



Distribution, Possible Sources, Ecological and Health Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Water of Niger Delta Creeks, Nigeria

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<https://doi.org/10.36263/nijest.2023.1.0404>

ABSTRACT

This study evaluates concentrations, probable sources, potential ecological and health risks of 16PAHs in the surface water from Buguma, Krakrama and Bonny communities along River Niger, Nigeria. Surface water sampling were undertaken in these communities and PAHs were analysed using gas chromatography–mass spectrometry (GC–MS). The GC-FID analyses of the PAHs were made on a Hewlett Packard Agilent 6890 series with a flame ionization detector (FID). The concentrations of total PAHs (Σ PAHs) ranged from 32.89 to 81.60 mg L⁻¹ in surface water with a mean value of 53.32 mg L⁻¹, while that of carcinogenic PAHs (Σ c-PAHs) was 10.27 mg L⁻¹, which corresponds to 19.3 % of the Σ PAHs. Low molecular weight (LMW) PAHs were recorded higher in concentrations (59.4%) as compared to high molecular weight (HMW) PAHs (40.6%). Phenanthrene with the maximal concentration of 16.51 mg L⁻¹ was the dominant PAH in surface water. Results revealed the alarming levels of PAHs and the unsuitability of water for drinking purpose. PAHs in water exerted very high ecological risks with phenanthrene (20.8%), naphthalene (14.6%), pyrene (14.1%), and chrysene (10.4%) as the main contributors. The primary source of PAHs was both pyrolytic and petrogenic. The sum of the ingestion and dermal lifetime cancer risk is 2.40×10^{-2} , which was higher than the acceptable value recommended by WHO. It means 1 lifetime cancer case in 42 residents in the three communities, indicating significant carcinogenic risk through long-term exposure via ingestion and dermal routes.

Keywords: Polycyclic Aromatic Hydrocarbon, Surface Water, Health Risk, dermal contact, Molecular Diagnostic Ratios

1.0. Introduction

Water is an essential component of existence, ubiquitous in nature, and the foundation of who we are. It is a crucial natural resource that sustains and preserves all forms of life on this world. (WHO, 2011) and makes up about 70-80% of man's body (Iwar *et al.*, 2021). Less than 3% of the Earth's water supplies are freshwater, and only one hundredth of one percent of this is suitable for human consumption, despite its relative copiousness (Ha and Schleiger 2022). Surface water, mainly in the form of rivers and lakes, supply one-third of drinking water necessity of the world (Edokpayi *et al.*, 2017) and meet the local water needs of the rural communities in developing countries. Since it has a profound impact on human and aquatic biome health, surface water contamination by organic compounds, many of which are known to be noxious, has been studied by numerous environmental

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experts around the globe (Huang *et al.*, 2021; Abbass *et al.*, 2022). A significant quantity of obstinate organic pollutants (POPs), primarily PAHs, have been released into water bodies as a result of increased human-induced activities brought on by rapid development and unintentional urbanization (rivers, lakes and groundwater) (Chabukdhara *et al.*, 2012).

PAHs are semi-volatile, hydrophobic, highly lipophilic chemicals that bioaccumulate in living organisms, are resistant to degradation as well as possess toxic properties (Abdel-Shafy and Mansour, 2016). Also referred to as polynuclear aromatics (PNAs), PAHs are hydrocarbons that are only made up of hydrogen and carbon atoms and are organized as two or more fused benzene rings that are bonded in a cluster, a linear bond, or both. They can be found in the biota, soil, water, and air, and they frequently exist in combinations that are highly persistent in the environment because of their natural characteristics (such as heterocyclic aromatic ring structures, hydrophobicity, thermostability). Due to their ubiquity, long-range transportability, chronic persistence, and possible negative effects on living things, as well as evidence of their documented carcinogenicity in experimental animals, PAHs are a major environmental concern (Gearhart-Serna *et al.*, 2018). PAHs can exist in more than 100 different combinations formed primarily by pyrolytic processes, especially the incomplete combustion of organic (carbonaceous) materials (e.g. biomass, coal and fossil fuel) at high temperatures. Sixteen PAHs have been identified as priority pollutants of significant public health concern due to their high toxic, carcinogenic, mutagenic, teratogenic, and immunotoxicogenic as well as act as endocrine disrupting chemicals (EDCs) to various life forms and ecological environment (EU, 2013; USEPA, 2014; Liu *et al.*, 2020; Sun *et al.*, 2021). Its composition within the aquatic environment (the surface waters and sediments) reflects the diverse origins from which they were derived. The PAHs of pyrolytic or pyrogenic origin come from incomplete combustion of industrial production (mining, steelworks, aluminium smelters, etc.), energy production (oil, gas or coal power stations), domestic combustion (wood, coal, etc.), automotive fuel or incinerators (Abdel-Shafy and Mansour, 2016). Petrogenic PAHs are derived from petroleum and other fossil fuel containing sources (Mojiri *et al.*, 2019) while PAHs of biogenic origin are those from biological processes - synthesized by terrestrial or aquatic biological entities like plants, animals, microorganisms, phytoplankton, bacteria, macro- and microalgae and early stages of diagenesis - formed during the slow degradation of organic matter in soil and anoxic sediment (Rocha and Palma, 2019; Honda and Suzuki, 2020). Only pyrogenic and petrogenic sources are the main contributors of environmental PAH pollution in aquatic ecosystems. Direct discharge pathways (municipal and industrial effluents, surface (agricultural and urban) runoff, river transport, and unintentional oil leaks or spills) and indirect sources (atmospheric fallout - dry and wet deposition) are the two main ways that the released PAHs may reach the water bodies (Zanardi-Lamardo *et al.*, 2019; Li *et al.*, 2020).

