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Chemical Fingerprinting, PAHs Characterization and Ecological Risks of Carcinogenic PAHs in Surficial Sediments of Egi Crude Oil Producing Communities, Niger-Delta, Nigeria

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Abstract

In order to do PAHs rings analysis, its source identification, extent to which cPAHs present and what kind of ecological risk they pose, the surface sediments from various freshwaters in the Egi crude oil producing cities in the Niger Delta, Nigeria were analyzed. Sediments collected from the research areas for PAHs loadings (in mg/kg dry weight) ranged from 0.020 to 1.790, 0.050 to 1.880, and 0.020 to 1.640, respectively for Obite, Obagi, and Ibewa cluster areas, as measured by gas chromatography-mass spectrometer. In these clusters, the respective average concentration of the three dominant carcinogenic PAHs were Indeno(1,2,3-cd)pyrene (1.170.0mg/kg), Dibenz[a,h]anthrancene (0.870.0 mg/kg), and Dibenz[a,h]anthrancene (1.3670 mg/kg) for Ibewa, Obagi and Obite cluster areas. The findings showed that dominant PAHs rings are of high molecular weight (HMW) PAHs in these sediments are, 5 member rings, which are benzo(b)fluoranthene, Benzo(k)fluoranthene, and Benzo(a)pyrène, and 6-member ring which are, Indeno(1,2,3-cd)pyrene, Dibenz[a,h]anthrancene, and Benzo[ghi] perylene, respectively. Their fingerprints points majorly to pyrogenic sources, combustion of coal, biomass, petroleum, and other related anthropogenic petroleum activities as the primary source of PAHs in the environment. Notably, the RQ_{NCs} and RQ_{MPCs} for single PAHs molecule are both less than 1, it means the contamination it generates is considered of low ecological risk. Again, the research area experiences frequent flooding, it is believed that this contributes to the low ecological risk of PAHs chemical pollution. Consequently, the area is deemed to be quite safe.

Keywords: Sediment, Source Identification, Ecological Risk, Carcinogenicity, cPAHs

Introduction

The Niger Delta area of Nigeria exhibited a notable oil production output of 101.4 million metric tons in the year 2019, positioning the country as one of the leading oil producers in the African continent according to Faria (2020) [11]. Obida *et al*., (2018) [19] buttressed that the Niger Delta located in Nigeria holds the distinction of being the largest delta in Africa and ranks as the third-largest delta globally. The Niger Delta is situated in the southern region of Nigeria, serving as the initial point of departure for the river originating from central Nigeria. The Niger Delta was identified by Obida *et al*., (2018) [19] as one of the ten largest marine and wetland ecosystems globally. This region has a wide array of ecological systems, such as mangrove forests, estuaries, lakes, rivers, and creeks. According to Ofori *et al*., (2020) [20], the Niger Delta region is inhabited by various human settlements, including states, metropolises, cities, and Local Government Areas (LGAs).

According to the study conducted by Ite *et al*., (2018) [13], the Niger Delta region has significant environmental and socioeconomic consequences as a result of oil exploration and exploitation activities.

The following are several undesirable outcomes: The effects of burning and releasing natural gas include air pollution (Ite *et al*., 2018) [13], pollution of marine ecosystems (Iniaghe *et al*., 2013; Osuagwu and Olaifa, 2018) [12, 21], contamination of surface and groundwater (Ite *et al*., 2018) [13], and the exacerbation of socioeconomic problems and environmental degradation.

Environmental heavy metals, persistent organic pollutants, total petroleum hydrocarbons (TPHs), and polycyclic aromatic hydrocarbons (PAHs) have been introduced to the land and water ecosystems in the Niger Delta region as a result of oil exploration and production. Environmental and public health problems have been heightened globally due to the current scenario, according to Emoyan (2020) [10] and the UN Environment Programme (2019) [26].

Rapid urbanization and commercialization contribute to pollution in many ways, including the emission of PAHs (Mojiri *et al*., 2019) [18]. Researchers Ehigbor *et al*., (2020) [9] and Iwegbue *et al*., (2020) [16] found that PAHs showed toxicity profiles that could indicate they could interact with the immune and endocrine systems, create mutations, and perhaps cause cancer. Since polycyclic aromatic hydrocarbons (PAHs) are very mobile, they can contaminate areas that are far away from their original release site. The primary contributors to these pollutants include automobiles, incinerators, industrial emissions, oil spills, biomass combustion, and insufficient fossil fuel combustion (Iwegbue *et al*., 2021). Many other types of plant-based materials are considered biomass, such as wood, grass, and other similar compounds. Anomalous solid molecules containing two or more fused aromatic rings composed of carbon and hydrogen atoms are known as polycyclic aromatic hydrocarbons, according to both Abdel-Shafy and Mansour (2016) [1] and Suman *et al*., (2016) [25]. Abdel-Shafy and Mansour's 2016 study discovered three different spatial arrangements for aromatic rings: Angular, cluster, and linear. There is a correlation between the amount of aromatic rings found in a PAH and its molecular weight, which determines whether it is an LMW or an HMW PAH. Polycyclic aromatic hydrocarbons (PAHs) can leach into the environment as gases or particles, depending on their molecular weight. It is feasible to classify PAHs according to their ring structures.

