Research Article

Characterization of Contaminated Sediments Containing Polycyclic Aromatic Hydrocarbons from Three Rivers in the Niger Delta Region of Nigeria

Festus-Amadi Ijeoma*, Erhabor, O. Destiny[1], Ogwuche Christiana E[2], Erienu Obruche K[3]

*Chemistry Department, Ignatus Ajuru university of Education, Port Harcourt, Nigeria
[1]Chemistry Education Department, Federal College of Education (Technical), Umunze, Anambra, Nigeria
[2]Chemistry Department, Federal University of Petroleum Resources, Delta State
[3]Chemistry Department, Federal University of Agriculture, Makurdi, Nigeria
Corresponding Author: kenkennedy767@gmail.com

Abstract In this study, 16 priority polycyclic aromatic hydrocarbons (PAHs) were determined in sediment samples in three Rivers (i.e. Orashi River, Aluu River and Woji River) in Port Harcourt, River State Nigeria. Pretreatment of the samples were performed to increase the homogeneity of the soil and to increase the extractability of the analytes in the sediment was carried out using dichloromethane. The samples were extracted using the soxhlet extractor and clean-up by Solid phase extraction (SPE) clean up, using a 12- port vacuum manifold from SUPELCO with 6 mL Supelco C18 SPE cartridges. Under the optimized conditions, the ranges of extraction recoveries and SPE clean-up of the PAHs in the sediments were in the range of 71-90%. Gas chromatography-mass spectrometry (GC-MS) was used for the extraction and determination of the 16 PAHs in the samples. The method prescribed United States Environmental Protection Agency (USEPA) priority polycyclic aromatic hydrocarbons (PAHs) was used throughout the analysis. The detection of PAHs in the present study shows that there are serious pollutants in the water and sediments; it also indicates the inefficiency of water resources management in the three Rivers in Port Harcourt, River state Nigeria.

Introduction

The term polycyclic aromatic hydrocarbon (PAHs) also known as Poly-aromatic hydrocarbons or polynuclear aromatic hydrocarbons are a class of organic chemical consisting refers organic compounds comprised of two or more benzene rings bonded in linear, cluster, or angular arrangements [1, 2]. Polycyclic aromatic hydrocarbons (PAHs) are organic compounds that are mostly colorless, white, or pale yellow solids [3]. They are a ubiquitous group of several hundred chemically related compounds, environmentally persistent with various structures and varied toxicity. Polycyclic aromatic hydrocarbons (PAHs) are organic pollutants that are widely found in the environment [4]. They may found in air attached to dust particles, soil, sediments, water and food. Most PAHs enter the environment during burning of most organic materials such as coal, bones, refuse, oil, wood, gasoline, garbage and tobacco [5-7]. They are an important class of environmental contaminants because of their potential adverse health effects. They are known to have carcinogenic, mutagenic, teratogenic and genotoxic properties [8]. Genotoxic effects for some PAH been demonstrated both in rodents and in vitro tests using mammalian (including human) cell

