Concentration And Risk Assessment of Selected Polycyclic Aromatic Hydrocarbons in Water and Sediment Samples from Ezu-River, Anaku, Anambra State

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Abstract- ***This study was undertaken to investigate the occurrence of selected polycyclic aromatic hydrocarbons (PAHs) in sediments and water samples of Ezu River. The PAHs of interest were the ones with carcinogenic characteristics. Collected samples were carefully analyzed using Gas chromatography with mass spectrometer detector. benzo [a] pyrene and benzo[b] fluoranthene were detected in the samples analyzed in large quantity as compared to other detected PAHs. Risk assessments were carried out on the analyzed samples using the USEPA model. Results shows that the water samples can be recommended for consumption as the hazard index were found to be less than one.***

Indexed Terms- PAHs, Risk Assessment, Hazard Index.

I. INTRODUCTION

Pollution of water bodies originates from municipal, domestic, agricultural and industrial activities and may contain persistent organic pollutants such as polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). Many PAHs are known to be carcinogenic, mutagenic or teratogenic, which pose serious health effects to population exposed to them (Wang *et al.* 2007,). There has been notable presence of PAHs in the environment with increased detrimental health effects over the years; however, global concentrations may have stabilized due to water and air quality regulation (Van Drooge, 2013). High concentrations of PAHs in the environment are hazardous to human and aquatic life through its discharge from various sources, therefore the level of PAHs in water and sediment should be within the permissible limits. In most rural areas, large amount of the waste comprises of mainly organic materials, though there are considerable proportions of incomplete combustion of plastic, paper, coal, oil, wood, bushes which are known to be real sources of polycyclic aromatic hydrocarbons and heavy metals.
The concentration of PAHs in sediments is dependent on the size and type of the sediment, areas where they are located, water migration and other environmental factors. When there is a change in environment condition, the adsorbed PAHs may be re-released into the water by biological and chemical processes, which leads to secondary pollution of the surrounding environment. (Wang *et al.,*2010, Lu *et al.,* 2012). Polycyclic aromatic hydrocarbons in the environment may be generated from three sources which are petrogenic, pyrogenic, and biogenic processes (Wang *et al.,* 2007).

PAHs are not synthesized chemically for industrial purposes. The major sources of PAHs are the incomplete combustion of organic material such as coal, oil and wood. Kafilzadeh *et al.,* (2011) determined the levels polycyclic aromatic hydrocarbons in water and sediments by using Liquid-liquid extraction water samples, while PAHs in sediments were extracted using Soxhlet Extraction and finally analyzed by means of Gas chromatography with mass spectrometer detector. Results showed that in water samples, the highest concentration was found in acenaphthene whereas fluoranthene was the most important pollutant in sediments. This study is aimed at assessing the level of polycyclic aromatic hydrocarbons (PAHs) in water and sediments in Ezu-

River, Anaku, Anambra state, Nigeria with the various risks associated via different exposure route and also help to generate a toxicology profile for the distribution of PAHs in water and sediment and fish in the studied river.

II. MATERIALS AND METHODS

2.1 Apparatus Used

The equipment used in this study includes: 25ml Burettes, 250ml conical flasks, volumetric flask, Erlenmeyer flask 100ml and 250ml, Separatory funnel, Fractionating column, Beakers, Filter papers, Aluminum foil, Spatula, Crucible, Desiccators, Water bath, Magnetic stirrer/Glass rod, Electro-thermal heater, Fume cupboard, pH meter, Mortar and pestle, Oven, Heating mantle, Centrifuge tube, Glass wool, Rotatory evaporator, Sonicator, Gas chromatograph (Agilent 6890/Agilent mass detector 5973N, USA),

2.2 Chemical reagents used

Concentrated H2SO4, Distilled-water, Concentrated perchloric acid (HClO4), O-phosphoric acid (H3PO4), n-Hexane, Anhydrous sodium sulphate, 1:1 nitric acid, Sodium hydroxide (50%), Phenolphthalein (1%) and Boric acid (2%), Dichloromethane, Anhydrous sodium sulphate (Analar grade), Silica gel, concentrated nitric acid (HNO3), Ferrous ammonium sulphate, Ethanol, pH 4.0 and 7.0 buffer solutions, Mixed standard containing the USEPA 16 priority PAHs (sigma).

