



Source identification and diagnostic evaluation of polycyclic aromatic hydrocarbons (PAHs) in the sediments and Seafood of kaani River in ogoni axis of Rivers State, South-South, Nigeria

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Abstract

In the Kaani River in the Ogoni axis of Rivers state, Nigeria, this study evaluates the origins and diagnostic assessment of polycyclic aromatic hydrocarbons in sediment and seafood. Polycyclic Aromatic Hydrocarbons (PAHs) were detected in surface water shrimp, tilapia, mudskipper, crab, and sediment samples that were collected from four (4) different locations. The locations were identified as station 1 (Maa di binnise Igbara waterside), station 2 (Mann Stream), station 3 (Woman Stream), and station 4 (Nwii ke ma kor stream). The samples were treated in accordance with laboratory standards. The concentrations of PAHs in sediment and seafood were first determined by extraction using a soxhlet extractor with 125 milliliters of methanol. Then, the concentrations of PAHs from the purified extract were measured using Gas Chromatography equipped with Flame Ionization Detector, which provided the concentration degrees of the various components present in the sediment and seafood. Results were obtained. The contaminant's mean concentrations varied from 9.8643±1.0977 mg/kg to Not Detected in the sediment samples. The results for the average content of polycyclic aromatic hydrocarbons in seafood samples taken from the Kaani River at various sites were also obtained. In the seafood sample, the average concentration of PAHs varied from 0.3787±0.0229 mg/kg to Not Detected. The source diagnostic ratio of PAHs in sediment samples taken from the Kaani River: An/(An + Ph) varied from Not Detected-0.9008, Flu/(Flu + Py) ranged from Not Detected – 0.7447, and BaA/(BaA + Ch) ranged from 0.2612-0.9665. The Σ LMW PAHs and Σ HMW PAHs were measured in mg/kg and ranged from 6.5599–14.7869, respectively. The source diagnostic ratio of PAHs in seafood samples from the Kaani River were ranged as follows: Σ LMW PAHs: 0.1126-0.4863 mg/Kg; Σ HMW PAHs: 0.2789-0.6241 mg/Kg; LMW/HMW: 0.3541-1.7436; An/(An + Ph): 0.3288-0.8983; Flu/(Flu + Py): Not Detected – 1.000; and BaA/(BaA + Ch): 1.0000-1.0000. The studies' findings demonstrated that the PAH concentrations varied from 0.008 to 0.249 mg/kg. The contaminants' quantities were found to be greater than the USEPA's recommended limits for drinking water, which range from 0.20 to 400 parts per billion. Some of the PAHs that were detected were highly prevalent close to the point source and hazardous even at low doses. During the examination, variations in the concentrations of PAHs were noted in the stations and the seasons, with the dry season of the year yielding greater values. Both pyrogenic and petrogenic sources were shown to be the origins of PAHs in the sediment, with the pyrogenic source having higher amount in the river's seafood. The research comes to the conclusion that, until a full remediation exercise is completed, both the use of the River for domestic purposes and the ingestion of any aquatic habitat creature from these rivers should be immediately suspended.

Keywords: Diagnostic evaluation, polycyclic aromatic hydrocarbons, sediments, seafood

Introduction

In any given context, the distribution pattern or spread of polycyclic aromatic hydrocarbons has a profound impact on the makeup and origins of PAHs, and it may be utilized to evaluate the total negative impact of PAHs on the environment (Adeniji *et al.*, 2019) ^[1]. In order to diagnose and identify or anticipate the sources of PAHs in the environment, as well as to distinguish between their various sources of input, behavioral traits related to the ratio of PAHs have proven to be very helpful (Campbell, 2008; Tao *et al.* 2017) ^[2, 32].

In the environment, polycyclic aromatic hydrocarbons, or PAHs, are a common type of organic pollution. They are well known to bio-accumulate in both human and animal tissue and to have mutagenic and carcinogenic properties. According to Liang *et al.* (2007) ^[10], incomplete combustion of organic materials, fossil fuels, and petroleum are the main anthropogenic and natural sources of PAHs. Fish that has been smoked at high temperatures or grilled meat can also produce PAHs. For instance, a small number of writers (Storelli *et al.*, 2003; Purcaro *et al.*, 2006) ^[27, 31] have documented that, depending on the method of cooking, preservation, and storage, PAHs can be discovered in significant levels in specific foods. However, it is important to remember that the permeability of each fish species'

membrane and the enzyme system that powers it determine how much of the PAHs are absorbed. As a result, different PAHs accumulate in different orders in different fish samples, and this is a highly species-specific phenomenon (USEPA 2011) ^[33].