lines [9]. Most of the PAHs are not genotoxic by themselves and they need to be metabolized to the diol exposed which react with DNA, thus inducing genotoxic damage. Genotoxicity plays important role in the carcinogenity process and maybe in some forms of developmental toxicity as well [10-13]. The main sources of exposure to PAHs are from breathing PAHs (in wood smoke, traffic exhaust and other contaminated air) [14], from eating contaminated food and drinking contaminated water. PAHs are generally carcinogenic and mutagenic and may induce lung, bladder as well as skin cancer [15, 16]. In addition, exposure to high levels of PAHs has been shown to produce immunosuppressive effects and causing oxidative stress during its metabolism [17, 18]. The maximum allowable concentrations of PAHs in soil and water are presented in Table 1. PAHs may contain four-, five-, six-, or seven- membered rings, but those with five or six are most common. PAHs comprised only of six-membered rings are called alternant PAHs. Certain alternant PAHs are called benzenoid PAHs [19]. PAHs containing up to six fused aromatic rings are often known as small PAHs and those containing more than six aromatic rings are called large [20]. PAHs are lipophilic compounds that show high affinity for organic matter and their determination in soil always requires powerful extraction techniques to release the strongly sorbed contaminants from the soil material. They can have a faint, pleasant odor [21-24]. A few PAHs are used in medicines and to make dyes, plastic and pesticides [25]. Over 100 compounds existing in indoor air have been identified to date, two of the more common ones are benzo (a) pyrene and naphthalene[26,27]. Different water sources can be contaminated with PAHs from dry and wet deposition, road runoff, industrial wastewater and petroleum spills [28-30]. Which later settle on the River bed, to contaminate the sediment. PAHs are ubiquitous in the environment, which can be frequently found in food, air, soil, and sediments [31-33]. Additionally, they can be detected in street dust [34], rain water [35], and urban runoffs [36]. PAHs can reach water bodies mainly through dry and wet deposition, road runoff, industrial wastewater, leaching from creosote-impregnated wood, petroleum spills, and fossil fuel combustion [37, 38]. Due to the low water solubility and hydrophobicity of PAHs, they rapidly become associated with inorganic and organic suspended particles and subsequently deposited in sediments [39]. Thus, analysis of sedimentary mixture of contaminants such as PAHs can be used for assessment and interpretation of the impact of these anthropogenic pollutants on the aquatic environment. Various methods of extraction and analysis of PAH have been carried out to compare the traditional extraction methods of extraction with modern techniques [40-42]. In contaminated soils and sediments, apart from the PAHs, which are the target analytes, other components may interfere with the determination of the PAHs. In addition, the PAHs in the extraction solution from the soil and sedimente cannot be determined directly because of their lower concentrations. Many methods can be used for dried soils, Soxhlet extraction is the most frequently applied technique to extract PAHs from dried soils. Analytical chemists have used Soxhlet extraction for more than 100 years [43]. This method is the classic approach for extracting solid samples [43, 44] for a spectrum of non and semivolatile organic compounds. In addition, solid phase extraction (SPE) offers a faster, more cost-effective sample preparation method with dramatic time savings [45].

The aim of this research was to determine the sediment quality of three Rivers in Rivers state, to

Investigate the levels of some toxic Polycyclic Aromatic Hydrocarbons (PAHs) in selected rivers, which are Woji Creek, Aluu and Orashi in Rivers State of Nigeria.

Table 1: Maximum allowable Concentrations (MACs) of PAHs in water and soil, [1]

PAH	MAC (water), ppm	MAC (soil), ppm
Pyrene	3.0	3.0
Naphthalene	3.0	1.0
Phenanthrene	3.0	3.0
Benzo[h,g,i]perylene	3.0	3.0
Benzo[a]pyrene	0.005	3.0
Anthracene	3.0	3.0
Fluoranthene	3.0	3.0
Acenaphthene	3.0	3.0
Acenaphthylene	3.0	3.0

Benzo[a]anthracene	0.005	0.15
Benzo[b]fluoranthene	0.005	3.0
Dibenzo[a]anthracene	0.005	3.0
Fluorene	3.0	3.0
ndeno[1,2,3-ghi]pyrene	0.005	3.0
Indene	3.0	----

Materials and Methods

Study Areas

This research work covers both fresh water and brackish water. The Rivers include Orashi River, Aluu River and Woji Creek. Orashi and Aluu rivers are both fresh water while Woji Rivers is brackish water, in Port Harcourt, River State, Nigeria [46].