2.3 Sample collection

2.3.1 Sampling location

The sampling site is Ezu-river, located in Anaku, Anambra State between Latitude: 6° 21' 40" N and Logitude: 6° 51' 38" N in Ayamelum Local Government Area. It is bordered by "Omambala", the native name of Anambra River. It is mostly dominated by the Igbo's. Occupations in the community are mostly fishing, farming and hunting.

2.3.2 Sediment sample

Sediment samples of 100 grams were collected with a clean bottle in four different locations in the water at 5cm depth and homogenized into a composite sample. It was stored in labeled polythene bags and taken to the laboratory for analysis. Furthermore, they were air dried for 2 days, stones and debris were removed from the samples and then pulverized and passed through a 2mm mesh sieve to remove debris.

2.3.3 Water sample

Water samples (2.5L) were collected in a clean glass bottles at the water surface and 50cm below water level from four different sites. The samples were homogenized to get a composite sample and pH test was carried out. The bottles were tightly capped and immediately transported to the laboratory for further analysis.

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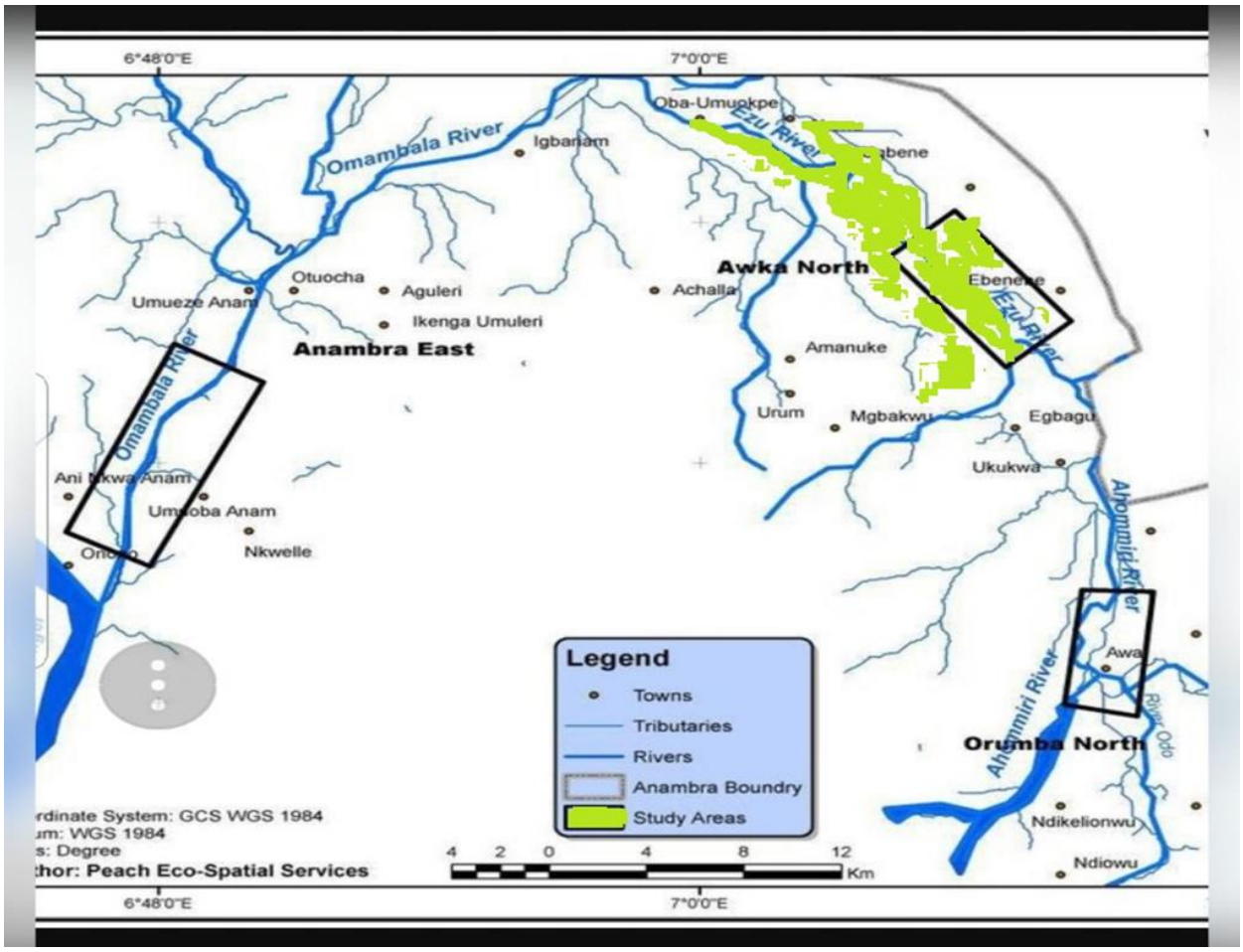