The primary cause for concern after human exposure to these substances, according to Llobet *et al.* (2006) ^[11], is the fact that several PAHs are carcinogenic. Dietary exposure to PAHs has been linked to an elevated risk of some human malignancies, according to a number of recent epidemiological studies (Ekpete *et al.*, 2019; Purcaro *et al.*, 2006; IARC, 1987) ^[4, 27]. The majority of chemical molecules known as polycyclic aromatic hydrocarbons (PAHs) are solid, colorless, white, or pale yellow. These are a common set of several hundred chemically related compounds that have different structures and varying degrees of toxicity. They are also persistent in the environment. Through a variety of mechanisms, they poison organisms (Obiakor *et al.*, 2014) ^[22]. In general, PAHs are found in the environment in mixtures including two or more of these chemicals, such as soot, and are introduced through a variety of pathways (EFSA, 2008) ^[5].

The incomplete burning of organic materials including coal, oil, and wood is the main source of PAHs. According to the EU (2014) ^[6], PAHs are not chemically produced for

industrial use. However, several PAHs have a few commercial applications. According to Zhang *et al.* (2017)^[34], they are primarily employed as middlemen in the chemical industries that produce medications, agricultural goods, photographic products, thermosetting polymers, lubricants, and other things. On the other hand, several PAHs are generally used for: Acenaphthene: used in the production of polymers, pigments, dyes, and medications. Anthracene is a diluent used in the production of pigments and dyes as well as wood preservatives. Production of pharmaceuticals, dyes, and agrochemicals using fluoranthene. Fluorene: used in the production of thermoset plastic, pigments, dyes, and medicines. Phenanthrene: production of insecticides and resins

Pyrene: pigment production. In addition to roofing tar, asphalt used in road building may also contain other PAHs. Moreover, the fields of electronics, functional polymers, and liquid crystals all employ particular refined PAH compounds (Hajisamoh, 2013; Singh *et al.* 2008)^[7,30].

The processes referred to as pyrolysis are of three types: pyrogenic, petrogenic, and biological. When organic materials are subjected to high temperatures with little or no oxygen, pyrogenic PAHs are created (Poster *et al.* 2006)^[25]. Pyrolysis is the purposeful conversion of coal residues into lighter hydrocarbons through thermal cracking or the destructive distillation of coal into coke and coal tar. Meanwhile, incomplete combustion of wood in fireplaces and forest fires, incomplete combustion of motor fuels in vehicles and trucks, and incomplete combustion of fuel oils in heating systems are all unintended processes (Qian *et al.* 2017)^[28]. The range of temperatures at which pyrogenic reactions take place is from 3500C to over 12000C. In general, urban regions and areas near significant PAH sources have higher quantities of pyrogenic PAHs (WHO, 2003)^[33]. Furthermore, PAHs can develop at lower temperatures.

It is important to note that PAHs found in crude oils were generated at temperatures as low as 100–1500C over millions of years (Qiu *et al.*, 2009)^[29]. In this sense, petrogenic refers to PAHs produced during the maturation of crude oil and related processes. Because crude oil and its products are used, stored, and transported so widely, petrogenic PAHs are prevalent.

Material and methods

Table 1: Sample locations' geographic positions along the Kaani River

River	Sample Identity	Location	Geographic Location (Coordinates)
Kaani. Kaani. Kaani. Kaani	1	Maa di binnise Igbara waterside	Lat. 4.6793 ⁰ N
	2	Mann Stream	Long. 7.3809 ⁰ E
	3	Woman Stream.	Lat. 4.6791 ⁰ N
	4	Nwii ke ma kor stream	Long. 7.3850 ⁰ E

Sample collection and preparation

Using a hand-held van Veen grab, silt samples were collected from multiple locations along the River. Representative or composite samples were then produced, placed in sterile glass bottles, and transported to the laboratory. Local fishermen collected seafood from several study sites by using fishing gear. After that, the seafood was delivered in an ice freezer to the lab (Prycek *et al.* 2007)^[26]. Four (4) distinct locations were used to gather sediment samples, shrimp, tilapia, mudskipper, and crab from surface water. These locations include station 1 (Maa di binnise Igbara waterside), station 2 (Mann Stream), station 3 (Woman Stream), and station 4 (Nwii ke ma kor stream). Being handled in accordance with laboratory guidelines while being checked for polycyclic aromatic hydrocarbons (PAHs). First, the concentration of PAHs in sediment and seafood was determined by extraction and purification using a soxhlet extractor with 125 milliliters of methanol. Then, the concentrations of PAHs from the purified extract were measured using Gas Chromatography equipped with a Flame Ionization Detector, which provided the concentration degrees of the various components present in the sediment and seafood (Onojake *et al.* 2020)^[24].

For sediment and seafood samples, the amount of PAHs found at every particular chromatogram was expressed in mg/kg (Obayori and Salam 2010)^[21].