PAHs are divided into two groups based on their physical, chemical, and biological characteristics; lower-molecular-weight (LMW) PAHs (2-3-ring), most often come from natural resources (petrogenic), are prone to biodegradation as well as to photolysis and higher-molecular-weight (HMW) PAHs (4-6-ring) often originate from combustion (pyrolytic), and have greater resistance to degradation (Friedman *et al.*, 2014). The LMW PAHs, for example, naphthalenes, fluorenes, phenanthrenes, and

anthracenes, have significant acute toxicity to aquatic organisms. The HMW PAHs, from benzo[a]anthracene to indeno[1,2,3-cd]pyrene, do not cause acute toxicity but are known to be carcinogenic. Seven of the sixteen PAH compounds namely benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[ah]anthracene, indeno[1,2,3-cd]pyrene have been recognized as being carcinogenic to animals and to humans by the World Health Organisation (WHO, 2011) and the International Agency for Research and Cancer (IARC, 1987). Human beings are exposed to PAHs through inhalation (nose and mouth) from atmosphere, direct ingestion (mouth) and dermal absorption (skin) (Ali, *et al.*, 2019). A number of harmful health impacts are linked to prolonged exposure to PAHs. As some PAHs are potent carcinogens (IARC, 2017), short-term and long-term exposure to PAHs humans, even at low concentrations, cause long-lasting damage such as reproductive defects, neurotoxicity, immunotoxicity, cancers of the skin, oesophagus, lung, breast, bone, colon, bladder, ovary and scrotum; kidney and liver damage; decreased immune function, form DNA adducts and induce mutations, leukaemia as well as cardiovascular disease (CVD), including atherosclerosis, thrombosis, hypertension, and myocardial infarction (MI) to humans and wildlife (Abdel-Shafy and Mansour, 2016; Mallah *et al.*, 2022). There is evidence of DNA damage, genotoxic impacts, and growth inhibition linked to PAH exposure in aquatic organisms (Taioli *et al.*, 2007; Al-Khion, 2018).

The Niger Delta region have been identified to be among the five most polluted ecosystems in the world as a result of petroleum production (Ayuba, 2012) and these include oil extraction and spills (World Bank, 2008; UNEP, 2011), discharge of oil produced water into water sources (Ajuzieogu *et al.*, 2018) and increase of artisanal refining along the creeks (The Guardian International edition, 2020). Other human activities in the Niger Delta include construction and fabrication of marine boats, disposal of industrial and domestic wastes and sailing (Moslen and Miebaka, 2016), and use of pesticides for farming (Akpan and Ajayi, 2016). Oil spills have occurred repeatedly for the past five decades in the Niger Delta and large parts of the land and wetlands are chronically affected by oil spills (Linden and Jonas, 2013); Nigeria recorded 9,343 cases within 10 years (Albert *et al.*, 2018).

In this present study, we chose communities along Buguma, Krakrama and Bonny estuaries of River Niger and collected surface water samples from these estuaries. Accordingly, the main objectives of this study were to (1) determine the concentrations of 16 priority PAHs with a view to evaluate the suitability for human use, (b) identify the possible sources of PAHs in the water body through diagnostic ratio and multivariate statistical analyses such as hierarchical cluster analysis (HCA) and principal component analysis (PCA), (c) apply and calculate potential ecological risk index for pollution assessment of surface water and (d) appraise and quantify the corresponding human health risk associated with oral and dermal exposure to PAHs, especially carcinogenic risk for different age groups (i.e. children, adults) and lifetime based on USEPA risk model.

2.0. Materials and methods

2.1. Materials

A standard mixture of PAHs consisting of naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo(a)anthracene (BaA), chrysene (Chr), benzo(b)fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz(a,h)anthracene (DahA), indeno(1,2,3-cd)pyrene (InP) and benzo(g,h,i)perylene (BghiP) was purchased from Accustandard (USA). All chemicals used were of analytical grade.

2.2. Study Area Description

Water samples were collected from three sampling stations. Location of the stations was determined by the global positioning system (GPS) ([Table 1](#)).

2.2.1. L1 sampling station

Buguma River (L1) is situated with Oil Mining Lease 18 (OML 18). It is criss-crossed by oil and gas flowlines, an oil manifold and delivery line to Krakama flowstation. Within this site, anthropogenic activities like illegal bunkering of crude oil, fishing, two-engine boat for human and goods transportation.

2.2.2. L2 sampling station

Krakama River (L2) is situated with OML 18. It is criss-crossed by oil and gas flowlines, and a flowstation. Within this site, anthropogenic activities like gas flaring from the flowstation, vandalism of oil flowlines and delivery pipeline, illegal bunkering of crude oil, illegal artisanal refineries, fishing, two-engine boat for human and goods transportation.

2.2.3. L3 sampling station

Bonny River (L3) is situated with Oil Mining Lease (OML 11). It is crisscrossed by oil and gas flowlines, high pressure water wells, delivery oil pipelines. The following facilities are located in this site: Oloma flow station and associated gas gathering (AGG) plant operated by Eroton Exploration and Production, Natural gas liquefaction plant and terminal operated by Nigerian Liquefied Natural Gas (NLNG), Bonny Oil and Gas export Terminal operated by Shell Production Development Company, and Bonny River Export Terminal operated by Mobil Producing Nigeria (MPN), a subsidiary of ExxonMobil. Within this site, anthropogenic activities like continuous gas flaring at the terminals and flow station, vandalism of oil flowlines and delivery pipeline, illegal bunkering of crude oil, illegal artisanal refineries, fishing, two-engine boat for human and goods transportation.

Water samples from each of the rivers were collected in 2500 mL amber glass bottles with Teflon lined tops and sealed with Teflon tape. For each river, water samples were collected from three different sampling locations. These were stored in an ice-packed cooler at 4°C while being transported to the laboratory prior to analysis.

Table 1: Location of sampling stations and coordinates

No	Station code	Station name	Coordinates	
			Latitude (N)	Longitude (E)
1	L1	Upper stream of River Niger -Buguma River	4° 44'10.10"	6° 51' 44.50"
2	L2	Middle section of River Niger -Krakrama River	4° 33' 04.00"	6° 57' 03.00"
3	L3	Downstream of River Niger -Bonny River	4° 22' 59.99"	7° 05' 60.00"

The samples were properly labelled for identification of sources and immediately transported to the laboratory as soon as after sampling for preservation and analysis. The duration of preservation of the water samples was seven days at a temperature of 40°C (in a fridge) by adding HNO₃ to maintain a pH < 2, according to the industrial waste resource guidelines (USEPA 2022).