Figure 1: Map of sampling location

2.4 Extraction of polycyclic aromatic hydrocarbon (PAHs) in water sample (USEPA, 2016, Method).

Twenty grams (20g) of 100mm mesh silica gel was baked at 105^{o}C in an oven overnight. The baked silica gel was mixed with 30ml hexane to form slurry. The fractionating column was packed with glass wool followed by the slurry silica gel and 3grams of anhydrous sodium sulphate was then added to absorb water. 100ml of water sample was measured using a graduated cylinder into a clean separating funnel and 50ml of 1:1 Hexane-Acetone mix solvent was added. The separating funnel was sealed and shaken for 2 minutes with periodic venting to release the inbuilt pressure. The mixture was allowed to stand for 10minutes for separation into distinct layers. The organic layer (i.e the upper layer) was collected in a round bottom flask. The extraction procedure was repeated until all the oil is extracted and concentrated to 2ml using Rotary evaporator. The sample is then ready to be fractionated into aromatic (PAH) fractions using fractionating column. The concentrated sample was transferred into the fractionating column using 1ml pipette and eluted with 10ml dichloromethane into a flat bottom flask. The eluate was transferred into a round bottom flask and re-concentrated again to 2ml. The concentrated 2ml sample was pipetted into a Teflon screw-cap vial and analyzed for PAH using the Gas Chromatography-mass spectrometer.

2.4.1 Extraction of polycyclic aromatic hydrocarbon (PAHs) in sediment sample (USEPA, 2016 method).

Ten grams (10g) of 100mm mesh silica gel was baked at 105^{o}C in an oven overnight. The baked silica gel was mixed with 15ml dichloromethane to form slurry. The fractionating column was packed with glass wool followed by the slurry silica gel and 3grams of anhydrous sodium sulphate was then added to absorb

water. 10 grams of sediment sample was weighed and homogenized in a mortar with 10grams of anhydrous sodium sulphate until a completely dried homogenate was obtained. 20 ml of dichloromethane was added to the dried homogenate sediment samples inside a 100ml beaker and the beaker containing the sample was then placed in the sonicator for about 15minutes at about 70°C. (Note this was done in triplicates to extract all analyte present in the sample). After sonication, 10g of anhydrous sodium sulphate was added to the sample to remove any residual water molecules. This was allowed to stand for about 15minutes. The extracts were then transferred into a round bottom flask and then concentrated at about 2ml using a rotary evaporator. The sample is ready to be fractionated into aromatic (PAH) fractions using fractionating column or silica gel cartridge. 1.5ml of the concentrated sample was pipetted into the already conditioned column and eluted with 15ml of dichloromethane. The eluate was collected in a solvent rinsed round bottom flask and then concentrated to 1.5ml. The concentrated sample was pipette into a clean GC vial bottle and capped tightly. The sample was then injected into the GC for PAH analysis using the Gas Chromatography Agilent HP 5890 series II model.

2.5 Human Health Risk Assessment Model

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 through exposure to sediment and consumption of contaminated water studied area. Assessment was carried out for both adults and children for carcinogenic health risk. The reference table for Heavy metals and polycyclic aromatic hydrocarbons (PAHs) carcinogenic and non-carcinogenic risk assessments are presented in Table 3.1 and 3.2 respectively. Risk assessment conducted on PAHs was used by determining the chronic daily intake (CDI); thereafter evaluate the carcinogenic impact to adults and children through ingestion and dermal pathway as shown in equation (1– 2) (USEPA 2020).