Results

Table 2: Mean Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediment Samples from Kaani River at different Stations

PAHs (mg/Kg)	Stations				
	1	2	3	4	Control
Na	ND	ND	ND	ND	ND
Ace	ND	ND	ND	ND	ND
Acy	ND	ND	0.0543±0.0162	ND	ND
Fl	ND	0.1289±0.0225	1.0021±0.2231	0.8131±0.1264	ND
Ph	0.2454±0.0176	0.0373±0.0035	0.5065±0.0351	0.7062±0.0437	0.0003±0.0001
An	0.2258±0.0122	0.3386±0.0124	0.1455±0.0043	ND	ND
Flu	0.0000±0.0000	0.1758±0.0006	3.1670±0.2195	0.6699±0.0514	0.0004±0.0001
Py	3.7727±0.2214	0.2713±0.0050	1.0859±0.4471	0.9345±0.0669	0.0005±0.0001
BaA	1.6951±0.1398	0.4547±0.0244	0.6663±0.0395	0.5514±0.0451	0.0002±0.0001
Ch	0.0587±0.0027	0.0534±0.0023	0.8324±0.0067	1.5595±0.05394	0.0002±0.0000
BbF	0.0033±0.0004	9.8643±1.0977	0.1646±0.0269	0.2006±0.0866	0.0000±0.0000
BkF	0.1156±0.0046	0.0737±0.0050	ND	ND	ND
BaP	0.3780±0.0655	1.4521±0.2116	0.0011±0.0004	0.1575±0.0044	0.0012±0.0003
BP	0.0000±0.0000	0.0538±0.0032	1.3819±0.0659	ND	ND
DA	1.4742±0.0504	1.3218±0.0352	1.5653±0.3269	2.2366±0.1139	0.0004±0.0001
IP	0.0169±0.0012	1.0660±0.0299	ND	0.2498±0.0072	0.0001±0.0000
Total	7.9857±0.5158	15.346±1.4695	10.5186±1.3954	8.0791±1.0850	0.0033±0.0008

ND (Not Detected)

Naphthalene (Na), acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Fl), phenanthrene (Ph), anthracene (An), fluoranthene (Flu), pyrene (Py), benzo [a] anthracene (BaA), chrysene (Ch), benzo [b] fluoranthene (BbF), benzo

[K] fluoranthene (BkF), benzo [a] pyrene (BaP), indeno [1,2,3 – cd] pyrene (IP), dibenzo [ah] anthracene (DA) and benzo [g,h,i] perylene (BP)

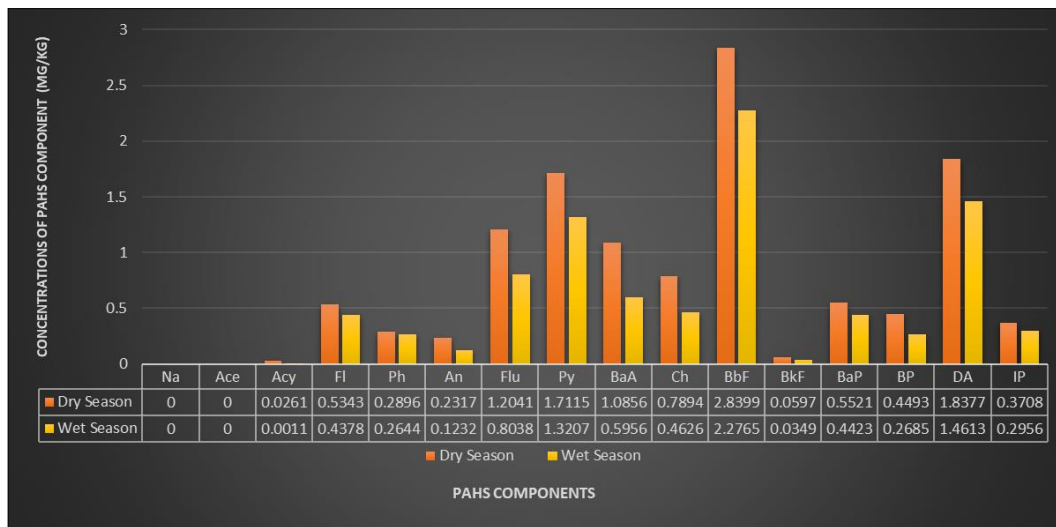


Fig 1: Mean Variations of PAHs (Components) Concentrations in Dry and Wet Seasons in the Sediment of Kaani River

Table 3: Mean Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in Seafood Samples from Kaani River at different Stations

