. The study research have not been taken into consideration and generally ignored in Nigeria despite the cases of cancer related illness. Hence, results from this study would assist the State and Federal Environmental Protection Agencies, Nigeria and the public on the levels of PAHs in the study environment.

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