2.3. Sample preparation, extraction, analysis and clean-up

The target analytes were the 16 PAHs stipulated by USEPA (2009). They are (Nap, Acy, Ace, Flu, Phe, Ant, Fla, Pyr, BaA, Chr, BkF, BbF, BaP, DahA, BghiP, InP). Water samples were filtrated under vacuum with 0.45 µm and 0.22 µm hydrophilic filters to separate the particulates within 7 days after collection. The entire sample were poured the into a 1 litre separatory funnel. The methylene chloride extract was collected into a 250 ml Erlenmeyer flask. Subsequently, 20 ml of methylene chloride was used to rinse both the separatory funnel and the column into the flask and the process was repeated thrice. This was purified by passing through a pasture pipette packed with silica gel and anhydrous sodium sulphate on a membrane and concentrated by blowing it down with nitrogen gas to about 2 ml. This was transferred into 2 well-labelled vial (1 ml each) and stored at 4°C until GC analysis (USEPA 2022).

2.4. Gas chromatograph–mass spectrometry (GC/MS) analysis

Gas chromatography-flame ionization detector (GC-FID) analysis

The GC-FID analyses of the PAHs were made on a Hewlett Packard Agilent 6890 series with a flame ionization detector (FID) and cold on-column injection. Calibration of the PAHs was done using their respective standard. Exactly 1 µl portion of the sample was injected and analyzed for TPHs (C 9 - C 40). An HP-5 column having the dimensions 30 m x 0.25 mm with a stationary phase thickness of 0.25 µm was used for analytical separation. The carrier gas was purified nitrogen held at a flow rate of 5 ml min⁻¹. The operating temperature program was started at 60 °C for 2 min and then increased at a rate of 10 °C per minute to 300 °C for 10 min. The injector and detector temperatures were maintained at 250 °C and 300 °C respectively. The minimum detection limit for all the compounds analyzed was 0.1 µg kg⁻¹ wet weight. As the samples appeared from the column (at constant flow rate) the FID detector automatically detected them and this response is based on the components of the vapour (Enuneku *et al.*, 2015; Oyibo *et al.*, 2018).

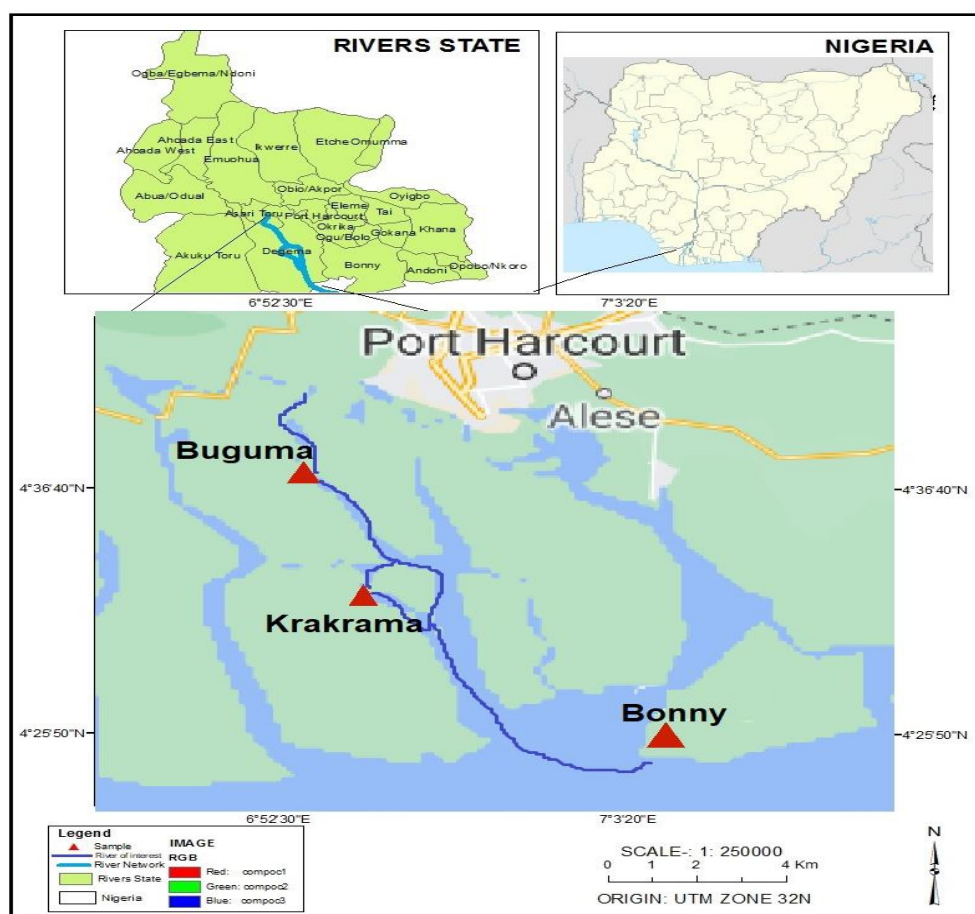


Figure 1: Map showing the study area (Onyegeme-Okerenta *et al.*, 2022)

2.5. Quality Assurance and Quality Control

Average recoveries and relative standard deviations (RSDs) of PAHs were monitored under strict quality assurance. The residue levels of PAHs were quantitatively determined by multiple analyses of 10 replicate spiked water samples with a concentration of 10 ng L^{-1} for PAH congeners. In order to monitor procedural performance and matrix effects, surrogate standards were added to all the samples (Sun *et al.*, 2009). Before sample analysis, working standard solutions of PAHs were detected to determine peak response and evaluate peak resolution. Average recoveries of PAHs in 10 replicate spiked water samples were between 78% and 116%. Quality assurance and quality control procedures were ensured by using standard reference materials with each batch of samples, adding a solvent blank and a procedure blank. The precision of analytical data for each sample was determined by three consecutive measurements of the standard reference solution. Each sample was detected three times and the mean value was accepted.

2.6. Risk assessment

It is crucial to assess the risk posed by PAHs for ecological environment security and to protect human health.