Plate 1: Map showing the study areas

Standards and Reagents

A standard mixture of the USEPA [47] priority PAHs (2000 µg/mL, dichloromethane: benzene): Naphthalene (Naph.), acenaphthene (Ace.), fluorene (Fl.), phenanthrene (Phen.), anthracene (Ant.), anthracene-d10 (Ant.d10), pyrene (Pyr.), benzo [a] anthracene (B[a]A), chrysene (Chy.), benzo [b] fluoranthene (B[b]F), benzo [k] fluoranthene (B[k]F), benzo [a] pyrene (B[a]P), dibenz [a, h] anthracene (D[ah]A) and benzo [ghi] perylene (B[ghi]P) with purity higher than 98% were purchased from Sigma-Aldrich/Fluka/Supelco (Germany) [48]. Serial dilutions of the standard solution using HPLC grade isooctane, toluene, acetonitrile, dichloromethane, tetrachloroethylene, n-hexane, ethanol, 2-propanol, methanol, acetone and chloroform were obtained from Chem-lab Belgium. Ultrapure water was obtained from a Milli-Q plus ultra-pure water system (Millipore, Molsheim, France) [49].

Calibration standards

Individual stock standard solutions (1 mgmL^{-1}) of the polycyclic aromatic hydrocarbon (PAHs) were prepared in toluene [50]. All the solutions were transferred to amber glass vials and stored at 4˚C. They were kept for 30 min. at ambient temperature prior to their use. A mixed intermediate standard solution at a concentration of 100 ngmL^{-1} was prepared via appropriate dilution of the stock solutions in methanol. This solution was used as a spiking solution for validation experiments. Spiked calibration standards at concentration levels of 0.35, 0.7, 1.4, 2.8, and 5.6 ngmL-1 were prepared by addition of 35 µL, 70 µL, 140 µL, 280 µL and 560 µL of mixed standard stock solution to 10 mL

of blank water samples in each case. A stock solution of anthracene-d10 in toluene at concentration of 1 mgmL^{-1} was used as internal standard. An aliquot of 70 µL of anthracene-d10 in methanol (100 ngmL^{-1}) was added to the spiked water sample as internal standard [51].

Collection of Water Samples

A random sampling technique was adopted as described by Na [51]; in collecting the sediments samples from the three rivers (Orashi River, Aluu River and Woji Creek). Nine samples (i.e. 3 samples each) were collected from the three Rivers. Sample were taken to a depth of 0.6 m to account for the toxic zone where aerobic respiration takes place and therefore, ease of chemical flow from the sediment to the water column. Samples were randomly collected with a good wide range depending on the size and shape of the River to be able to ascertain for the total heavy metals in the River. The samples were collected almost like a circular pattern to cover the whole River. All water samples were collected in 1000 – 2000 mL dark glass bottles with Teflon caps and stored at 4 °C prior to extraction (normally within 48 h) [52].

Pretreatment

Pretreatment of the samples were performed to increase the homogeneity of the soil and to increase the extractability of the analytes in the soil. Before taking a sub sample for analysis, the samples were sufficiently homogenized (with dichloromethane) [53]. PAHs can be extracted from wet or dried samples. However, storage, homogenization and extraction are much easier when the samples are dry.

Soxhlet extraction

10 g each of soil samples were weighed into Whatman extraction thimbles (that had been pre-extracted with dichloromethane). The samples were extracted using the soxhlet extractor with 250 mL DCM for 16 h. The extracts were further reduced to 10 mL using a rotary evaporator, transferred into 4 mL amber vials, and kept in the refrigerator for clean up and analysis [54].

Solid phase extraction (SPE) clean up of extracts

SPE clean-up of the sediment extracts was carried out using a 12- port vacuum manifold from SUPELCO with 6 mL Supelco C18 SPE cartridges. The sorbents of SPE cartridges were conditioned with 5 mL of extracting solvents and 40 % of the extracting solvent in water respectively to prepare the column for the cleanup process [55]. The extraction solutions were each loaded and aspirated through the cartridge under gentle vacuum at a flow rate of less than 2 ml/min.