2.5.1 Chronic daily intake (CDI) (mg/kg/day) of PAHs in sediment sample

$$CDI-ingestion = \left(\frac{CS \times IRs \times EF \times ED \times RBA \times TR}{BW \times AT}\right) (1)$$

$$CDI-dermal = \left(\frac{CS \times SA \times K_p \times EF \times AF \times ED \times TR}{BW \times AT \times GIABS}\right) (2)$$

Where CS is PAHs concentration in the sediment (mg/kg), IRs is sediment ingestion rate (mg/day) (100mg/day for adults and 200mg/day for children), EF is exposure frequency (350-day year^{-1}), ED is exposure duration (26 years for adults and 6 years for children), TR is target risk (1×10^{-6} mg/mg), BW is body weight (80kg for adults and 15kg for children), AT is average time, (carcinogen =70×365), SA is skin surface area (6032cm^2/day for adults and 2373 cm^2/day for children), K_p: dermal permeability constant (0.001); AF is water adherence factor: (0.2mgcm^{-2} for adults and 0.07mgcm^{-2} for children), GIABS is fraction of contaminant absorbed in gastrointestinal tracts (unit-less) (1.0 for adults and children).

Table 1: Reference value for polycyclic aromatic hydrocarbons (PAHs)

TPAHs	Dermal		Ingestion	
	CSF	RfD	OSF	RfD
Benzo[a]anthracene (BaA)	0.73*	0.03**	0.73*	0.03
Chrysene (Cry)	0.0073*	0.03**	0.0073*	0.03
Benzo[b]fluoranthene (BbF)	0.73*	0.03**	0.73*	0.03
Benzo[k]fluoranthene (BkF)	0.0073*	0.03**	0.0073*	0.03
Benzo[a]pyrene (BaP)	7.3*	0.03**	7.3*	0.03
Dibenzo[a,h]anthracene (DBA)	7.3*	0.03**	7.3*	0.03
Indeno [1,2,3-cd] pyrene (IND)	0.73*	0.03**	0.73**	0.03
Benzo[ghi]perylene (BghiP)	0.073*	0.03**	0.073*	0.03

Total PAHs	7.3*	0.03**	7.3*	0.03

Where: *(USEPA, 2005a; USEPA, 2005b), **(USEPA, CEPA, Verbruggen, 2012). CSF: cancer slope factor (mg/kg/day), OSF: oral slope factor (mg/kg/day), RfD: reference dose

III. RESULT AND DISCUSSION

Table 2: PAHs concentration of surface water and sediment

PAHs	Surface Water	Sediment
*Benz[a]anthracene (BaA)	<0.001	0.01
*Chrysene (Chy)	<0.001	<0.001
*Benzo[b]fluoranthene (BbF)	0.03	0.04
*Benzo[k]fluoranthene (BkF)	<0.001	0.17
*Benzo[a]pyrene (BaP)	0.03	0.02
*Indeno(1,2,3-cd) perylene (IND)	<0.001	0.03
*Dibenz[a,h]anthracene (DBA)	<0.001	0.01
*Benzo[ghi]perylene (BghiP)	<0.001	0.03
Total	0.06	0.49

*Values presented as mean ± standard error of mean; <0.001 = below detection limits (BDL); *PAHs: carcinogenic PAHs*

In the PAHs study conducted, different concentration was detected as shown in Table 2, where benzo [a] pyrene and benzo[b] fluoranthene were detected across all sample sources. According to USEPA (2020) and WHO (2017), benzo[a]pyrene (BaP) is used as a reference value for determining the carcinogenicity of any sample in relation to other 15 priority PAHs due to its ecological and health effect to human contact over a period of time in addition to different environmental matrices. Several studies have shown that PAHs is highly hazardous to human health with genotoxic, neurotoxic and behavioral changes to both adult and children (Loganathan *et al,* 2014). Continuous exposure of PAHs for a period of 350 days as stipulated by USEPA (2020) shows that PAHs can cause damages to human immune, nervous and reproductive system, as 1% of the toxicity of benzo[a]pyrene can damage or destroy red blood cells that is detrimental to persons with leukemia (Russo *et al.,* 2006). Benzo[b]fluoranthene has been associated with gasoline engine exhaust; emissions from burning coal and from oil-fried heating; broiled and smoke food; oils and margarine (Lawal, 2017); and soils, ground water and surface waters at hazardous waste site (WHO, 2017). An overview of carcinogenic PAHs has shown that continuous human exposure of these PAHs can lead to genetic disorder and other chronic health challenges (Ramesh *et al.,* 2010).