Polycyclic aromatic hydrocarbons (PAHs) deposit as sedimentary materials in a variety of aquatic habitats including rivers, lakes, lagoons, and oceans due to their hydrophobic character, which allows them to adsorb onto particulate matter (Souza *et al*., 2018; Aghadadashi *et al*., 2019) [3]. In addition to providing a home for benthic creatures, sediments also act as a repository for PAHs, which are a byproduct of human activity (Balgobin and Ramroop Singh, 2019) [4].

In addition, working with sediments can expose farmers and fishermen to polycyclic aromatic hydrocarbons (PAHs), which can be harmful if consumed or touched accidentally. Consequently, surface sediment analysis is crucial for a full picture of the contamination situation and the dangers involved. Because of their extremely harmful features, environmental matrices containing polycyclic aromatic hydrocarbons (PAHs), especially those with high molecular weights, require monitoring.

The river systems in the Niger Delta region are greatly stressed out by the freshwater rivers that flow through the Egi settlements, especially in their lower areas. Many factors are coming together to cause this phenomenon. These include the presence of large oil and gas reserves in the area where the observation was made, the effects of drilling and production, the discharge of urban waste, and various commercial and industrial activities, especially in the upstream parts of the nearby factories.

Researchers have looked at polluted soils in a number of different locations, including the Ibewa cluster, the Obagi flow station, the oil wells in the Egi hamlet, and the Obite gas plant. The abundant natural gas and crude oil deposits in the area draw research participants because of the huge economic impact these resources have on the local economy. The ecosystem in the area has been greatly altered by human activities such as urbanization, industrialization, agriculture, oil and gas extraction, and the introduction of eco-hazards. Plans to decrease pollution, systems to monitor environmental quality, and rules to insure compliance can't be formulated without accurate data on the degree of pollution in the area. Polycyclic aromatic hydrocarbons (PAHs) in Egi community freshwater sediments: Where they came from, how they got there and what kind of ecological damage they could do are the goals of this research.

The study area is known for its abundance of oil and gas wells, flare stacks, and pipelines that transport crude oil. These facilities have the potential to leak organic contaminants (PAHs) into the environment. Sediment contaminated with crude oil has the potential to release PAHs into the water, where they could be ingested by fish, people, and other species that inhabit such an unhealthy ecosystem. One way to do this is by consuming tainted food or water, breathing in contaminated air, or touching contaminated sediments with your skin. In order to understand the current pollution situation and the dangers it poses, it is necessary to analyze the surface sediments. Constant monitoring is necessary for PAHs in environmental matrices due to their significant toxicity, particularly for PAHs with large molecular masses.

The main aim of this research is to evaluate the PAHs distribution, sources and possible ecological risk of carcinogenic polycyclic aromatic hydrocarbons (PAHs) in surface sediments of selected contaminated freshwaters of Egi crude oil producing communities (Obagi, Obite and Ibewa) of the Niger Delta, Nigeria.

The objectives of the study are to determine of the concentration of PAHs, Carcinogenic PAHs in surface sediments from the study area, to determine the possible sources (fingerprinting) of the (carcinogenic) PAHs in the surface sediments and to determine ecological risk of PAHs in the surface sediment of study area.

Study Area

Description of the study area

The study area covers streams around Obagi flow station, Obite gas plant, Ibewa cluster and contaminated freshwaters around oil wells in the study area (Egi communities). Egi community is located in Ogba/Egbema/Ndoni Local Government Area, Rivers State. The area is located in the northern part of the state and shares boundary with Imo and Delta State respectively. It is a growing city with an estimated population of about 40000 (EPNL, 2005). The economy of the area relies mainly on agriculture and oil and gas, being one of the highest oil and gas producing communities in Rivers State. The climate is typically tropical with dry (November – March) and wet (June – October) seasons. Average temperature of the area ranges between $27^{O}C$ – $32^{O}C$, while average humidity is between 69% and 96%, EPNL(ELF Petroleum Nigeria Ltd) (2005).