GC–MS instrumentation and conditions

The analysis was carried out using GC model Agilent 7890A, Washington, USA, equipped with a split/splitless injection port, an autosampler model Agilent 7693, electronic ionization and a triple quadrupole mass analyzer model Agilent 7000 series. A HP-5MS 5% Phenyl Methyl Silox, Agilent 19091s-433 capillary column was used with 30 m × 0.25 mm I.D. and 0.25 µm film thickness. Helium with a purity of 99.99% and a flow rate of 1 mLmin^{-1} was used as carrier gas. The injector temperature was retained at 280˚C and injection performed in the splitless mode. The initial oven temperature was maintained at 60˚C for 0.5 min, increased to 230˚C at a ramp rate of 3˚C min^{-1} and kept for 0.5 min, then increased to 290˚C at 5˚C min^{-1} and hold for 10 min at the final temperature. Data acquisition was delayed for 12 min. The ionization was performed in ion source with electron impact mode (70ev). The ion source and triple quadrupole mass analyser temperature were kept at 230˚C and 280˚C, respectively. The vial was placed in autosampler and 2 µL of the contents was injected into the gas chromatograph for analysis. All samples were analysed in duplicate [56].

Risk Analysis due to PAHs

Health-risk due to contact with PAHs was estimated using the measured PAHs concentration USEPA [57].

Carcinogenic Risk

The possibility of cancer occurrences from contact with possible carcinogen [57]. The Incremental Lifetime Cancer Risk (ILCR) model USEPA [57] was employed to determine the risk of incidental exposure to PAHs in soils from the study area. The estimated daily intake of PAHs shows the PAHs in soil samples ingested into the bloodstream represented by EDI. The EDI (mg/kg/d) of PAHs via soil ingestion was estimated using the formula [57].

$$EDI = \frac{CS \times IR \times CF \times ED \times EF}{Bw \times AT} EDI = \frac{CS \times IR \times CF \times ED \times EF}{Bw \times AT} \qquad 1$$

where EDI is the Estimated daily intake related to soil particle ingestion (mg/kg/d), CS = PAHs concentrations in soil (mg/kg), IR = soil ingestion rate (m/gd), EF = exposure frequency (day/year), ED = exposure duration (year), BW is weight of the individual (kg), AT = averaging time which is 365 days per year for 70 years for lifetime exposure (70 years × 365 days/year), CF = conversion factor (1×10^{-6} kg/mg) [58].

$$\text{Cancer Risk} = SF \times EDI \qquad 2$$

CSF= cancer slope factor $(mg/kg/day)^{-1}$. Cancer risk (CR) is seen as the upper bound lifetime likelihood of a person developing cancer growth as a result of contact to a probable carcinogen" (Emrah, 2012). Risk management decisions are from 10^{-6} to 10^{-4} USEPA [57]. Cancer risks are estimated as the incremental possibility of a person developing cancerous growth over a while due to the exposure to cancer-causing substances. Human Health Toxicological Data for carcinogenic in PAHs and Parameters used in cancer risk assessment of PAHs risk in sediments and shown in table 2 and 3.

Table 2: Human Health Toxicological Data for carcinogenic PAHs.

PAHs	Relative Potency Factor	Cancer Slope Factor $(mg/kg/day)^{-1}$
benzo[a]anthracene (BaA)	0.1	7.3×10^{-1}
chrysene (Chy)	0.01	7.3×10^{-2}
benzo[b]fluoranthene(BbF)	0.1	7.3×10^{-1}
benzo[k]fluoranthene(BkF)	0.1	7.3×10^{-1}
benzo [a] pyrene	1	7.3
indeno[1,2,3-cd]pyrene(IcdP)	0.1	7.3×10^{-1}
dibenzo[a,h]anthracene(DahA)	1	7.3

Sources: [5,57]

Table 3: Parameters used in cancer risk assessment of PAHs risk in sediments

Definition	Unit	
	60	Years
Ingestion Rate (IR)	100	mg/day
Exposure Frequency (EF)	365	Years
Body Weight (BW)	65	Kg
Average Time (AT)	365 x 70	Days
Conversion Factor (CF1)	10^{-6}	mg/kg
Exposure Duration (ED)	70	Years
Concentration of PAHs (Cw)		

Sources: [5,57]

Results and Discussion

The results of the concentration of the PAHs in sediment from the Study Rivers are shown in table 4-6.

