Distribution Patterns of Polycyclic Aromatic Hydrocarbons in Marshy Soil and Sediments in Warri, Southern Nigeria

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Abstract: This study was carried out to determine the seasonal distribution patterns of Polycyclic Aromatic Hydrocarbons (PAHs) in marshy soil samples in Warri City, Southern Nigeria. The samples were collected during dry and rainy seasons from four locations within Warri and a control location in Agbarho, 20km away. Levels of 16 priority PAHs listed in United States Environmental Protection Agency (USEPA) were determined using Gas Chromatography coupled with Flame Ionization detector (GC-FID). This study was carried from January to March and June to August 2014, representing the dry and wet seasons respectively. Mean levels of individual PAHs for sediment samples in the dry season ranged from 0.001mg/kg low for Acenaphthene to 0.447mg/kg high for Benzo(a)pyrene while for soil samples in the dry season, mean levels ranged from 0.005mg/kg low for Acenaphtylene to 1.069mg/kg high for Benzo(a)pyrene. In the rainy season, individual PAH in sediments ranged from 0.001mg/kg low in acenaphthylene to 0.231mg/kg high for anthracene while for soil samples, mean levels of individual PAHs for rainy season ranged from 0.001mg/kg low in phenanthrene to 0.090mg/kg high for Benzo(b,k)Fluoranthene. Overall, the highest total concentration of individual PAH was recorded for benzo(a)pyrene with 3.302mg/kg in soil samples in the dry season while the lowest total concentration was Acenaphthylene with 0.012mg/kg in sediments in the rainy season. It was observed that PAHs concentration was generally higher in dry than rainy seasons for soil and sediment samples. This can be attributed to dissolution and washing-off of the PAHs during the rainy season.

Keywords: PAHs; Marshy Soil; Marshy Sediments; Seasonal Distribution Patterns; Benzo(a)pyrene; Gas Chromatography; Flame Ionization detector

INTRODUCTION

Marshy environments cannot be isolated from the effects of different environmental variables; and soil and sediments may act as a temporary or long-term reservoir of contaminants accompanied by natural origin compounds. Polycyclic aromatic hydrocarbon compounds are omnipresent components of marshy environments and derive from natural and anthropogenic sources. The natural concentration of chemical compounds is characterized as a base and background for identifying the portion of anthropogenic sources [1, 2].

PAHs (polycyclic aromatic hydrocarbons) originate mainly from incomplete combustion of organic materials as well as petroleum. Due to their hydrophobic nature, PAHs in the aquatic environment rapidly bind with particles and deposited sediments become their primary reservoirs [3]. The occurrence of PAHs in soils, sediments, aerosols, waters, animals and plants is of increasing environmental concern because some PAHs may exhibit mutagenic [4] properties. The levels of PAHs commonly found in many aquatic environments which an important risk factor for various health aspects [5]. PAHs represent a major problem to urban environments since these are among the most toxic compounds [6]. Because of their low aqueous solubility PAHs adsorb to particulate material and are deposited in sediments, where they can accumulate in higher concentrations. They also tend to accumulate in biota [4].

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Marshes provide a unique opportunity to assess the chronic input of land-derived pollutants to aquatic ecosystems. Contaminants that accumulate on land and are eroded by rain result in runoff that carries the chemical signature of the land it traverses. Since residential and undeveloped land uses are associated with different levels of PAH accumulation, adjacent wetland sediment should reflect the differences in PAH concentration as they scavenge particles from runoff [7, 8]. PAH compounds have been listed as priority pollutants by the USEPA (United States Environmental Protection Agency) and the European Union. Consequently, increasing attention has been paid to the environmental behaviour of PAHs on a global scale. This is in addition to their long-range transport potentials; as the global oceans are a likely gigantic sink for organic contaminants derived from a variety of sources [9].

Given the numbers of oil and gas wells and complex transportation pipelines within Warri, determining the concentration levels of PAHs in soil and sediments of this region is necessary for risk assessment and evaluation of ecosystem health. This study was therefore carried out to achieve this aim and also to assess the seasonal variation of PAHs in soils and sediment of the City.

Warri is a major hub of the oil and gas industry in Southern Nigeria. Given the numbers of oil and gas wells and complex transportation pipelines within Warri and its environs, concentration levels of PAHs in soils and sediments of the city must be quantified to evaluate their ecological impacts. Considering that PAHs account for 10-45% of total hydrocarbons in crude oil [10, 11] and the importance of this region to fisheries stock, other edible aquatic lives as well as farming, it is also important to understand the distribution of PAHs in this area. Unfortunately, there is a paucity of data for PAH concentrations and distribution in soils and sediments in Warri City. This study, therefore, is essential not only to determine the seasonal distribution patterns of PAHs in soils and sediments in the city, but also to provide baseline data for the city. Having this type of baseline information available will be critical to developing effective responses to future potential disasters such as oil spills and oil-related disasters.