Obagi flow station is an onshore oil field located on OML

58, 85 km north-west of Port-Harcourt, Nigeria. It is composed of 26 stacked reservoir levels with an estimated total OOIP(original oil in place) of 1.2 Gbbls. It was discovered in 1964 and has been producing since 1966 through 123 wells and 257 completions. 21 layers have been developed. The Obite Gas Plant processes Non-Associated Gas (from HP-high pressure Gas wells) and Associated Gas (from Obagi Gas Compression) which it exports on an extended capacity of 10.65 Million Standard Metric Cubes of Gas to the Nigeria LNG Plant in Bonny.

Materials and Method

Soil sample collection

Sediment samples were collected from freshwater around Obagi flow station, Obite gas plant, Ibewa cluster and contaminated sediments around oil wells between July and December 2022, to reflect the dominant seasons in the study area – wet and dry seasons.

Twenty-seven (27) grab sediment samples (about 1kg each) were collected at different depth from the various sampling stations. The sediments were collected in an aluminium foil using soil auger. Each sampling was carried out in triplicate. With the exception of suspected source point, the sampling points were evenly spread in order to give a true representative sample of the study area. The samples were kept in a cooler containing dry ice (≤4ºC) to initiate cooling process and sample preservation prior to transportation to the laboratory for preparation and analysis. Control samples were taken 100 meters away from each sample site.

Sample Preparation

The sediment samples were air-dried for more than 48 hours until there was no visible moisture remaining. Each of the air-dried samples were thoroughly homogenized in a mortar and then sieved with a 2mm metal sieve. Sonication extraction technique was used to extract the PAHs in the sediment. 1:1 solvent mixture of acetone and dichloromethane was prepared. About 10 g aliquot of the well homogenized sediment sample was measured into a solvent rinsed beaker. 50 ml of the solvent mix was added to the sample. The sample was then place in a Sonicator and sonicated for about 10-15 minutes at 70ºC. About 10 g of anhydrous sodium sulphate was added to the sample until a clear extract developed. The extracted solvent was poured into a round bottom flask and concentrated to about 2ml using vacuum rotary evaporator. Clean up of PAH extracts from the sediment was achieved through solid phase extraction with alumina/silica gel. The 2 ml concentrated solvent was transferred into the packed column and fractionated with 10 ml dichloromethane. Saturated aliphatic hydrocarbons were eluted with 20 ml of n-hexane and the aromatic hydrocarbons eluted with 30 ml of a mixture of hexane and dichloromethane (90:10) (v/v). The eluted solvent (aromatic hydrocarbon) was re-concentrated and then transferred to the vial bottle. The elute (aromatic fraction) was analyzed using an "HP5890 Series ii'' gas chromatography equipped with a flame ionization detector (GC/FID).