Table 4: PAHs concentration in sediment of Mbiama river sediment in mg/kg

PAHs	Station 1	Station 2	Station 3	Total
Naphthalene (Naph)	5.35E-5	9.82E-6	8.00E-5	1.43E-4
acenaphthene (Ace)	ND	3.04E-5	ND	3.04E-5
fluorene (Fl)	1.00E-5	5.42E-6	ND	1.54E-5
Acenaphthylene(Acen)	ND	3.68E-7	ND	3.68E-7
Phenanthrene(Phen)	3.47E-6	4.26E-6	9.53E-7	8.68E-6
Anthracene(Anth)	6.61E-6	6.13E-6	1.02E-6	1.38E-5
Fluoranthene(Fluo)	3.17E-6	3.58E-6	3.57E-6	1.03E-5
Pyrene(Pyr)	3.43E-4	9.89E-5	1.05E-5	4.52E-4
benzo[a]anthracene (BaA)	2.75E-5	2.78E-5	6.14E-6	6.14E-5
chrysene (Chy)	2.82E-4	3.77E-5	1.28E-4	4.48E-4
benzo[b]fluoranthene(BbF)	4.66E-6	8.84E-6	2.40E-6	1.59E-5
benzo[k]fluoranthene(BkF)	3.52E-5	3.12E-5	3.55E-5	1.02E-4
benzo [a] pyrene	1.24E-4	9.58E-6	4.96E-6	1.38E-4
dibenzo[a,h]anthracene(DahA)	5.59E-4	3.74E-3	9.93E-5	4.40E-3
indeno[1,2,3-cd]pyrene (IcdP)	1.51E-2	3.03E-3	1.69E-2	2.90E-2
benzo[g,h,i]perylene(BghiP)	5.41E-3	1.95E-3	2.68E-3	1.00E-2
tPAHs	2.20E-2	9.00E-3	1.40E-2	4.50E-2

Table 5: PAHs concentration in sediment of Aluu river sediment in mg/kg

PAHs	Station 1	Station 2	Station 3	Total
Naphthalene (Naph)	2.330	1.10E-1	3.200	5.640
acenaphthene (Ace)	2.370	1.30E-1	3.120	5.480
fluorene (Fl)	1.300	2.30E-1	1.680	3.210
Acenaphthylene(Acen)	ND	ND	ND	ND
Phenanthrene(Phen)	1.10E-1	ND	ND	1.10E-1
Anthracene(Anth)	2.20E-1	3.00E-2	0.280	0.530
Fluoranthene(Fluo)	3.10E-1	2.00E-2	0.360	0.690
Pyrene(Pyr)	ND	ND	ND	ND
benzo[a]anthracene(BaA)	1.90E-1	1.00E-2	0.180	0.380
chrysene (Chy)	4.00E-1	4.00E-1	0.350	0.780
benzo[b]fluoranthene(BbF)	0.150	3.00E-2	0.130	0.310
benzo[k]fluoranthene(BkF)	1.20E-1	3.00E-2	0.320	0.470
benzo [a] pyrene	7.10E-1	7.00E-2	0.660	1.440
dibenzo[a,h]anthracene(DahA)	2.20E-1	2.00E-2	0.140	0.380
indeno[1,2,3-cd]pyrene (IcdP)	2.50E-1	2.00E-2	0.150	0.420
benzo[g,h,i]perylene(BghiP)	1.90E-1	1.00E-2	0.120	0.320
tPAHs	8.880	0.760	10.680	20.32