2.6.1. Potential ecological risk

IARC (1987) has identified seven PAH compounds (BaA, Chr, BkF, BbF, BaP, DahA and InP) as possible carcinogens. PAHs are of great environmental concern due to their bioaccumulation and potential carcinogenicity. In this study, the total toxicity equivalent quotient of C-PAHs, TEQ_{CARC} (TEQ relative to BaP), an assessment tool (Tsai *et al.*, 2009; Zanardi-Lamardo *et al.*, 2019), was used to assess the environment risks of PAHs in the aquatic environments. The total toxicity equivalent quotient of C-PAHs (TEQ_{carc}) is expressed as total sum of the products of measured C-PAH concentrations in water and the corresponding toxicity equivalency factor (TEF) relative to BaP. The toxic equivalent quotient (TEQ_{carc}) for the studied C-PAHs in each sampling station is calculated by adding the weighted toxicities of all PAHs using equation 1 (Rojas *et al.*, 2011):

$$TEQ_{CARC} = \sum(CPAH_i \times TEF_i) \quad (1)$$

Where TEQ_{CARC} is the sum of the toxic equivalent quotients, TEQs, of CPAHs relative to that of BaP ($mg L^{-1}$); $CPAH_i$ ($mg L^{-1}$) the concentration of *i*th CPAHs in water and TEF_i (unitless) is corresponding toxicity equivalent factor of individual CPAH congener in water respectively. Four CPAHs were detected and include benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF) and benzo[k]fluoranthene (BkF), and their corresponding TEF values are 0.1, 0.1, 0.1 and 0.01 respectively (Nisbet and Lagoy, 1992). To better understand the risk level of TEQ_{CARC} values, the lowest risk concentration of BaP was converted to a TEQ of $5 \times 10^{-7} mg L^{-1}$ (TEQ_{QV}) (Chen *et al.*, 2020). Then, TEQ_{CARC} is categorized according to TEQ_{QV} values as follows: $TEQ_{CARC}/TEQ_{QV} < 0.1$, showing that PAHs concentrations have the no risk or negligible risk to the ecological environment; 0.1–1 represents the low risk; 1–10 represents the low-moderate risk; 10–100 represents moderate-to-high risk; and ≥ 100 represents the high risk.

2.6.2. Human health risk

Health risk assessment evaluates the harmful effects of exposure to chemicals in the contaminated environment on humans. PAHs in surface water exert health risks through ingestion (drinking water) and dermal contact (such as shower) hence risk assessment in aquatic environments usually considers two pathways, direct ingestion and dermal contact (Xiao *et al.*, 2019).

The health risks were evaluated using cancer risk (CR) and lifetime cancer risks (LCR). Health risks through ingestion pathway posed by *i*th PAHs in surface water of the study area were calculated by equations 2 and 3 (USEPA 2015a; USEPA, 2016):

$$CR_{ing, i} = \frac{TEQ_{wi} * IR * ABS_{gi} * EF * ED * SF}{BW * AT} \quad (2)$$

$$CR_{ing} = \sum CR_{ing, i} \quad (3)$$

Where TEQ_{wi} and IR represent the toxic equivalent quotient of c-PAHs in surface water ($mg L^{-1}$) and the daily water ingestion rate ($L day^{-1}$), respectively; EF_i means ingestion exposure frequency ($day yr^{-1}$), ED_i refers to ingestion exposure duration (yr); BW refers to body weight (kg); AT means average lifespan (yr); SF refers to cancer slope factor ($kg d mg^{-1}$). The values of SF could be obtained from the USEPA guidelines (USEPA, 2016).

Health risks through dermal contact for ith PAHs were calculated by the following equations (USEPA, 2004):

$$CR_{der\ i} = TEQ_{wi} * K_{pi} * ABS_d * t_{event} \frac{SA * ET * EF_d * ED_d}{BW * AT} * \frac{SF}{ABS_g} \quad (4)$$

$$CR_{der} = \sum CR_{der,i} \quad (5)$$

where K_p , ABS_d , and t_{event} refer to dermal permeability coefficient of pollutant; dermal absorption factor and event duration, respectively; EV , ED_d , and EF_d represent the event frequency, dermal contact exposure duration, and dermal contact exposure frequency, respectively; SA refers to skin surface area; ABS_g is the gastrointestinal absorption. The values of parameters were obtained from the references and shown in Table 2.

Table 2: Parameters and input assumptions for exposure assessment of PAHs

Parameter/Definition (units)	Values		Reference
	Adult	Child	
Contaminant concentration in water (C_w) (mg L ⁻¹)	value in this study	value in this study	
Incidental water ingestion rate per event (during swimming) (IR_s) (L d ⁻¹)	0.053	0.098	USEPA, 2011
Event frequency (EV) (day ⁻¹)	1	1	USEPA, 2004
Event duration (T_{event}) (h day ⁻¹)	0.58	1	USEPA, 2004
Exposure frequency (EF) (y)	350	350	USEPA, 2004
Exposure frequency (ED) (d y ⁻¹)	24	6	
Total exposure frequency (EDt) (d y ⁻¹)	39.7	15	
Exposed skin surface area (SA) (cm ²)	18000	6600	
Gastrointestinal absorption factor (ABS_g)	BaP and other PAHs: 0.89		USEPA, 2004
Dermal Absorption factor, ABS_d	BaP & other PAHs: 0.13		USEPA, 2004
Dermal permeability constant (K_p) (cm h ⁻¹)	BaA, Chr: 0.47; BaP, BbF: 0.7		USEPA, 2004
Unit conversion factor (CF) (L cm ⁻³)	0.001	0.001	
Body weight (Bw) (Kg)	70	15	USEPA, 2004
Average time (AT) (d)	54.7 x 350 (carcinogenic)		
Ingestion Slope Factor (SF_{ing}) (kg d mg ⁻¹)	BaA, BbF, BkF: 0.73; Chr: 0.073		
Dermal Slope Factor (SF_{der}) (kg d mg ⁻¹)	BaA, BbF, BkF: 2.5; Chr: 0.25		

Health risks posed for each pollutant in surface water for the subgroups were calculated using equation 6.

$$CR_i = CR_{ing} + CR_{der} \quad (6)$$

Carcinogenic risk was calculated for the carcinogens (BaA, Chr, BbF and BkF) observed in the study area. The total carcinogenic risk (TCR) was evaluated using the single health risk index (CR) for carcinogenic PAHs is shown in equation 7.

$$CR = \sum CR_i \quad (7)$$

CR_i is the carcinogenic risk of PAH_i due to ingestion and dermal contact.

The lifetime carcinogenic effect (LCR) of a pollutant is computed over the course of a lifetime, taking into consideration exposures during both childhood and adulthood (Zhang *et al.*, 2013; Wang *et al.*, 2016; Liu and Ma, 2020); a child aged 0-15 years (ED is 15years) and an adult aged 15-54.7 years (ED is 39.7years) (UNDP, 2020). Hence the lifetime cancer risk due to PAHs is expressed as the summation of the aggregate cancer risks of both age groups and given in equation 8.

$$LCR = CR_{child} + CR_{Adult} \quad (8)$$

In general, when the CR value is less than 10^{-6} , it is considered that the carcinogenic risk can be negligible; when the CR value is higher than 10^{-4} , the carcinogenic risk is unacceptable; when the value of CR is between 10^{-6} and 10^{-4} , the carcinogenic risk is considered to be acceptable (Xiao *et al.*, 2019).