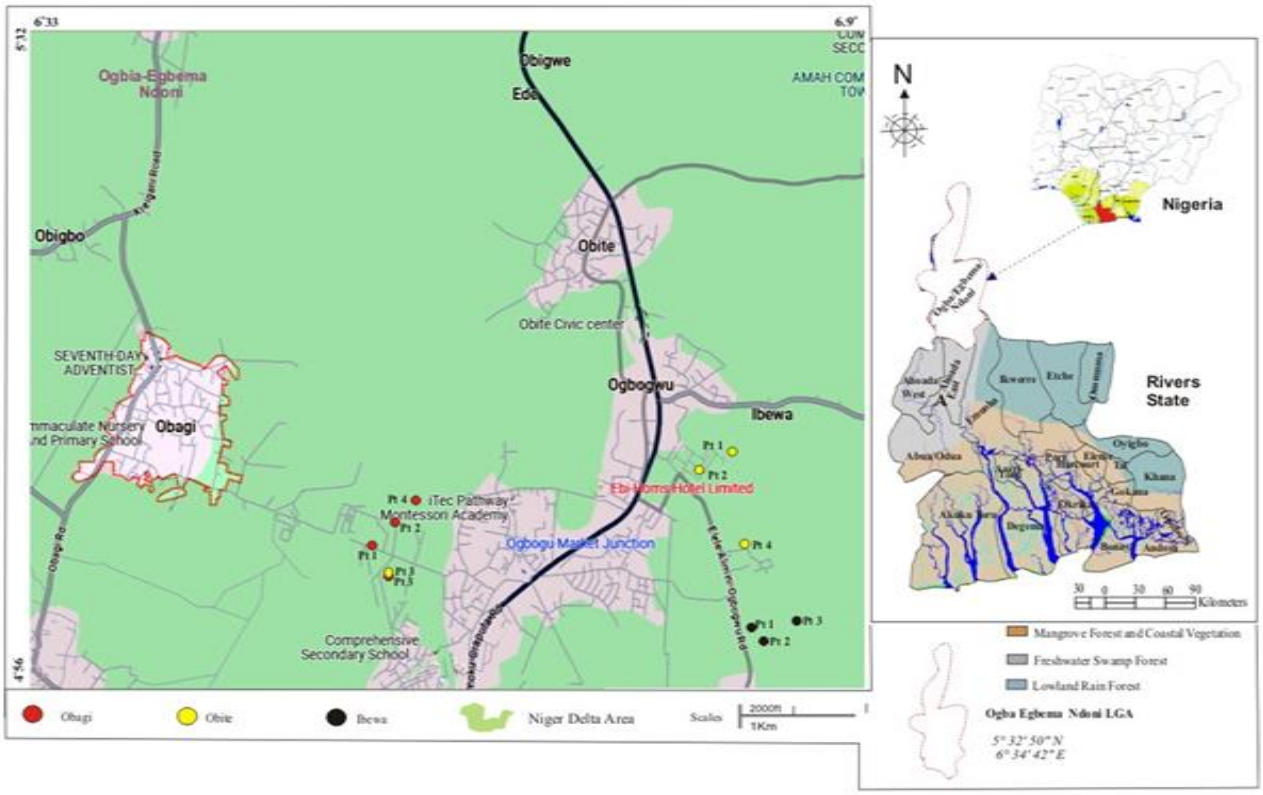

Fig 1: Map of Rivers state, Nigeria showing study area

Quality assurance/quality control (QA/QC)

The reagents/ chemicals used were of analytical standard grade. The process of sample collection, storage and preparation were carefully carried out so as to maintain the integrity of the samples. Field blanks were taken to the site for site contaminant levels. All apparatus used in the preparatory stage of the GC analysis were solvent rinsed with a mixture of acetone and dichloromethane. The round bottom flask used for sample concentration was rinsed with acetone after each round of concentration. This was to avoid cross-contamination of the samples. The surrogate standard, orthoterphenyl was used to determine the efficiency of the

extraction procedures. The surrogate standards recovery rate ranged from 71 % to 108 %. All the spiked blanks (standards spiked into solvents) had surrogate standard recoveries in the range of 75–98%. Quantification was by external calibration techniques.

Equipment calibrations were done following manufacturer guidelines or established protocols. Samples were prepared and handled with care to avoid contamination or degradation and Protocols were implemented for proper storage, labeling, and tracking of samples.

Method of Data Collection/Instrumentation

Computerized system for collecting, storing and processing MSD output was used. Before samples were analyzed, the instrument was calibrated for the analysis. This was done by injecting a series of 1µL PAHs Accu-Standards. A five-point calibration curve was prepared using the PAHs mixture that was commercially obtained. The range of the curve was 5mg/L, 10mg/L, 15mg/L, 20mg/L and 25mg/L. The acceptable linear correlation was 0.95. Calibration verification was used to confirm that the instrument performance had not changed significantly since initial calibration. It was done by analyzing midpoint concentration of standards within the calibration range and if calculated concentrations deviated by more than 30% from known values, then corrective actions of recalibrating the instrument must be done before sample analysis. The concentration of each analyte in a sample was determined by calculating the amount of analyte injected, from the peak response, based upon the analyte.

Soil/Sediment Samples

$$Cf = Area\ (p) \times Rf \times \frac{Vf}{Wi} \times DF \times 1000$$

Where:

Cf = Final Sample concentration (ug/L)
Area (p) = Measured area of peak (peaks)
Wi = initial weight extracted (g dry weight)
Vf = Final extract volume (mL).
Df = Dilution factor of sample or extract.
Rf = Response factor from the calibration standard calculation.

Ecological Risk Assessment

The risk posed to the ecosystem by the concentrations of PAHs found in sediments from the study areas was evaluated by making use of the risk quotient (RQ) approach of Kalf *et al*., (1997) [17] with the modifications introduced by Cao *et al*., (2010) [6]. The risk assessment was based on a set of negligible concentrations (NCs) and a set of maximum permissible concentrations (MPCs) for PAHs in sediment which were developed by Kalf *et al*., (1997) [17]. The RQs for PAHs in these river sediments were determined by using Equations below:

$$RQ_{NCs} = \frac{C_{PAHs}}{C_{QV\,(NCs)}} \quad (2)$$

$$RQ_{MPCs} = \frac{C_{PAHs}}{C_{QV\,(MPCs)}} \quad (3)$$

Where:

RQ_{MPCs} is the Risk quotient for maximum permissible concentration
RQ_{NCs} is the Risk quotient for negligible concentration
C_{PAHs} is the concentrations of PAHs in the sediments
C_{QV} is the corresponding sediment quality value concentration for these PAHs.