MATERIALS AND METHOD

Study Area
This study was carried out in Warri located between latitude $5^0$31'N and longitude $5^0$45'E. The city, also known as 'Oil City', is one of the cosmopolitan cities and a major hub of petroleum activities and businesses in Southern Nigeria. It is a commercial capital city in Delta State, in the oil rich Niger Delta region, comprising originally of Itsekiri, Urhobo and Ijaw people.

The region experiences moderate rainfall and moderate humidity for most part of the year. The area is characterized by tropical equatorial climate with mean annual temperature of 32.8^0C and annual rainfall amount of 2673.8 mm. There are high temperatures of 36^0C and 37^0C. The natural vegetation is a rainforest with swamp forest in some areas. The forest is rich in timber trees, palm trees, as well as fruit trees.

As a result of the unique location of Warri at the bank of the Niger Delta, there are rivers, creeks, ponds and wetland areas around the city hence most places in the city are swampy areas and marshes. Majority of the people especially those living close to the waters are either fishermen/women or take fishing as a hobby. Warri River which is one of the most important coastal rivers of the Niger Delta distributed in various tributaries around the city and beyond is responsible for the marshy soil and swampy area that characterise the city [12].
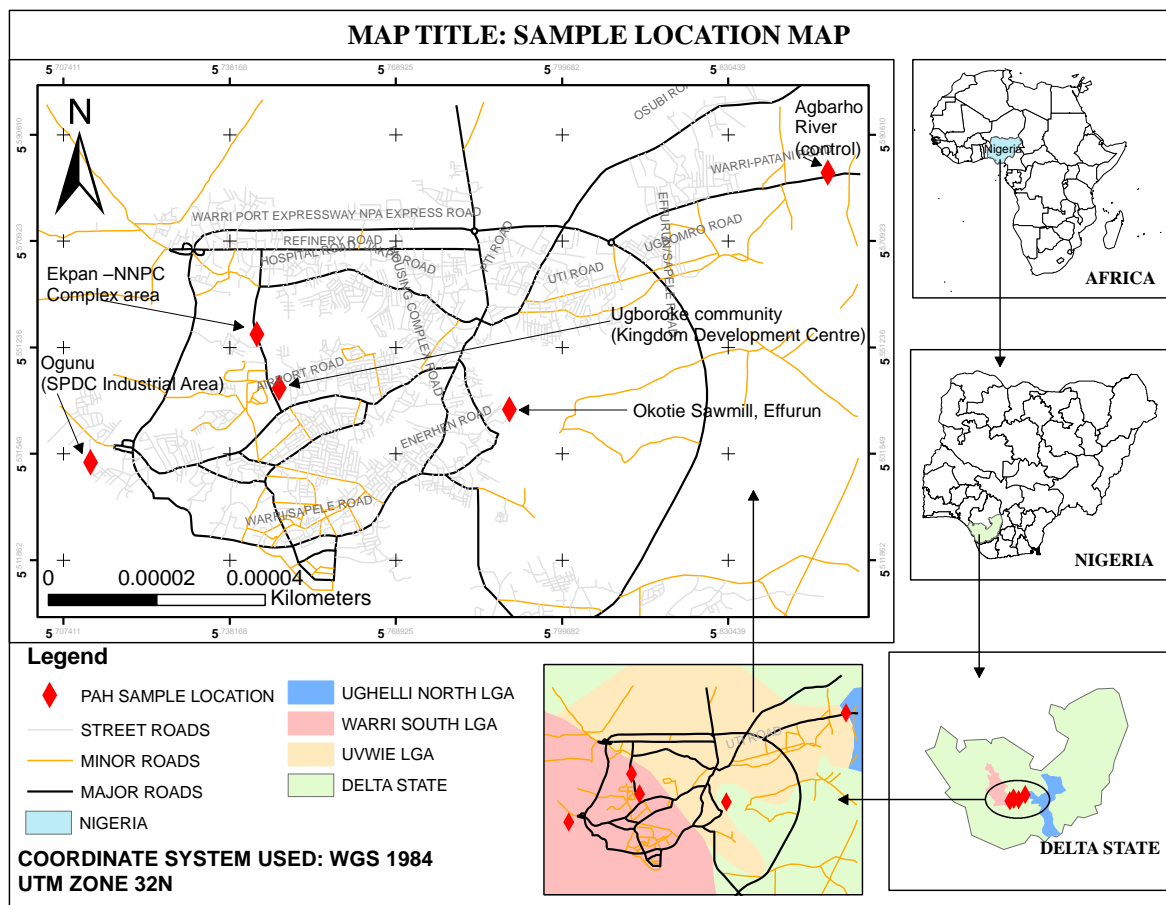
Fig. 1: **GIS based Map of Study Area**

The coordinates of the locations of the sample in the study area are as shown in Table 1 below:

Table 1: Showing Sample Locations and their GPS Coordinates

Sampling Location	Coordinates	
	Northings	**Eastings**
Ekpan – NNPC Complex Area	05º 33´13.5''	005º 44´35.8''
Ugboroke community (Kingdom Development Centre)	05º 32´37.6''	005º 44´50.5''
Ogunu (SPDC Industrial Area)	05º 31´48.1''	005º 42´44.9''
Okotie Sawmill, Effurun	05º 32´23.3''	005º 47´24.0''
Agbarho River (Control)	05º 35´01.1''	005º 50´56.0''

Sample Locations
Five (5) areas were strategically chosen, four within Warri and one outside Warri; the one outside Warri was chosen as the control.