PAHs (mg/Kg)	Stations				
	1 Shrimps	2 Tilapia	3 Mudskipper	4 Crab	Control
Na	ND	0.3604±0.0238	ND	ND	ND
Ace	ND	ND	ND	ND	ND
Acy	ND	0.0226±0.0022	ND	ND	ND
Fl	ND	0.0679±0.0049	0.1563±0.0218	0.0323±0.0034	0.0004±0.0001
Ph	0.0636±0.0028	0.0036±0.0006	0.0328±0.0033	0.0647±0.0036	0.0001±0.0000
An	0.0490±0.0028	0.0318±0.0049	0.0522±0.0019	0.0317±0.0012	0.0002±0.0001
Flu	ND	0.0050±0.0007	0.0318±0.0062	ND	ND
Py	ND	ND	0.3787±0.0229	ND	ND
BaA	0.0779±0.0029	0.1425±0.0272	0.2015±0.0136	0.0741±0.0032	0.0003±0.0001
Ch	ND	ND	ND	ND	ND
BbF	0.2126±0.0271	ND	ND	0.2009±0.0111	ND
BkF	0.0275±0.0020	0.1314±0.0016	0.0121±0.0006	0.0333±0.0042	0.0002±0.0000
BaP	ND	ND	ND	ND	ND
BP	ND	ND	ND	ND	ND
DA	ND	ND	ND	ND	ND
IP	ND	ND	ND	ND	ND
Total	0.4306±0.0376	0.7652±0.0659	0.8654±0.0703	0.4370±0.0267	0.0012±0.0003

ND (Not Detected)

Naphthalene (Na), acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Fl), phenanthrene (Ph), anthracene (An), fluoranthene (Flu), pyrene (Py), benzo [a] anthracene (BaA), chrysene (Ch), benzo [b] fluoranthene (BbF), benzo [K] fluoranthene (BkF), benzo [a] pyrene (BaP), indeno

[1,2,3 – cd] pyrene (IP), dibenzo [ah] anthracene (DA) and benzo [g,h,i] perylene (BP)

n Variations of PAHs (Components) Concentrations in Dry and Wet Seasons in the Seafood of Kaani River.

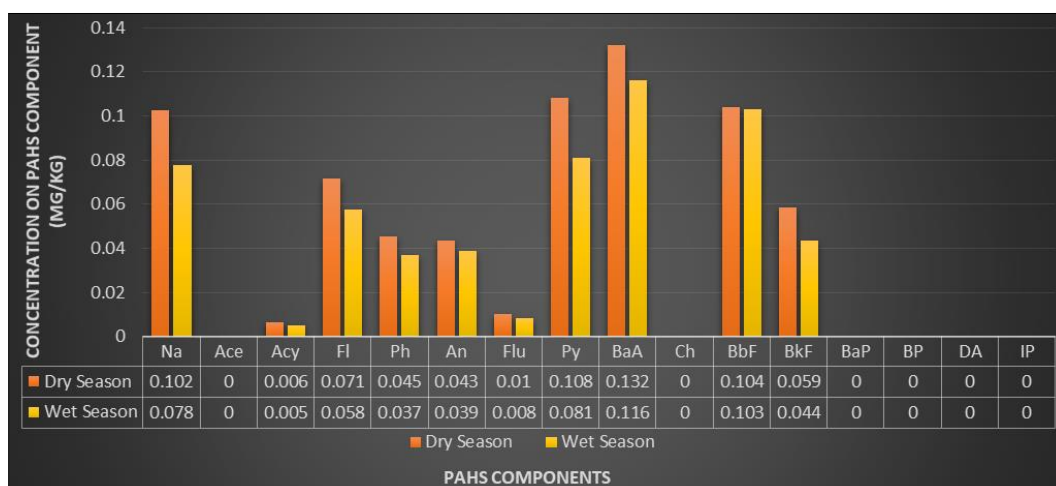


Fig 2: Mean Variations of PAHs (Components) Concentrations in Dry and Wet Seasons in the Seafood of Kaani River

Table 4: Diagnostic Ratios of PAHs in sediment Sample from Kaani River

Stations	Σ LMW PAHs	Σ HMW PAHs	LMW/HMW	An/(An+ Ph)	Flu/(Flu + Py)	BaA/(BaA+ Ch)
1	0.4712	7.5145	0.0627	0.4792	-	0.9665
2	0.5591	14.7869	0.0378	0.9008	0.3932	0.8949
3	1.6541	8.8645	0.1866	0.2232	0.7447	0.4446
4	1.5193	6.5599	0.2316	-	0.4175	0.2612
Petrogenic			> 1	< 0.1	< 0.4	< 0.2
Pyrogenic			< 1	> 0.1	> 0.5	> 0.35

Either the numerator or denominator or both are not detectable (ND)

LMW (low molecular weight), HMW (high molecular weight), an (anthracene), Ph (phenanthrene), Flu (fluoranthene), Py (pyrene), BaA (benzo [a] anthracene), Ch (chrysene)

Table 5: Diagnostic Ratios of PAHs in Seafood Samples from Kaani River

Stations	Σ LMW PAHs	Σ HMW PAHs	LMW/HMW	An/(An+ Ph)	Flu/(Flu + Py)	BaA/(BaA+ Ch)
1	0.1126	0.3180	0.3541	0.4352	-	1.0
2	0.4863	0.2789	1.7436	0.8983	1.0	1.0
3	0.2413	0.6241	0.3866	0.6141	0.0775	1.0
4	0.1287	0.3083	0.4175	0.3288	-	1.0
Petrogenic			> 1	< 0.1	< 0.4	< 0.2
Pyrogenic			< 1	> 0.1	> 0.5	> 0.35