The maximum permissible concentration (MPCs) is the concentration above which the risk of adverse effects is considered to be unacceptable. The negligible concentration (NCs) is defined as the MPC/100.

Results And Discussion

Table 1: Mean of Carcinogenic Polycyclic Aromatic Hydrocarbons (cPAHs) from the Study

PAHs	Obagi	Obite	Ibewa
Benz(a)anthracene	0.1900[a]	0.0800[a]	0.1370[a]
Chrysene	0.1170[a]	0.1370[a]	0.1300[a]
Benzo(b)fluoranthene	0.2370[a]	0.4200[a]	0.4900[a]
Benzo(k)fluoranthene	0.3870[a]	0.5470[a]	0.4270[a]
Benzo(a)pyrene	0.6500[a]	0.2830[a]	0.6230[a]
Diben(a,h)anthracene	0.8700[a]	1.3670[a]	1.0230[a]
Indeno(1,2,3-cd) pyrene	0.3530[a]	1.0830[a]	1.1170[a]
	2.804	**3.917**	**3.947**

Table 1, presents the mean of carcinogenic concentration of PAHs (cPAHs) in Obagi, Obite and Ibewa Cluster study areas. The level of cPAHs concentration was 2.804, 3.9170 and 3.9470 mg/kg for Obite and Ibewa Cluster study areas respectively. In Obagi study area, Diben(a,h)anthracene (0.8700 mg/kg) had the highest concentration among the PAHs. Obite and Ibewa Cluster had Diben(a,h)anthracene (1.367 mg/kg) and Indeno(1,2,3-cd)pyrene (1.117 mg/kg) as highest PAH respectively. The lowest concentration of PAH in Obagi was chrysene with a concentration of 0.1170 mg/kg. In Obite, the lowest concentration of PAH was Benz(a)anthracene (0.0800 mg/kg) while Ibewa cluster also had chrysene (0.130 mg/kg) as the lowest concentration of PAH.

Characterization of the PAHs (Ring Analysis)

The analysis of the individuals PAHs by ring concentration was carried out for ring-4, ring-5 and ring-6 which are displayed in Table 2 and Fig 2, Ring-4: - Fluoranthene, Pyrene, Benzo (a) Athrancene, Chrysene, ring-5: - benzo (b) Fluoranthene, Benzo (k) Fluoranthene, and Benzo (a) Pyrene, and ring-6: - Indeno (1,2,3-cd) pyrene, Dibenz [a,h] anthrancene, and Benzo [ghi] perylene.

Table 2: Overall PAHs Ring Analysis for Obagi, Obite and Ibewa Cluster locations

Location/Rings		4-ring (%)	5-ring (%)	6-ring (%)
Obagi	Site 1	9.95	30.89	48.68
	Site 2	5.77	32.69	51.92
	Site 3	5.06	57.59	27.22
		6.93	**40.39**	**42.61**
Obite	Site 1	4.39	36.59	52.68
	Site 2	6.47	30.94	51.80
	Site 3	4.55	39.90	45.45
		5.14	**35.81**	**49.98**
Ibewa Cluster	Site 1	3.29	28.81	52.67
	Site 2	6.45	43.87	38.06
	Site 3	7.95	36.42	46.36
		5.90	**36.37**	**45.70**

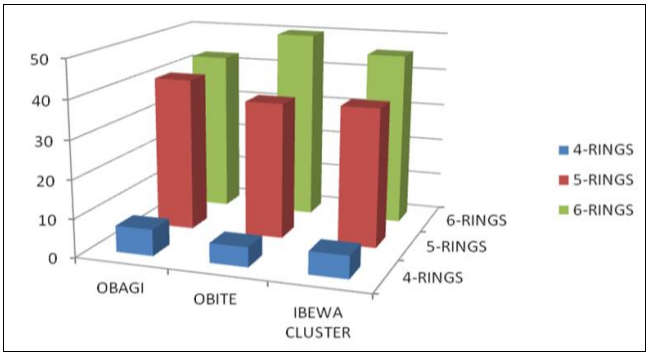

Fig 2: Overall PAHs ring analysis for Obagi, Obite and Ibewa Cluster from the study