3.1 Health and exposure risk assessment of polycyclic aromatic hydrocarbons

Table 3: Carcinogenic CDI of polycyclic aromatic hydrocarbons

	Water		Sediment	
Adult Exposure	Oral Ingestion	Dermal	Oral Ingestion	Dermal
BaA	No Data	No Data	5.14E-09	2.17E-11
BkF	No Data	No Data	8.73E-08	3.69E-10
BbF	2.63E-10	2.12E-07	2.05E-08	8.68E-11
BaP	2.63E-10	2.12E-07	1.03E-08	4.34E-11

DBA	No Data	No Data	5.14E-09	2.17E-11
IND	No Data	No Data	1.54E-08	6.51E-11
BghiP	No Data	No Data	1.54E-08	6.51E-11
∑ PAHs	5.25E-10	4.24E-07	2.52E-07	1.06E-09
Children Exposure	Oral Ingestion	Dermal	Oral Ingestion	Dermal
BaA	No Data	No Data	1.1E-08	2.6E-11
BkF	No Data	No Data	1.86E-07	4.42E-10
BbF	4.73E-10	2.09E-07	4.38E-08	1.04E-10
BaP	4.73E-10	2.09E-07	2.19E-08	5.2E-11
DBA	No Data	No Data	1.1E-08	2.6E-11
IND	No Data	No Data	3.29E-08	7.8E-11
BghiP	No Data	No Data	3.29E-08	7.8E-11
∑ PAHs	9.47E-10	4.19E-07	5.37E-07	1.27E-09

No Data: Analytical data below detection limit; ∑PAHs: sum total of polycyclic aromatic hydrocarbons

Table 3 shows the carcinogenic risk assessment conducted on the samples using USEPA risk formulas as regards different exposure patterns measured in mg/kg/day. The cumulative PAHs for both adults and children are: Surface water – oral (5.25E-10; 9.47E-10), surface water – dermal (4.24E-07; 4.19E-07), sediment – accidental ingestion (2.52E-07; 5.37E-07), sediment – dermal (1.06E-09; 1.27E-09). The cumulative PAHs CDI influence of adults to children was evaluated using similar model in to assess carcinogenic and non-carcinogenic PAHs, as shown in Figure 4.4. The results are: surface water – oral (55.4%; 11.0%), surface water – dermal (101%; 20%), sediment accidental ingestion (46.9%; 47.0%), sediment dermal (83.5%; 16.4%), as such this shows that surface water – dermal exposure was dominant.

Table 4: Cancer Risk of polycyclic aromatic hydrocarbons in adults and children

	Water		Sediment		
Adult Exposure	Oral Ingestion	Dermal	Oral Ingestion	Dermal	Total CR
BaA	No Data	No Data	3.75E-09	1.58E-11	3.77E-09
BkF	No Data	No Data	6.38E-10	2.69E-12	6.40E-10
BbF	1.92E-10	1.55E-07	1.5E-08	6.33E-11	1.70E-07
BaP	1.92E-09	1.55E-06	7.5E-08	3.17E-10	1.62E-06
DBA	No Data	No Data	3.75E-08	1.58E-10	3.77E-08
IND	No Data	No Data	1.13E-08	4.75E-11	1.13E-08
BghiP	No Data	No Data	1.13E-10	4.75E-13	1.13E-10
∑ PAHs	2.11E-09	1.7E-06	1.47E-07	6.23E-10	1.85E-06
Children Exposure					Total CR
BaA	No Data	No Data	8E-09	1.9E-11	8.02E-09
BkF	No Data	No Data	1.36E-09	3.23E-12	1.36E-09
BbF	3.46E-10	1.53E-07	3.20E-08	7.59E-11	1.85E-07
BaP	3.46E-09	1.53E-06	1.60E-07	3.8E-10	1.69E-06
DBA	No Data	No Data	8.00E-08	1.9E-10	8.02E-08
IND	No Data	No Data	2.4E-08	5.7E-11	2.41E-08