Either the numerator or denominator or both are not detectable (ND)

LMW (low molecular weight), HMW (high molecular weight), an (anthracene), Ph (phenanthrene), Flu (fluoranthene), Py (pyrene), BaA (benzo [a] anthracene), Ch (chrysene)

According to Table 2 and Figure 1, which provide the mean amounts of polycyclic aromatic hydrocarbons in the sediment samples for various sites, the pollutant ranged from Not Detected to 9.8643±1.0977 mg/kg. The values of Na varied: ND-ND for Ace, ND-0.0543±0.0162 for Acy, ND-1.0021±0.2231 for Fl, 0.0373±0.0035-0.7062±0.0437 for Ph, ND-0.3386±0.0124 for An, and 0.0000±0.0000-3.1670±0.2195 for Flu., Py's result was 0.2713±0.0050-3.7727±0.2214; BaA's result was 0.4547±0.0244-1.6951±0.1398; Ch's result was 0.0534±0.0023-1.5595±0.5394; BbF's result was 0.0033±0.0004-9.8643±1.0977; BkF's result was ND-0.1156±0.0046; BaP's result was 0.0011±0.0004-1.4521±0.2116; BP's result was ND-1.3819±0.0659; DA's result was 1.3218±0.0352-2.2366±0.1139; and IP's result was ND-1.0660±0.0299, respectively. However, the analysis's findings showed that the sediments are only mildly contaminated, which, if ignored, might eventually provide a major risk (Okoro 2008) [23].

Table 3 and Figure 2 show the findings for the mean concentration of polycyclic aromatic hydrocarbons in seafood samples from the Kaani River at various sites. The values varied from 0.3787±0.0229 mg/kg to Not Detected. The values of Na were 0.0741±0.0032-0.2015±0.0136, ND-ND for Ace, ND-0.0226±0.0022 for Acy, ND-0.1563±0.0218 for Fl, 0.0036±0.0006-0.0647±0.0036 for Ph, 0.0317±0.0012-0.0522±0.0019 for An, ND-0.0318±0.0062 for Flu, and ND-0.3787±0.0229 for Py, For BaA, ND-ND for Ch, ND-0.2126±0.0271 for BbF, 0.0121±0.0006-0.1314±0.0016 for BkF, ND-ND for BaP, ND-ND for BP, ND-ND for DA, and ND-ND for IP. Although there is no immediate health risk to the environment from these creatures' ostensibly low amounts of PAHs, there may be harmful effects down the road due to the contaminant's bioaccumulation (Meng *et al.* 2019) [13].

Table 4 displays the findings for the source diagnostic ratio of PAHs in sediment samples from the Kaani River.

An/(An + Ph) ranged from Not Detected-0.9008, Flu/(Flu + Py) ranged from Not Detected – 0.7447, and BaA/(BaA + Ch) ranged from 0.2612-0.9665. The Σ LMW PAHs were found to be between 0.4712-1.6541 mg/Kg, the Σ HMW PAHs ranged between 6.5599-14.7869 mg/Kg, and the LMW/HMW varied from 0.0378-0.2316. According to the research, HMW PAHs predominate over LMW PAHs, and their primary origins are petrogenic.

Table 5 displays the findings for the source diagnostic ratio of PAHs in seafood samples from the Kaani River. The PAH ranges that were measured were as follows: Σ LMW PAHs were 0.1126–0.4863 mg/kg, Σ HMW PAHs were 0.2789–0.6241 mg/kg, LMW/HMW was 0.3541–1.7436, An/(An + Ph) was 0.3288–0.8983, Flu/(Flu + Py) was Not Detected – 1.000, and BaA/(BaA + Ch) was 1.0000-1.0000. It has been determined that the analysis's sources of PAH input are a combination of pyrogenic and petrogenic sources. This research supports the findings of Storelli *et al.* (2003) [31] and Nyarko *et al.* (2011) [20].

Discussion

The Kaani River sediment sample results (Table 4) showed that all of the stations had a low molecular weight/high molecular weight PAHs (LMW/HMW) ratio less than 1, which denotes a pyrogenic source of input. The ratio of benzo[a] anthracene/benzo [a] anthracene + chrysene (BaA / BaA + Ch) gave value greater than 0.35 indicating PAHs sources arising from pyrogenesis. In station 1, the ratio of anthracene/anthracene + phenanthrene (An / An + Ph) was 0.4792, indicating pyrogenic sources of PAHs in the aquatic environment. The data from station 2 indicates that there were pyrogenic sources of PAHs input, as indicated by the ratio of anthracene/anthracene + phenanthrene (An) being greater than 0.1, the ratio of fluoranthene/fluoranthene + pyrene (Flu/Flu + Py) being less than 0.4, indicating a petrogenic source of input, and the ratio of benzo[a] anthracene/benzo [a] anthracene + chrysene (BaA / BaA + Ch) being greater than 0.35, indicating pyrogenic input source.