Table 6: PAHs concentration in sediment of Woji river sediment in mg/kg

PAHs	Station 1	Station 2	Station 3	Total
Naphthalene (Naph)	24.62	33.57	29.45	357.6
acenaphthene (Ace)	31.29	34.39	29.23	94.91
fluorene (Fl)	39.47	55.23	57.00	50.57
Acenaphthylene(Acen)	35.09	32.87	30.26	98.22
Phenanthrene(Phen)	49.61	69.89	67.48	187.0
Anthracene(Anth)	107.9	118.9	109.5	336.3
Fluoranthene(Fluo)	107.2	119.2	118.4	344.8
Pyrene(Pyr)	116.9	108.3	118.7	343.9
benzo[a]anthracene(BaA)	94.83	114.6	109.9	319.3
chrysene (Chy)	88.16	109.9	107.2	305.3
benzo[b]fluoranthene(BbF)	87.40	99.55	90.55	277.5

benzo[k]fluoranthene(BkF)	109.9	146.7	110.6	367.2
benzo [a] pyrene	53.13	64.39	67.22	184.7
dibenzo[a,h]anthracene(DahA)	10.32	11.79	10.05	32.16
indeno[1,2,3-cd]pyrene (IcdP)	54.68	82.11	59.18	196.0
benzo[g,h,i]perylene(BghiP)	38..54	48.30	56.70	143.7
tPAHs	1049	1250	1171	3470

Table 7: Average PAHs concentration in sediment of the studied rivers measured in mg/kg

PAHs	Mbiama	Aluu	Woji	USEPA
Naphthalene(Naph)	4.77E-5±2.89E-5	1.880±1.301	119.2±3.658	1.43E-4
acenaphthene (Ace)	1.01E-5±1.41E-5	1.830±1.270	31.64±2.121	3.04E-5
fluorene (Fl)	5.13E-6±4.09E-6	1.070±0.614	50.57±7.880	1.54E-5
Acenaphthylene(Acen)	1.23E-7±1.73E-7	ND	32.74±1.974	3.68E-7
Phenanthrene(Phen)	2.89E-6±1.41E-6	0.037±0.52	62.33±9.046	8.68E-6
Anthracene(Anth)	4.60E-6±2.53E-6	0.176±0.107	112.1±4.852	1.38E-5
Fluoranthene(Fluo)	3.43E-6±1.91E-7	0.230±0.150	114.9±5.478	1.03E-5
Pyrene(Pyr)	1.51E-4±1.41E-4	ND	114.6±4.538	4.52E-4
benzo[a]anthracene(BaA)	2.05E-5E1.01E-5	0.126±0.083	106.4±8.433	6.14E-5
chrysene (Chy)	1.49E-4±1.01E-4	0.260±0.159	101.7±9.675	4.48E-4
benzo[b]fluoranthene(BbF)	5.30E-6±2.27E-6	0.103±0.052	92.50±5.148	1.59E-5
benzo[k]fluoranthene(BkF)	3.40E-5±1.96E-6	0.156±0.121	122.4±17.18	1.02E-4
benzo [a] pyrene	4.60E-5±5.51E-5	0.480±0.291	61.58±6.086	1.38E-4
dibenzo[a,h]anthracene(DahA)	1.47E-3±1.62E-3	0.126±0.082	47.91±7.421	4.40E-3
indeno[1,2,3-cd]pyrene (IcdP)	9.67E-3±5.00E-3	0.140±0.094	10.72±0.764	2.90E-2
benzo[g,h,i]perylene(BghiP)	3.33E-3±1.49E-3	0.106±0.074	65.30±12.01	1.00E-2
tPAHs	1.50E-2±5.35E-3	6.773±4.315	1157±82.68	4.50E-2

Table 8: Concentration of Carcinogenic (cPAHs) and non-carcinogenic PAHs (ncPAHs

Settlements	Carcinogenic (cPAHs)	non-carcinogenic PAHs (ncPAHs)s
Woji river	436.81	720.19
Aluu river	1.2645	5.508
Mbiama river	0.0113743	0.0036257