Table 2, displays the ring characterization of PAHs found in the sediments of the research region. The results showed a range of 3.29 to 57.59% in the sediments of the studied location. In the Obagi area, the largest concentrations of 6-ring PAHs were found at sites 1 and 2, while the highest concentrations of 5-ring PAHs were found at site 3. Site 1's PAH concentrations were shown to be lowest, but only ring 4's PAH concentrations were lowest at sites 2 and 3 within the Obagi study region. The concentration of 6-ring PAH was consistently higher in the Obite research area. In the Ibewa cluster region, 6-ring PAHs were more prevalent and concentrated at sites 1 and 3, while 5-ring PAHs were more plentiful at site 2, according to the data. Whereas 4-ring PAH concentrations were highest at sites 3 and 2. Fig 2, illustrates the percentage distribution and PAH ring analysis visually in the study area.

Finger printing/ Source of the PAHs

The finger printing and isomeric ratios of the PAHs to check for the possible sources of the cPAHs in the biota and the following PAH/PAH ratio as was used. The potential sources of cPAHs specifically if detected can be differentiated using its distribution pattern (Wang and Fingas, 1999). The ratios of Ant/(Ant+Phe) and Flt/(Flt+Pyr) was employed to differentiate petrogenic combustion from pyrogenic combustion and Ant/(Ant+Phe) < 0.1 indicates a petrogenic derivation, while Ant/(Ant+Phe) > 0.1 indicates a pyrogenic derivation. In addition, Flt/(Flt+Pyr) < 0.40 is characteristic of a petrogenic source; Flt/(Flt+Pyr) > 0.50 is characteristic of biomass/coal combustion sources; and ratios between 0.4 and 0.5 characterize petroleum combustion (Yunker *et al.*, 2002) [29]. In some situations, where Ant and Phe were not detected due to their volatility, the diagnostic and ring analysis is done with other PAHs (Lu & Zhu, 2012). BaA/(BaA+Chr) below <0.25 implies a petrogenic source, while values > 0.25 is of pyrogenic sources. Fluo/Pyr >1.0 implies petroleum sources while <1.0 implies pyrolytic sources. Phe/Anth <10 signifies combustion sources and >10 implies petrogenic sources. IcdP/(IcdP+BghiP) <0.2 Petroleum sources, >0.5 biomass and coal sources, and between 0.2 to 0.5 represent petroleum combustion.

Table 3: Fingerprinting of the possible sources

Isometric ratio	Obagi	Obite	Ibewa
Ant/(Ant + Phe)	0.5500	0.7800	0.4500
Flt/(Flt + Pyr)	0.5200	0.6200	0.5200
IndP/(IndP + BghiP)	0.3100	0.6000	0.6500
BaA/(BaA + Chry)	0.6200	0.3700	0.5100

Polycyclic Aromatic Hydrocarbons detectable isomeric ratios results revealed that PAH sources in this study were of mixed origin. Table 3, presented the result of the isometric ratio for sediments in Obagi, Obite and Ibewa Cluster study areas. The results showed that Ant/(Ant + Phe) isomeric ratio was greater than 0.1 for the study areas which indicated that PAHs were derived from a pyrogenic sources. Flt/(Flt+Pyr) isometric ratio indicated that all the study areas were polluted with biomass/coal combustion sources since their ratios were greater than 0.5. IcdP/(IcdP+BghiP) isometric ratio indicated that Obagi town with a ratio of 0.31 possibly could describe sources associated with burning of liquid petroleum while Obite (0.60) and Ibewa Cluster area (0.65) were polluted by petroleum sources. BaA/(BaA+Chry) isometric ratio for the study area also indicated a pyrogenic source for PAHs since all ratios were greater than 0.25.

Ecological Risk of Carcinogenic PAHs using RQ_{NCs} and RQ_{MPCs}

The risk posed to the ecosystem by the concentrations of PAHs found in sediments from the Obagi, Obite and Ibewa Cluster study area was evaluated by making use of the risk quotient (RQ) approach of Kalf *et al.*, (1997) [17] with the modifications introduced by Cao *et al.*, (2010) [6]. The significance of the RQ values is as follows: $RQ_{NCs} < 1.0$ signifies that the individual PAH compounds are probably of negligible concern, while $RQ_{MPCs} \geq 1$ implies that contamination by the individual PAH compound is severe and there is an urgent need for some control and remedial action to be undertaken to minimize the risk. In a situation where $RQ_{NCs} \geq 1.0$ and RQMPCs < 1, it suggests that the contamination caused by a single PAH compound might be classified as a moderate risk, and some control and remedial actions are required.