At station 3, the ratio of anthracene/anthracene + phenanthrene (An / An + Ph) was greater than 0.1, indicating pyrogenic sources of PAHs input in the environment; the ratio of fluoranthene/fluoranthene + pyrene (Flu/Flu + Py) gave value of 0.7447, indicating pyrogenic sources of PAHs; and the ratio of benzo[a] anthracene/benzo [a] anthracene + chrysene (BaA / BaA + Ch) gave value greater than 0.35, indicating sources of PAHs resulting from pyrogenesis.

At station 4, the ratio of benzo[a] anthracene/benzo [a] anthracene + chrysene (BaA / BaA + Ch) gave value not greater than 0.35 indicating PAHs sources arising from petrogenesis, while the ratio of fluoranthene/fluoranthene + pyrene (Flu/Flu + Py) gave value not greater than 0.5, suggesting petrogenic sources of PAHs.

Seafood samples from the Kaani River (shrimps, tilapia, mussels, and crab) produced results (Table 5) that showed that in stations 1, 3, and 4, the ratio of low molecular weight/high molecular weight PAHs (LMW/HMW) was less than 1, indicating pyrogenic sources of input; in station 2, however, the ratio was greater than 1, indicating petrogenic sources of PAHs input in the station. All of the stations (1-4) had ratios of anthracene/anthracene + phenanthrene (An / An + Ph) greater than 0.1, which indicates pyrogenic sources of PAHs in the aquatic environment.

At station 2, the ratios of benzo[a] anthracene/benzo [a] anthracene + chrysene (BaA / BaA + Ch) and fluoranthene/fluoranthene + pyrene (Flu/Flu + Py) produced values more than 0.5 and 0.35, respectively, confirming PAH sources originating from pyrogenesis. At station 3, the ratio of benzo[a] anthracene/benzo [a] anthracene + chrysene (BaA / BaA + Ch) gave value greater than 0.35 signifying pyrogenic sources of PAHs, while the ratio of fluoranthene/fluoranthene + pyrene (Flu/Flu + Py) gave value less than 0.4 indicating petrogenic sources of PAHs input in the station. The benzo[a] anthracene/benzo [a] anthracene + chrysene (BaA / BaA + Ch) ratio in station 4 was higher than 0.35, indicating that pyrogenic input is one of the sources of PAHs.

Anthropogenic input of PAHs into the water body, primarily from combustion sources, was indicated by the increased proportion of combustion-based or pyrogenic source of PAHs found in the water body from the examined stations (Ilechukwu *et al.*, 2016)^[8]. Anthropogenic activities abound in the suburb and Kaani River towns, including the careless dumped of untreated home and agricultural garbage into bodies of water. Main contributing factors to pyrogenic sources of PAHs in the aquatic environment are the use of agrochemicals to improve soil fertility and the illicit dredging and commercial sand conveyance by engine boats (Nyarko *et al.* 2011)^[20]. While there are no known instances of illegal bunkering, also known as "Kpoo fire," in the Kaani River communities, there have been reports of such activities in the surrounding areas. This is likely due to the transportation of low molecular weight hydrocarbons from the illegally refined crude oil combustion, which can end up in the River.

The results of this study support those of previous research on PAHs in the Niger Delta's aquatic environment (Neff *et al.*, 2004; Meador *et al.*, 2006; Mzoughi and Chouba, 2011)^[12, 14, 15]. While the overall findings of this work indicated a higher prevalence of HMW compared to LMW, the various diagnostic ratios used to identify the input sources favored

pyrogenic input sources. This is consistent with findings from other writers (Nkpaa and Essien., 2013; Nwineewii and Ibok, 2014)^[17, 19] as well as researchers that examined the sources of PAHs that have an impact on the ecosystem in the Niger Delta (Nozar and Zakaria, 2013; Ekpete *et al.*, 2019)^[4, 18]. Liang *et al.* (2007)^[10] state, while pyrogenic polycyclic aromatic hydrocarbons are released first into the air and then precipitate down to water through gravity, rainfall, or other forms of atmospheric depositions, petrogenic polycyclic aromatic hydrocarbons are released directly into the aquatic environment (Onojake *et al.* 2020)^[24].

Conclusion

Monitoring the aquatic environment, which includes seafood and sediments, is crucial to the assessment and evaluation process that aims to revitalize and repair the ecosystem. By providing safety and protection to the plants and animals that live in the aquatic environment, such evaluation will maintain the aquatic ecosystem's integrity. The aquatic medium's PAH level further demonstrated the low amounts in the Kaani River. The majority of the data documented indicated that, during the course of the inquiry, HMW PAHs outnumbered LMW PAHs in the river's silt.