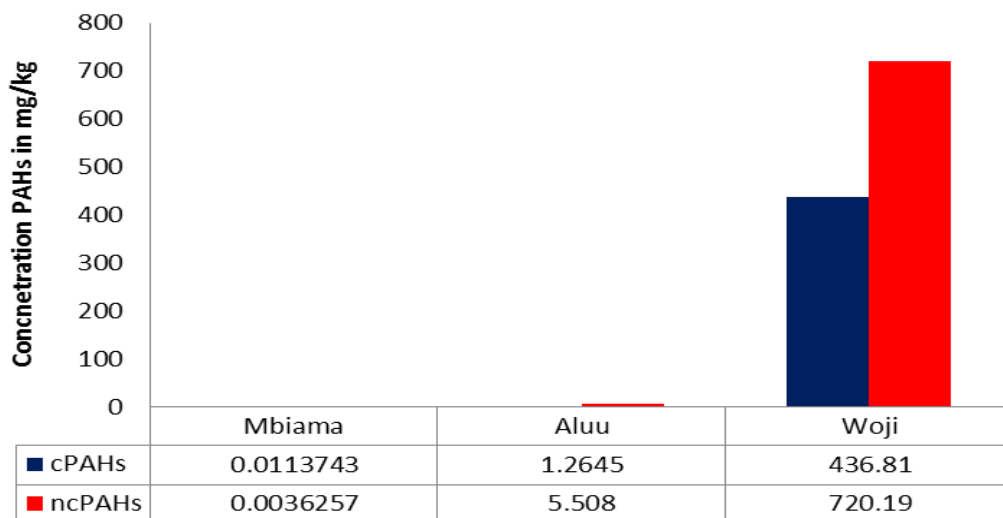|	Mbiama	Aluu	Woji
■ cPAHs	0.0113743	1.2645	436.81
■ ncPAHs	0.0036257	5.508	720.19

Figure 2: Concentration of Carcinogenic (cPAHs) and non-carcinogenic PAHs (ncPAHs)

Health risk due to cancer from PAHs concentration in the study area
The cancer risk estimated due to PAHs from the three Rivers is depicted in tables 9 and 10.

Table 9: Estimated daily intake of PAHs in sediment samples from the study area

PAHs	Mbiama	Aluu	Woji
chrysene (Chy)	2.13E-10	3.71E-7	1.45E-4
benzo[b]fluoranthene(BbF)	7.57E-12	1.47E-7	1.32E-4
benzo[k]fluoranthene(BkF)	4.86E-11	2.23E-7	1.75E-4
benzo [a] pyrene	6.57E-11	6.86E-7	8.80E-5
dibenzo[a,h]anthracene(DahA)	2.10E-9	1.80E-7	6.84E-5
indeno[1,2,3-cd]pyrene (IcdP)	1.38E-10	2.00E-7	1.53E-5

Table 10: Cancer risk of PAHs in sediment samples from the study area

PAHs	Mbiama	Aluu	Woji
chrysene (Chy)	1.55E-11	2.60E-8	1.06E-5
benzo[b]fluoranthene(BbF)	1.15E-12	1.07E-7	9.64E-5
benzo[k]fluoranthene(BkF)	3.41E-11	1.63E-7	1.28E-4
benzo [a] pyrene	4.74E-10	5.00E-6	6.42E-4
dibenzo[a,h]anthracene(DahA)	1.53E-8	1.31E-6	4.99E-3
indeno[1,2,3-cd]pyrene (IcdP)	1.01E-10	1.46E-7	1.12E-5

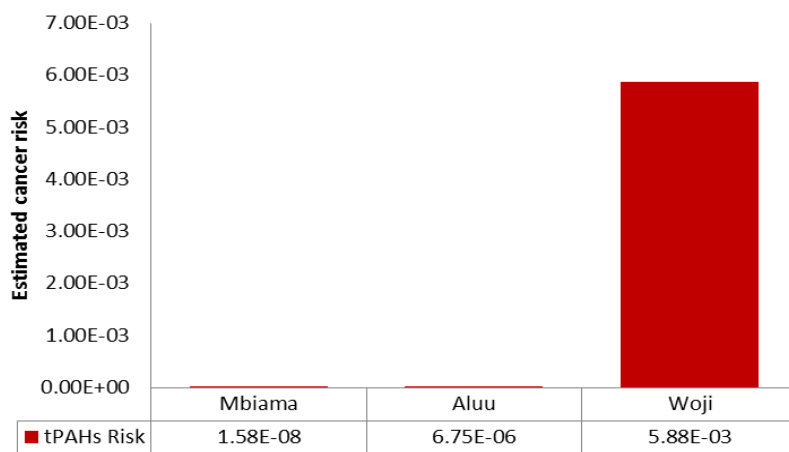|	Mbiama	Aluu	Woji
■ tPAHs Risk	1.58E-08	6.75E-06	5.88E-03