Table 4: Ecological Risk of Carcinogenic PAHs using RQ_{NCs}

PAHs	Obagi	Obite	Ibewa
Benz(a)anthracene	0.0530	0.0220	0.0380
Chrysene	0.0011	0.0013	0.0012
Benzo(b)fluoranthene	0.0660	0.1170	0.1360
Benzo(k)fluoranthene	0.0160	0.0230	0.0180
Benzo(a)pyrene	0.0240	0.0100	0.0230
Diben(a,h)anthracene	0.0320	0.0510	0.0380
Indeno(1,2,3-cd)pyrene	0.0060	0.0184	0.0189

Table 4 and 5 showed the ecological risk of carcinogenic PAHs using RQ_{MPCs} and RQ_{NCs}. From Table 4, all values of carcinogenic PAHs for RQ_{NCs} were less than 1.0 indicating that each individual PAH compound was probably of negligible concern, which could be due to lots of factors like flood incidence that washed away the soil surfaces, low crude oil production activities within the period of this work. This was also the same with tables 5.0 as all the values for RQ_{MPCs} in carcinogenic PAHs was less than 1 indicating that the PAHs were of negligible quantity and may not need any urgent sort of control or remedial action to minimize the risk. Though the risk might be low but provided oil activities continues the possibility of increase in ecological risk might there, therefore the need for intermittent survey of the environment.

Table 5: Ecological risk of carcinogenic PAHs using RQ_{MPCs}

PAHs	Obagi	Obite	Ibewa
Benz(a)anthracene	0.0005	0.0002	0.0004
Chrysene	0.000011	0.000013	0.000012
Benzo(b)fluoranthene	0.00070	0.00120	0.00140
Benzo(k)fluoranthene	0.00016	0.00023	0.00018
Benzo(a)pyrene	0.00024	0.00010	0.00023
Diben(a,h)anthracene	0.00032	0.00051	0.00038
Indeno(1,2,3-cd)pyrene	0.000060	0.00018	0.00019

Discussion

The quantities of carcinogenic polycyclic aromatic hydrocarbons (PAH) in the sediment at the research sites were found to be below the intervention level set by the Nigerian rule (40,000 µg/kg; 4000 mg/kg) and did not surpass the goal value of 1000 µg/kg (100 mg/kg), as reported by the Department of Petroleum Resources (DPR) in 2012. The research sites exhibited minimal impact from PAH concentrations, so rendering the implementation of rigorous pollution control measures and sustainable management strategies for their reduction and mitigation of ecological consequences unnecessary. Baumard *et al*., (1998) [5] have delineated four distinct levels of carcinogenic polycyclic aromatic hydrocarbon (cPAH) contamination in sediment. (a) The concentrations are classified as very low, surpassing 10 ng/g; (b) they are considered moderate, ranging from 100 to 1000 ng/g; (c) they are classified as high, ranging from 1000 to 5000 ng/g; and (d) they are classified as extremely high, surpassing 5000 ng/g. According to Baumard *et al*., (1998) [5], in order to categorize sediments from these research locations as having "low" contamination, the average PAH readings should fall within the range of 0 to 10 ng/g.

The quantities of carcinogenic polycyclic aromatic hydrocarbons (cPAHs) in the research zones are presented in Table 1. The cluster region of Ibewa exhibited the highest concentration, whilst Obagi demonstrated the lowest concentration. The Obagi and obite study zones had the highest concentration of Diben(a,h)anthracene, whereas the Ibewa cluster region displayed the highest concentration of Indeno(1,2,3-cd) pyrene. All of the samples exhibited significantly higher levels of carcinogenic polycyclic aromatic hydrocarbons (PAHs). The utilization of ANOVA to analyze the concentrations did not yield statistically significant changes in the levels of PAHs across the several research locations, regardless of their carcinogenic nature ($p<0.05$). Nevertheless, a significant disparity was seen in the homologous composition and levels of the various polycyclic aromatic hydrocarbons (PAHs). The study locations were deemed contaminant-free as the individual quantities were much below the maximum contamination levels set by the USEPA. Researchers observed a rise in the concentration of ring 6 polycyclic aromatic hydrocarbons (PAHs) across all the studied sites. Rings 6, 5, and 4 in the Obagi research area demonstrate a progressive increase in values. In the research locations, it was shown that 4-ring polycyclic aromatic hydrocarbons (PAHs) accounted for 49.98% and 45.70% of the total PAHs discovered in the Obite and Ibewa clusters, respectively. Identifying the sources of PAHs is essential for formulating control strategies, mitigating hazards, and implementing environmental governance frameworks. This study aimed to investigate the ratios of carcinogenic polycyclic aromatic hydrocarbon (PAH) isomers.