BghiP	No Data	No Data	2.4E-10	5.7E-13	2.41E-10
∑ PAHs	3.80E-09	1.68E-06	3.15E-07	7.47E-10	2.00E-06

No Data: Analytical data below detection limit; No CSF: reference value unavailable; ∑PAHs: sum total of polycyclic aromatic hydrocarbons.

The cancer risk was evaluated as shown in Table 4 to derive the cumulative cancer risk (cancer-total). In water, dermal contact appears to be more carcinogenic to human health while in sediment, oral ingestion poses serious carcinogenic risk with respect to time in adult and children. The cumulative total cancer risk for adults and children are 1.85E-06 and 2.00E-06 respectively, which were within USEPA reference values respectively (Verbruggen, 2012).

Hazard quotient was evaluated using non-carcinogenic CDI for different exposure medium in assessed samples to derive the hazard index as shown in Table 5, with the cumulative hazard quotient (hazard index) for adults and children were 4.98E-05 and 2.02E-04, which means that both population conglomerate will not have significant health related issues over a period of time (USEPA, 2020).

Table 5: Hazard Index of polycyclic aromatic hydrocarbons in adults and children

	Water		Sediment		
Adult Exposure	Oral Ingestion	Dermal	Oral Ingestion	Dermal	Total HQ
BaA	No Data	No Data	4E-07	1.69E-09	4.01E-07
BkF	No Data	No Data	6.79E-06	2.87E-08	6.82E-06
BbF	2.04E-08	1.65E-05	1.6E-06	6.75E-09	1.81E-05
BaP	2.04E-08	1.65E-05	7.99E-07	3.37E-09	1.73E-05
DBA	No Data	No Data	4.00E-07	1.69E-09	4.01E-07
IND	No Data	No Data	1.2E-06	5.06E-09	1.2E-06
BghiP	No Data	No Data	1.2E-06	5.06E-09	1.2E-06
∑ PAHs	4.08E-08	3.3E-05	1.67E-05	6.33E-08	4.98E-05
Children Exposure					Total HQ
BaA	No Data	No Data	8.52E-07	1.03E-08	8.65E-07
BkF	No Data	No Data	1.45E-05	1.74E-07	1.47E-05
BbF	1.87E-07	8.25E-05	3.41E-06	4.1E-08	8.62E-05
BaP	1.87E-07	8.25E-05	1.7E-06	2.05E-08	8.44E-05
DBA	No Data	No Data	8.52E-07	1.03E-08	8.63E-07
IND	No Data	No Data	2.56E-06	3.08E-08	2.59E-06
BghiP	No Data	No Data	2.56E-06	3.08E-08	2.59E-06
∑ PAHs	3.73E-07	1.65E-04	3.56E-05	3.85E-07	2.02E-04

No Data: Analytical data below detection limit; ∑PAHs: sum total of polycyclic aromatic hydrocarbon.

Human health risk assessment conducted showed varying chronic daily intake for ingestion and dermal contact via carcinogenic models in all samples. The cancer risk and hazard index were within acceptable USEPA standards, which makes all samples sources fit for human consumption, as extreme care must be taken into consideration for children exposure as compared to adults. As such, the exposure period of any population is dependent on age, sex, body weight, location and proximity to pollution (Verbruggen, 2012).

CONCLUSION

Human health risk assessment showed that both hazard index and total cancer risk were within acceptable limit, as such, proper advocacy and sensitization is needed to assist inhabitants on the health impact of heavy metals and PAHs for their survival. To minimize pollution in the study area:

i. Public awareness and education about the sources and health effects of exposure to heavy metals and PAH should be improved.
ii. Human exposure and health risk assessment studies should be adequately studied to establish risk posed by diverse pollutants and exposure sources to human health and wellbeing.

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