2.7. Statistical analysis

The pollution status, ecosystem risk assessment, and human health risk assessment of PAHs were analysed by using Microsoft Excel 2007 software. The analysis of source characteristics of PAHs was based on use of Excel 2020 and SPSS 20.0 software.

3.0. Results and Discussion

3.1. Distribution of PAH isomers in Niger Delta creeks water

The mean concentration of individual PAHs in surface water samples from the three sampling sites is shown in Figure 2. While the overall mean concentrations of individual PAHs, of on ring sizes, level ranges, and carcinogenic PAHs found at various sampling sites are presented in Table 3. Most of the 16 EPA priority PAHs were detected in a majority of surface water samples, 4 PAHs (two 5 -ring PAHs: BaP and DahA, and two 6-ring PAHs: InP and BghiP) were not detected in all the sampling sites. The mean concentrations of the detected PAHs in the surface water of sampling sites of river in this study varied from 1.02 to 16.5 mg L⁻¹. The distribution pattern of the PAHs in the water across sites is in the order of: Phe > Nap > Pyr > Chr > Flu > Fla > Ace > Acy = BkF > BbF > Ant > BaA. Based on the overall mean concentration, Phe (11.11 mg L⁻¹) from 3-ring PAHs, Nap (7.81 mg L⁻¹) from 2-ring PAHs, Pyr (7.51 mg L⁻¹) from 3-ring PAHs, and Chy from 4-ring PAHs (5.52 mg L⁻¹), with a content percentage of 21%, 15%, 14% and 10% of the $\sum PAHs$ ($\sum PAHs$ is the sum of PAHs detected; (12 PAHs in this case), respectively, are the dominant PAH compounds found in the water samples (Table 3). The mean concentrations in water in this study were several orders of magnitude higher than that of the Annual Average Environmental Quality Standards (AA-EQS) of European Water Framework Directive (WFD) for individual PAHs, which state that the safe range for PAHs is from 2.0×10^{-5} to 2.4×10^{-3} mg L⁻¹ (Werres *et al.*, 2009) and EU (2014) permissible limit of and 1.0×10^{-4} mg L⁻¹ for individual PAHs in water intended for consumption by humans and posed harm to human health and ecosystem.

The Σ PAHs levels varied from 32.89 mg L⁻¹ at Bonny to 81.60 mg L⁻¹ at Buguma with mean level of 53.32 mg L⁻¹. These Σ PAHs values are significantly higher than the maximum admissible concentrations of EU (2014) and the Environmental Quality Criteria of the United States (USEPA, 2015b), 5.0×10^{-5} mg L⁻¹, 2×10^{-4} mg L⁻¹ and 3×10^{-5} mg L⁻¹, respectively, for protection of human consumers of aquatic life. Additionally, the results showed that Σ PAHs concentrations in the surface water of all sampling creeks exceeded 1×10^{-2} mg L⁻¹ and implied that the water was heavily contaminated by PAHs and existed high hazard to exposed organisms (Zhang *et al.*, 2012).

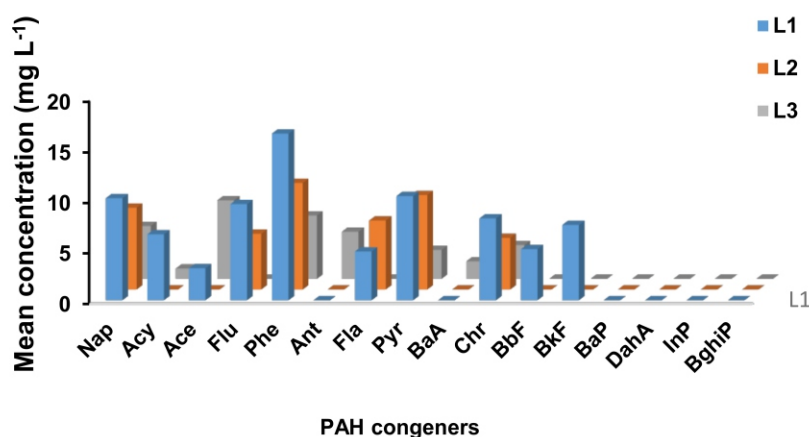


Figure 2: Mean concentrations (mg L⁻¹) of individuals PAHs in the sample waters of Niger Delta mangrove creeks

In the present study, the Σ PAHs concentrations found in the creek water at three different sampling creeks (53.32 mg L⁻¹) are several orders of magnitude higher than those reported in Versova and Malad Creek near Mumbai, India (Singare and Shirodkar, 2021) and some creeks of Niger Delta, Nigeria (Nwineewii and Marcus, 2015). The level of PAHs as reported in the present study was comparable with the PAHs level in the Mvudi and Nzhelele Rivers, South Africa (Edokpayi *et al.*, 2016). The Σ PAHs concentrations found in surface water of the present study are compared with those reported earlier by other researchers in water bodies from different part of the world (Table 4).

Table 3: Overall mean concentration of individual PAHs, ring sizes and carcinogenic PAHs in the surface water samples from River Niger (values in mg L⁻¹)

PAHs	Ring	Overall mean	Range	% Contribution to Σ PAHs	% Contribution to Σ CPAHs
Naphthalene (Nap)	2	7.81	5.23-10.1	14.6%	
Acenaphthylene (Acy)	3	2.52	Nd-6.53	4.7%	
Acenaphthene (Ace)	3	3.65	Nd-3.17	6.8%	
Fluorine (Flu)	3	5.01	Nd-9.52	9.4%	
Phanthrene (Phe)	3	11.11	6.27-16.5	20.8%	
Anthracene (Ant)	3	1.55	Nd-4.66	2.9%	
Fluoranthene (Fla)	4	3.89	Nd-6.83	7.3%	
Pyrene (Pyr)	4	7.51	2.86-10.32	14.1%	