According to Mojiri *et al.*, (2019) [18], cPAHs pollution is mostly attributed to two primary groups of sources: Human activities and natural processes. Minor or negligible natural emission sources include fires occurring in forests, volcanic eruptions, and moorland fires caused by lightning (Srogi, 2007; Ravindra *et al.*, 2008; Abdel-Shafy and Mansour, 2016) [24, 22, 1]. Ravindra *et al.*, (2008) [24] assert that the primary sources of PAH contamination are predominantly derived from four distinct categories of anthropogenic origins, including industrial, mobile, residential, and agricultural. The ratios of Ant/(Ant+Phen) and Flt/(Flt+Pyr) enable the differentiation of polycyclic aromatic hydrocarbon (PAH) sources linked to the combustion of petroleum from those linked to biomass, wood, and coal. A petrogenic derivation is indicated when the ratio of Ant to (Ant+Phe) is less than 0.1, while a pyrogenic derivation is indicated when the ratio is more than 0.1. The Ant/(Ant+Phe) ratio was employed for petrogenic combustion, whilst the Flt/(Flt+Pyr) ratio was utilized for pyrogenic combustion. Furthermore, according to Yunker *et al*., (2002) [29], Flut/(Flt+Pyr) values below 0.40 are indicative of petrogenic sources, while Flt/(Flt+Pyr) values above 0.50 suggest biomass/coal combustion sources. Additionally, ratios ranging from 0.4 to 0.5 are indicative of petroleum combustion. BaA/(BaA+Chr) readings below 0.25 indicate a petrogenic source, whereas those over 0.25 indicate a pyrogenic source. A Fluo/Pyr value beyond 1.0 signifies the presence of petroleum sources, whilst a value below 1.0 indicates the presence of pyrolysis sources. When the Phe/Anth ratio is less than 10, it indicates the presence of combustion sources, whereas a ratio more than 10 indicates the presence of petrogenic material sources. The range of IndP/(IndP+BghiP) is below 0.2 for petroleum sources, over 0.5 for biomass and coal sources, and between 0.2 and 0.5 for petroleum combustion. According to Table 4.3, the primary source of pollution in the Obagi area is pyrogenic, which refers to the combustion of biomass or coal. The isometric ratio of indP to (indP+BghiP) suggests that pollution is likely caused by the combustion of petroleum. Additionally, the isometric ratio of baA to (baA + chry) provides further evidence that pollution originates from pyrogenic sources. Based on the isometric ratios of Ant/(Ant + Phe), Flt/(Flt + Pyr), and BaA/(BaA + Chry), it may be inferred that the predominant kind of pollution in the surveyed region of Obite was pyrogenic in nature. According to the isometric ratio of IndP to (IndP + BghiP), the primary sources of pollution in the Obagi study region were predominantly attributed to the combustion of biomass and coal, rather than petroleum. The pollution sources in the Ibewa cluster region exhibited a same pattern, encompassing pyrogenic sources (Ant/(Ant + Phe), Flt/(Flt + Pyr), and BaA/(BaA + Chry)) as well as biomass/coal sources (IndP/(IndP + BghiP)).

Results from the use of RQNCs and RQMPCs to assess the environmental risk of cPAHs are presented in Table 4 and 5. All of the sites where these rivers' sediments were tested had RQNCs values for specific PAHs below 1. This suggests that, when considered separately, the PAHs pose little to no danger to ecosystems. Also, if the RQ_{MPC} score is less than 1, it means that the contamination from individual PAH chemical is not high enough to warrant urgent action to manage or remediate the situation. Because the RQ_{NCs} and RQ_{MPCs} for a single PAH molecule are both less than 1, the contamination it generates might be considered low risk.

Thus, few measures of control or correction would be required.

Conclusion

Based on the results, it seems that sustainable management and strict pollution control measures won't be necessary to lower carcinogenic PAH concentrations and their ecological effects in the studied regions. Possible causes for the reduced cPAH levels include the amount of oil and gas activity, which have slowed down, or the 2022 floods that occurred in the area, which washed away the top soils and transported toxins to faraway places. The risk may be minor, but intense oil and gas operations can also create pollution concentrations, which is why regular environmental audits are necessary.

Possible explanations for the reported concentration distribution pattern include photooxidation, PAH molecular weight, and volatility in the research region. Pyrogenic, petroleum, coal/biomass, and other anthropogenic petroleum-related sources were identified as the primary sources of the distinct PAHs, according to the study's findings. We can infer that a single PAH compound's contamination might be considered low risk, necessitating nothing in the way of control or cleanup efforts.

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