The dry season of the year exhibited greater values for variations in the concentrations of PAHs recorded in the stations and in the seasons during the experiment. Both pyrogenic and petrogenic sources were shown to be the origin of PAHs in the river, with pyrogenic sources having higher amounts in the sediment columns of the river.

Recommendation

To remove or lessen the amount of these environmental pollutants that are seen in the river, the government, through its agencies, should put in place appropriate and effective mechanisms to prevent the illegal refining and transportation of petroleum products that operate along the river's coasts. If the government is unable to offer sufficient monitoring mechanisms to check this threat, it should muster the political will to pass regulations that will encourage proper refining, management, and disposal of wastes at a designated site away from the river.

People who engage in illicit oil bunkering operations must to be made aware of the harm that these contaminants cause to the aquatic ecosystem and to the people who depend on the river for daily living.

To track the amount of these pollutants in the aquatic ecosystems, remediation plans should be properly implemented and with goals specified. This will lessen the possibility of water body contamination brought on by the buildup of PAHs and heavy metals.

References

1. Adeniji AO, Okoh OO, Okoh AI. Levels of polycyclic aromatic hydrocarbons in water and sediment of Buffalo River Estuary, South Africa and their health risk assessment. Archives of Environmental Contamination and Toxicology, 2019;76:657-669.
2. Campbell A. Polycyclic Aromatic Hydrocarbons PAHs, 2008. <https://thevkq308bm.wikispaces.com/Polycyclic+Aromatic+Hydrocarbons>.
3. Etori OS, Iyama WA. Source identification of polycyclic aromatic hydrocarbons in water at point of