Benzo[a]anthracene (BaA)	4	0.58	Nd-1.74	1.1%	5.6%
Chrysene (Chr)	4	5.52	3.34-8.11	10.4%	53.7%
Benzo[b]fluoranthene (BbF)	5	1.69	Nd-5.06	3.2%	16.4%
Benzo[k]fluoranthene (BkF)	5	2.49	Nd-7.46	4.7%	24.2%
Benzo[a]pyrene (BaP)	5	Nd	Nd	0.0%	
dibenzo[ah]anthracene (DahA)	5	Nd	Nd	0.0%	
Indeno[1,2,3-cd]pyrene (InP)	6	Nd	Nd	0.0%	
benzo[ghi]perylene (BghiP)	6	Nd	Nd	0.0%	
ΣCPAHs ^a		10.27	5.08-20.63	19.3%	100.0%
Σ2-ring PAHs		7.81	5.23-10.1	14.6%	
Σ3-ring PAHs		23.84	15.06-35.72	44.7%	
Σ4-ring PAHs		17.50	12.6-23.26	32.8%	
Σ5-ring PAHs		4.17	Nd-12.52	7.8%	
Σ6-ring PAHs		Nd	Nd	0.0%	
LMW PAHs (2+3-ring)		31.65	24.17-45.82	59.4%	
HMW PAHs (4+5+6-ring)		21.67	7.94-35.78	40.6%	
ΣPAHs (2+3+4+5+6-ring)		53.32	32.89-81.60	100%	

Nd: Not detected; ^aCPAHs = BaA + Chr + BbF + BkF + BaP + DahA + InP

The compositional pattern of PAHs by ring size in the water samples from the three sampling sites of the study area is shown in Figure 3A. Based on the ring size, the overall average percentage contribution of 2-, 3-, 4-, 5- and 6-ring PAHs to the ΣPAHs was 14, 41.5, 38.9, 5.6 and 0.0% respectively (Table 3). The percentage contribution of 12 PAHs based on ring size detected in the present study indicate the dominance of 3-ring PAHs followed by 4- ring PAHs; the two PAHs rings represent 70-89%. The mean concentration of the ring isomers followed the order: 3-ring > 4-ring > 2-ring > 5-ring > 6-ring (Figure 3B).

The LMW PAHs accounted for 59.4% while HMW PAHs accounted for 40.6%. The PAHs are likely derived from anthropogenic activities, such as the accidental oil spills/leaks from pipeline, gas flaring, indiscriminate disposal of used engine oil from boats and ferries for 3-rings PAHs as well as illegal artisanal refineries that littered the Niger Delta region, incomplete crude oil fuel combustion of the boats and ferries engines for 4-ring PAHs.

The results presented in this study comprise an attempt to report the levels, sources and degree of PAH contamination and carcinogenic risk of population exposed to surface water samples collected from Buguma, Krakrama and Bonny creeks of Niger Delta, Nigeria.

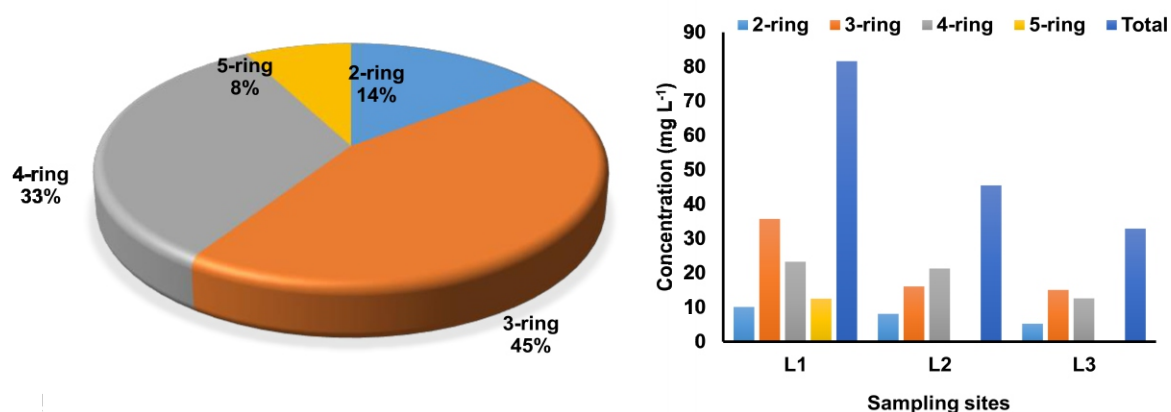


Figure 3A: Percentage of overall average concentration of PAHs by ring size in water of the Niger Delta creeks

Figure 3B: Composition pattern of PAHs isomers by rings in the surface water: A: Of different sampling sites of the study area

The total of LMW, HMW, CPAHs, PAHs concentration in surface water samples from the 3 sampling creeks are represented in Figure 4.

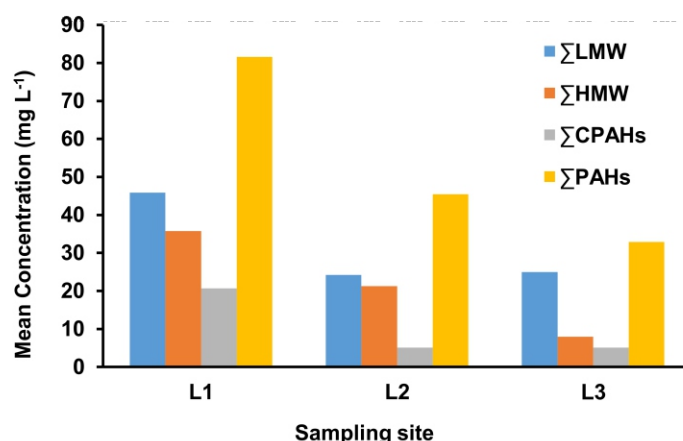


Figure 4: The total of LMW, HMW, CPAHs, PAHs concentration in surface water samples from the 3 sampling sites in the study area

The extent of carcinogenic burden of the study area was also determined by comparing the percent of total carcinogenic PAHs (Σ CPAHs) in Σ PAHs for the three sampling sites of the study area. The mean concentrations of Σ CPAHs (BaA, Chr, BbF, and B kF) detected ranged from 5.08 to 20.63 mg L⁻¹ with a mean of 10.27 mg L⁻¹, accounting for 19.3% of Σ PAHs in all water samples. These results are higher than the safe limits of the EPA National Recommended Water Quality Criteria for the protection of aquatic life and human health (2×10^{-5} mg L⁻¹) (USEPA, 2015b), which could have an adverse ecological effect in these areas. This concentration of Σ CPAHs was relatively higher in River Niger (19.3%) compared to Soan River (17.6%) and Gomti River (6.93%) (Aziz *et al.*, 2014). Thus, river quality should be controlled and the water treated adequately for PAHs contaminants.