Figure 3: tPAHs cancer risk estimate from the different rivers studied

The PAHs level ranges from ND to 3.2 mg/Kg. The following PAH; Acenaphthene and pyrene were below detection limit and tPAHs for the Aluu river was 6.773±4.315 mg/Kg. Woji River ranges from 10.05 to 119.2 g/Kg and tPAHs was 1157±82.68 mg/Kg while Orashi River ranges from ND to 9.93mg/Kg and tPAHs was 1.50E-2±5.35E-3. The three dominant PAHs were Naphthalene (Nap) (119.2±3.658), Fluoranthene (Fluo) (114.9±5.478) and Pyrene (Pyr), (114.6±4.538). The probable source estimation showed that the PAHs were of petroleum spills, combustion, leakages, and other combustion process (biomass, grass, pepper, wood, charcoal and coal). (ND=Not Detected) In the current study, the activities occurring in the area contribute to the input of PAHs in the water. However, the predominance of two and three rings PAHs (>40%) in water indicates that the major source of pollution in the water for all the studied stations comes from petroleum [58]. Other sources may come from the burning in the abattoir which releases sooth into the atmosphere and leads to direct air-water exchange. They may

also have been imputed from the boats that use the river as a means of transport and as a location for repairs, the direct input of hydrocarbons through spills from inadequate vessels also serve as a means of input [59]. PAHs study in Ubeji, Ifie, and Egbokodo creeks revealed similar results as those in the present study [60]. In contrast, in sediment samples, the percentage sum of two and three rings PAHs was about 30% (figure2), while a combination of 4,5, and 6rings PAHs made up about 70% of the PAHs composition in all the studied stations. This might be evidence that the PAHs is majorly from a combustion base source with an influence of petroleum combustion [59]. The source of PAH in this creek is similar to those assessed in Imo River. Results from the study was also higher that those obtained in the study of levels and risk assessment of polycyclic aromatic hydrocarbons in water and fish of Rivers Niger and Benue confluence Lokoja, Nigeria.

Conclusion

Polycyclic aromatic hydrocarbons (PAHs) are released into the environment through natural and synthetic (artificial) sources with emissions largely to the atmosphere. Natural sources include emissions from volcanoes and forest fires. Synthetic or artificial sources provide a much greater release volume than natural sources; the largest single source is the burning of wood in homes. Automobile and truck emissions are also major sources of PAHs. Environmental pollution like tobacco smoke, unvented radiant and convective kerosene space heaters, and gas cooking and heating appliances may be significant sources of PAHs in indoor air. Polycyclic aromatic hydrocarbon can enter sediment and soil through atmospheric deposition and from discharges of industrial effluents (including wood-treatment plants), municipal wastewater, and improper disposal of used motor oil. Several of the polycyclic aromatic hydrocarbons have been detected at hazardous waste sites at elevated levels. In air, Polycyclic aromatic hydrocarbon (PAHs) are found sorbed to particulates and as gases. Particle-bound PAHs can be transported long distances and are removed from the atmosphere through precipitation and dry deposition. In soil and sediments, microbial metabolism is the major process for degradation of PAHs. PAHs have a potential effect on the environment. Detection of PAHs in the present study shows that there are serious pollutants in the water and sediments; it also indicates the inefficiency of water resources management in those three (3) Rivers in port Harcourt, river state Nigeria.

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