- effluent discharge into the New Calabar River, Port Harcourt, Rivers State, Nigeria. *International Journal of Environment and Climate Change*,2019;9(6):343-349.
4. Ekpete OA, Etori OS, Iyama WA. Concentrations of polycyclic aromatic hydrocarbons from selected dumpsites within Port Harcourt Metropolis, Rivers State, Niger Delta, Nigeria. *International Journal of Environmental Sciences and Natural Resources*,2019;21(4):10-21.
 5. European Food Safety Authority (EFSA). Polycyclic aromatic hydrocarbons in food – Scientific Opinion of the Panel on Contaminants in the Food Chain, 2008.
 6. European Union Commission Regulation (EU). Amending regulation (EC) No 1881/2006 as regards maximum levels of polycyclic aromatic hydrocarbons (PAHs), 2014.
 7. Hajisamoh A. Pollution levels of 16 priority PAHs in the major rivers of Southern Thailand. *Research and Reviews: Journal of Chemistry*,2013;2(1):7-11.
 8. Ilechukwu I, Osuji LC, Onyema MO. Source apportionment of polycyclic aromatic hydrocarbons (PAHs) in soils within hot mixed asphalt (HMA) plant vicinities. *Journal of Chemical Society of Nigeria*,2016;41(2):10-16.
 9. International Agency for Research on Cancer (IARC). Monographs on the Evaluation of Carcinogenic Risk to Humans; PAHs, Part 1, Chemical, Environmental and Experimental Data,1987;32(2):57-62.
 10. Liang Y, Tse MF, Young L, Wong MH. Distribution pattern of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong. *Water Research*,2007;41(4):1301-1311.
 11. Llobet JM, Falcó G, Bocio A, Domingo JL. Exposure to polycyclic aromatic Hydrocarbons through consumption of edible marine species in Catalonia, Spanish *Journal of Food Protection*,2006;69(10):2493-2499.
 12. Meador JP, Sommers FC, Ylitalo GM, Sloan CA. Altered growth and related physiological responses in juvenile Chinook salmon (*Oncorhynchus tshawytscha*) from dietary exposure to polycyclic aromatic hydrocarbons (PAHs) *Canadian Journal of Fish and Aquatic Science*,2006;63(1):2364–76.
 13. Meng Y, Liu X, Lu S, Zhang T, Jin B, Wang Q, *et al.* Review on occurrence and risk of polycyclic aromatic hydrocarbons (PAHs) in lakes of China. *Science of Total Environment*,2019;651(6):2497–2506.
 14. Mzoughi N, Chouba L. Distribution of trace metals, aliphatic hydrocarbons and polycyclic hydrocarbons in sediment cores from the Sicily Channel and the gulf of Tunis (south-western Mediterranean Sea). *Environment and Technology*,2011;32(1-2):43-54.
 15. Neff JM, Stout AS, Gunstert DG. Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons in Sediments: Identifying Sources and Ecological Hazard. *Integrated Environmental Assessment and Management*,2004;1(1):22-23.
 16. Nemecek M. Low level PAH analysis using the Finigan Surveyor HPLC system with PDA detection. *Thermo Electron Corporation Applied Note*,2004;341:1-2.
 17. Nkpaa KW, Wegwu MO, Essien EB. Assessment of polycyclic aromatic hydrocarbons (PAHs) levels in two commercially important fish species from crude oil polluted waters of Ogoniland and their carcinogenic Health risk. *Journal of Environmental Earth Science*,2013;3(8):128–37.
 18. Nozar SL, Ismail WR, Zakaria MP. Residual concentration of PAHs in seafood from Hormozgan Province, Iran: human health risk assessment for urban population. *International Journal of Environmental Science Development*,2013;4(4):393–7.
 19. Nwineewii JD, Ibok UJ. Bioaccumulation of Polycyclic Aromatic Hydrocarbons (PAHs) Concentration in Biota from the Niger Delta, South- South, Nigeria. *Academic Research International*,2014;5(3):31-36.
 20. Nyarko E, Botwe BO, Klubi BE. Polycyclic aromatic hydrocarbons (PAHs) levels in two commercially important fish species from the coastal waters of Ghana and their carcinogenic health risks. *West African Journal of Applied Ecology*,2011;19(1):53–66.
 21. Obayori SO, Salam LB. Degradation of Polycyclic Aromatic Hydrocarbons: Role of Plasmids, 2010. <http://www.academicjournals.org>.
 22. Obiakor MO, Okonkwo JC, Ezeonyejiaku CD, Okonkwo CN. Polycyclic aromatic hydrocarbons (PAHs) in freshwater media: factorial effects and human dietary exposure risk assessment. *Resources and Environment*,2014;4(6):247-259.
 23. Okoro D. Source determination of polynuclear aromatic hydrocarbons in water and sediment of a creek in the Niger Delta Region. *African Journal of Biotechnology*,2008;7(3):282-285.
 24. Onojake MC, Nwokonko VN, Osakwe JO. Human health risks assessment of polycyclic aromatic hydrocarbons in selected seafood from Niger Delta Nigeria. *Nigerian Journal of Chemical Research*,2020;25(2):32-50.
 25. Poster D, Schantz M, Sander L, Wise S. Analysis of polycyclic aromatic hydrocarbons (PAHs) in environmental samples: A critical review of gas chromatographic (GC) methods. *Analytical and Bioanalytical Chemistry*,2006;386(6):859-881.
 26. Prycek J, Ciganek M, Simek Z. Clean-up of extracts for nitrated derivatives of polycyclic aromatic hydrocarbons analyses prior to their gas chromatography determination. *Journal of the Brazilian Chemical Society*,2007;18(6):1125-1131.
 27. Purcaro G, Navas JA, Guardiola F, Conte LS, Moret S. Polycyclic aromatic hydrocarbons in frying Oils and snacks. *Journal of Food Protection*,2006;69(5):199–204.
 28. Qian X, Liang B, Liu X, Liu X, Wang J, Liu F, *et al.* Distribution, sources, and ecological risk Assessment of polycyclic aromatic hydrocarbons in surface sediments from the Haihe River, a typical polluted Urban River in Northern China. *Environmental Science Pollution Resources*,2017;24(2):17153–17165.
 29. Qiu YW, Zhang G, Liu GQ, Guo LL, Li XD, Wai O. Polycyclic aromatic hydrocarbons (PAHs) in the water column and sediment core of Deep Bay, South China. *Estuarine, Coastal and Shelf Science*,2009;83(1):60-66.
 30. Singh VK, Patel DK, Jyoti RS, Mathur N, Siddiqui MK. Blood levels of polycyclic aromatic hydrocarbons in children and their association with oxidative stress indices: an Indian perspective. *Clinical Biochemistry*,2008;41(3):152-161.

31. Storelli MM, Stuffer RG, Marcotrigiano GO. Polycyclic aromatic hydrocarbons, polychlorinated Biphenyls, chlorinated pesticides (DDTs), hexachlorocyclohexane, and hexachlorobenzene residues in smoked Seafood. *Journal of Food Protection*,2003;66(4):1095-1099.
32. Tao Y, Yu J, Lei G, Xue B, Zhang F, Yao S. Indirect influence of eutrophication on air–water exchange fluxes, sinking fluxes, and occurrence of polycyclic aromatic hydrocarbons. *Water Resources*,2017;122(11):512–525.
33. U.S.E.P.A. Exposure Factors Handbook 2000 Edition (Final Report). U.S. Environmental Protection Agency, Washington, DC, EPA World Health Organization (WHO) (2003). Guidelines for Drinking water Quality. Polynuclear Aromatic Hydrocarbons in Drinking water, 2011. <http://www.who.int/water>.
34. Zhang S, Li C, Li Y, Zhang R, Gao P, Cui X, *et al.* Bio-accessibility of PAHs in contaminated Soils: Comparison of five *in vitro* methods with Tenax as a sorption sink, *Science and Total Environment*,2017;601(12):968-974.