Table 4: Distribution of PAH in the aquatic environment from various regions around the world (Values in mg L⁻¹).

Location	Year of Sampling	No	PAHs Range	References
Buguma, Krakrama, Bonny creeks	2019	16	32.89-81.6	Present Study
Malad and Versova creek, Mumbai	2017-18	17	0.114-0.347	Singare & Shirodkar (2021)
Bufalo River Estuary in the Eastern Cape Province, South Africa	2015-16	16	0.015-0.021	Adeniji <i>et al.</i> , (2019)
Alexandria coastal Sea water, Egypt	-	16	0.009-1.255	Omayma <i>et al.</i> , (2016)
Mvudi and Nzhelele Rivers, South Africa	-	16	13.174-26.382	Edokpayi <i>et al.</i> , (2016)
South East Rivers State, Niger Delta	-	16	0.008 - 0.249	Nwineewii & Marcus (2015)
Thohoyandou, Limpopo Province, South Africa	2005-06	6	0.029 - 3.065	Nekhavambe <i>et al.</i> , (2014)

3.2. Identification of Pollution Sources

PAHs introduced into surface waters affect both aquatic and human lives. In order to manage their potential human health hazard and protect the marine ecosystem, identification of their probable sources is of vital importance for studying the transport and fate of PAHs in the environment (Chen *et al.*, 2015). The molecular diagnostic ratios of PAHs isomers are widely used to identify the origin of the pollution emission due to their stability, physical and chemical attributes and by comparing PAH ratios and thus qualitatively distinguish pyrolytic and petrogenic sources (Zhang *et al.*, 2017; Ashayeri *et al.*, 2018). In this study the following isomer ratios Ant/(Ant+Phe), Fla/Pyr, Fla/(Fla+Pyr), Chr/BaA, BaA / (BaA + Chr), and LMW/HMW were applied to characterize source of PAH contamination in surface waters (Table 5).

The ratio of Ant/(Ant+Phe), in Bonny creek was > 1 which implies that the source of the PAHs was pyrogenic due to the combustion of biomasses (Nasher *et al.*, 2013) but was not applied to L1 and L2 as Ant was not detected in their samples. The ratio (LPAHs)/(HPAHs) gave values of >1 for all the sampling sites supporting the fact that the source of the PAHs was more likely to be due to the combustion of fuel. Also, the ratio of Fla/(Fla+Pyr) gave values of <0.4 in L1 which further confirms petrogenic sources due to the use of petroleum products. Value of the ratio of Fla/(Fla+Pyr) > 0.4 in L2 implies that the source of the PAHs was combustion of fuel. Fluoranthene/(Fluoranthene+Pyrene) was not applied to L3 as Fla was not detected in samples. In addition, the ratio (BaA/BaA + Chr) of <0.20 usually implies petrogenic origin, 0.20–0.35 indicates mixed petrogenic and pyrogenic origins, while >0.35 indicates pyrogenic origin (Yunker *et al.*, 2002). Hence, the mean value of this ratio from the Bonny surface water samples is 0.34 (Table 5) which might reflect mixed inputs from the direct discharge of two-stroke engine boats and the deposition of fuel combustion of boats. Generally, the source of PAHs in water samples can be attributed to pyrogenic and petrogenic sources.

Table 5: Molecular diagnostic PAHs ratios in surface water and their possible sources

Location	Ant/ (Ant+Phe) ^a		Fla/ Pyr ^b		Fla/ (Fla+Pyr) ^c		Chr/ BaA ^d		BaA/ (BaA+Chr) ^e		LMW/ HMW ^f	
Buguma	NC		0.47	Pet	0.32	Pet	NC		NC		1.28	Pet
Krakrama	NC		0.73	Pet	0.42	Pyr	NC		NC		1.14	Pet
Bonny	0.43	Pyr	NC ^g		NC ^g		1.92	Pyr	0.34	Pet/ Pyr	3.14	Pet
Petrogenic	<0.1		<1.0		<0.4		<0.4		<0.20		>1	
Pyrogenic	>0.1		>1.0		>0.4		>0.9		>0.35		<1	

3.3. Risk Assessment

3.3.1. Potential ecological risk of PAHs

Among the PAHs, carcinogenic PAHs possess extreme threat owing to their potentially carcinogenic toxicities. In the present study the ΣCPAHs levels in the sampling stations were L1 (20.63 mg L⁻¹), L2 (5.11 mg L⁻¹) and L3 (5.08 mg L⁻¹), and these account for 25.3, 11.2 and 15.4% of the ΣPAHs. The overall mean ΣCPAHs concentration level in the marine aquatic environment of the study area was 10.27 mg L⁻¹ which corresponds to 19.3% of the ΣPAHs.

The potential toxicity (TEQs) of carcinogenic PAHs relative to BaP, the most carcinogenic PAH, was used for potential ecological risk assessment. This method is often used to assess the ecological risk of PAHs in water environments and sediments (Tsai *et al.*, 2009; USEPA 2020). The TEQ_{CARC} values for various CPAHs detected in the aquatic environment of Niger Delta creeks are shown in Table 6. In the present investigation, the total of the carcinogenic PAHs, TEQ_{CARC}, computed for the surface water samples were L1 (1.333 mg TEQ L⁻¹), L2(0.051 mg TEQ L⁻¹) and L3(0.207 mg TEQ L⁻¹) with an overall mean value of 0.531 mg TEQ L⁻¹. The TEQ values for different carcinogenic PAHs detected in the aquatic marine environment of creeks of study area are presented in Table 6. According to the risk classification by TEQ_{CARC}/TEQ_{QV}, the PAHs in water sample is considered high risk (TEQ_{CARC}/ TEQ_{QV} ≥ 100). The TEQ_{CARC} of the carcinogenic PAHs detected accounted for 90% of the total TEQ of the PAHs (TEQ_{ΣPAHs}). The results show that the surface water in Niger Delta creeks was heavily polluted and may cause potential health risks. Therefore, efforts should be taken to control the PAH emissions. Among the 4 CPAHs detected, contributions to the total CPAHs (ΣCPAHs) in water samples followed the trend: BkF(46.9 %) > BbF (31.8%) > BaA(11.9%) > Chr(10.4%). The TEQ_{CARC} values at the different sampling creeks followed the trend: L1 > L3 > L2.

Table 6: TEF and TEQ_{CARC} values of PAHs surface water of study area

PAHs	TEF ^a	TEQ _{CARC} (mg TEQ L ⁻¹)		
		L1	L2	L3
BaA	0.100	-	-	0.174
Chr	0.010	0.081	0.051	0.033
BbF	0.100	0.506	-	-
BkF	0.100	0.746	-	-
BaP	1.000	-	-	-
BghiP	0.010	-	-	-
DahA	1.000	-	-	-
IdP	0.100	-	-	-
TEQ _{CARC}		1.333	0.051	0.207

^a TEFs: Toxic equivalency factors (Nisbet and LaGoy, 1992).

3.3.2. Health risk assessment

No K_p value was available for BkF; hence CR_{der} were not computed for it.

Cancer Risk (CR) and lifetime cancer risk (LCR)

The distribution of carcinogenic risk of children and adults, and lifetime cancer risk of PAHs exposure via the two pathways in the study area is shown in Figure 5. In the present study, cancer risk due to exposure to PAHs in water for adults and children were 1.8E-02 (1 cancer case per 56 people) and 6.0E-03 (1 cancer case per 167 people) respectively, and higher than the baseline of acceptable risk of 1E-04 (one cancer case per 10,000 people) (Maertens *et al.*, 2008), indicating a high carcinogenic risk. Considering exposure via dermal contact, it could be inferred that the water of the study area is unfit for recreational activities, because there is a chance that 1 in every 62 adults and 181 children who undertake recreational activity in the water are exposed to the risk of having cancer, respectively. It is pertinent to point out that the chances of adults' exposure to the carcinogenic risk is higher than for children (Adeniji *et al.*, 2019). Therefore, necessary caution should be taken by everyone using the water and regulatory authorities should ensure that the contamination of the aquatic environment is controlled to ensure the safety of human and aquatic lives.

The total estimated lifetime cancer risk (LCR) of ingestion and dermal exposure were 6.2E-04 and 2.3E-02. The mean estimated ingestion and dermal lifetime cancer risk (LCR) of PAHs was 2.4E-02 (1 cancer case per 42 people), exceeded the baseline of acceptable risk of 1E-04, indicating high lifetime cancer. This degree of cancer risk is unacceptable. The lifetime cancer risk in the study area (three communities) followed the trend: Buguma > Bonny > Krakrama.

The CR values of the 4 carcinogenic PAHs (BaA, Chr, BbF, and BkF) exceeded the baseline of acceptable risk of 1E-04. The BbF (86%) is the dominant contributor to the lifetime cancer risk (LCR) (Figure 6).

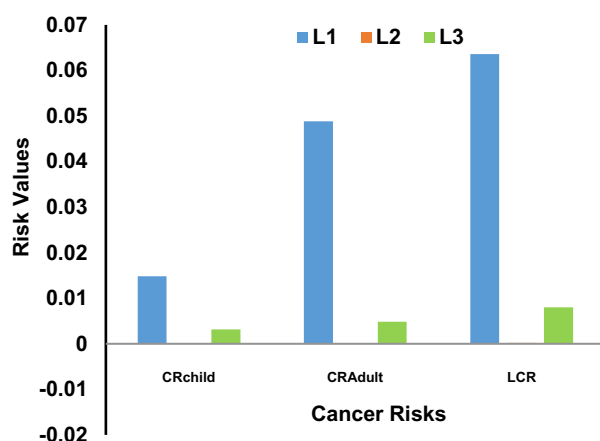


Figure 5: Distribution of cancer risk of PAHs in the sampling sections: CR_{Child}, CR_{Adult} and Lifetime Cancer Risk

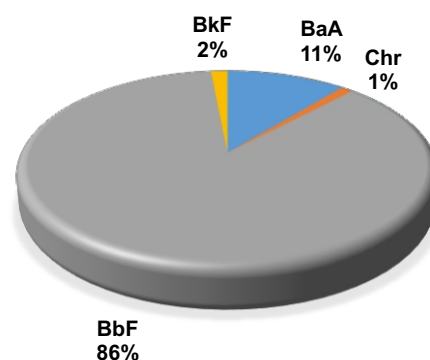


Figure 6. Mean contributions to Lifetime cancer from PAHs congeners

4.0. Conclusion

In this research, levels and sources of PAHs found in three sections of the River Niger's surface water were investigated, and related ecological and human health risks were estimated. Also water quality index, the toxicity load and removal of PAHs to make the water safe for human consumption were estimated. Selected PTEs concentrations were higher than the FAO/WHO recommended levels in all samples taken from the three riverine communities, which made up the sampled sites. The MDRs and multivariate analyses (PCA and Cluster analysis) demonstrated that PAHs were primarily petrogenic and pyrolytic by-products of human activities.

Due to similar pollution sources, PAHs have often been found to co-exist with PTEs, therefore risk computed must include the two contaminants. The average values of CR of surface waters samples from the three sections of River Niger were above the recommended threshold of 1×10^{-6} for PAHs. Increased concentrations of PAHs and associated risks to the environment and public health in the riverine towns of Buguma, Krakrama, and Bonny may be related to the indiscriminate discharge of untreated industrial effluents, domestic waste, and unlawful bunkering that takes place at the Niger Delta's creeks. The three parts of the River Niger's surface water were found to be highly polluted, and as a result, there is a risk that it will have a negative impact on both children's and adults' health. In view of this, it is therefore recommended that stakeholders and policymakers should help in crafting policies and strategies to mitigate the level of crude oil pollution, and consequently reduce PAH contamination as well as monitor PAHs pollution in surface waters of the communities along Buguma, Krakrama and Bonny creeks for sustainable ecosystem and human health.

Acknowledgements

The authors are indebted to Engr. Emenike Onyegeme-Okerenta for his guidance and support during sample collection, analysis and data presentation.

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Cite this article as:

Onyegeme-Okerenta, B.M., and West, O.L. 2023. Distribution, Possible Sources, Ecological and Health Risk Assessment of Polycyclic Aromatic Hydrocarbon (PAHs) in Surface Water of Niger Delta Creeks, Nigeria. *Nigerian Journal of Environmental Sciences and Technology*. 7(1) pp55-76. <https://doi.org/10.36263/nijest.2023.1.0404>