1. Ekpan –NNPC Complex area
This site is along the Ekpan bridge express, after the NNPC staff quarters. It is located between longitude 05º33´13.5''N and latitude 005º44´35.8''E. There is a company opposite the sampling point and a church beside it. The exact sampling point is a river under the bridge. One major characteristics of this location

is that there are not much human population here but the place is close to NNPC/Ekpan highway a major busy highway. The river could be a drain receiving waste water from neighbouring residential areas and industry.

2. Ugboroke community (Kingdom Development Centre)
This location can be said to describe the natural vegetation of Warri which is of rainforest with swamp forest in some areas; the forest in Warri is rich in timber trees, palm trees, as well as fruit trees. Ugboroke community is however one of the

emerging areas in Warri and developmental features such as roads, modern building structures are taking over the forest. The community is a densely populated area, made up of local indigenous people as well as others that have come to live within the community. One thing peculiar to this location is that, there are clusters of old, native houses, modern/semi-modern residential houses, small and medium scale businesses, factories, and companies, agricultural activities (poultry, fishing amongst others).

The sampling point is a pond at the back of a church (kingdom Development Centre). It is located between longitude 05º32´37.6''N and latitude 005º44´50.5''E. This point is actually like a wetland that is flooded most part of the year. Plantain trees, other trees, shrubs and plants are typical of this environment.

3.   Ogunu (SPDC Industrial Area)

This site is located between longitude 05º31´48.1''N and latitude 005º42´44.9''E, outside Shell Petroleum Development Company SPDC residential, recreational and mild administrative area. It is a local community that has been upgraded by virtue of the presence of the multinational companies in the area. Apart from SPDC, Ogunu community play host to, Pan Ocean Oil Company. The people in this community are majorly indigenes with few other non-indigenes. Their occupations are majorly petty trading, fishing, farming or idling. The exact

sampling point is Ogunu River. There are residential houses around and even in or on the river; there is also a local public toilet and a refuse dump close by.

4.   Okotie Sawmill, Effurun

This site is located between longitude 05º32´23.3''N and latitude 005º47´24.0''E, in the outskirt of Warri, in a place called Effurun. To many people, Effurun is not part of the Warri town ship but by geographical and political description, Effunrun is part of the larger Warri City and is usually called together as - Effurun Warri. The actual sampling area is a majorly industrial with few residential houses; some of the industries and companies in the area are – Nigeria Bottling Company (Coca Cola) Depot, Phyton Engineering Company, Thermosteel Nigeria Limited, Okotie Plank Sawmill and NISRIN Construction. Okotie Plank Sawmill and NISRIN Construction are just by the river where the sampling was carried out. The sampling point was close to one of the vessels-houseboat constructed by NISRIN.

5.   Agbarho River (Control)

Agbarho Community is a town outside Warri; it is along the Ughelli/Port Harcourt highway. The actual sampling site is the Agbarho River, located between longitude 05º35´01.1''N and latitude 005º50´56.0''E. Just by the side of this river is an open abattoir and cow meat market; as a result of which there are usually herd of cattle grazing by the side of the river.

Plate 1: Ugboroke Community showing the Swampy Forest of Warri; **Plate 2:** Kingdom Development Centre Ugboroke; **Plate 3:** Ogunu River; **Plate 4:** Agbarho Cow Market

Sample Collection and Analysis

Soil and sediments samples from the five sampling points were collected in the year 2012 for six months; three months in the dry season (January – March) and three months in the rainy season (June – August). The samples were collected using stainless steel hand auger and stainless steel spoon into an aluminium foil paper; while a stainless steel grab sampler was used for sediment samples that were collected when the river was full. Top (0-15cm) and bottom (15-30cm) samples were collected at each point to form one composite sample and a total of ten samples were collected for each month in the dry season (January-March) and in the wet season (June-August).

The samples were wrapped in aluminium foil and properly preserved by cooling in a refrigerator at (4ºC) before they were taken to the laboratory for analysis. Analysis was done using Gas Chromatography (GC) with Flame Ionization Detector (FID).

RESULTS AND DISCUSSION

Results

The results of analyses of the sediment and soil samples from the study area are as presented in Tables 2-6 below with their seasonal variation highlighted in Figures 2 and 3. The results including mean and standard deviation are presented for dry and wet/rainy seasons of sampling. The results were read as the detection limit on the gas chromatogram for individual PAHs which were in microgram per litre and these were converted to milligram per kilogram (mg/kg.). The minimum detection limit for GCFID used in the analysis on the chromatogram is 1×10^{-3} mg/kg.

Table 2: PAHs Concentrations in Marshy Soil Samples in Warri City in mg/kg

PAHs	Sampling Stations (ST)									
	ST 1 (Ekpan)		ST 2 (Ogunu)		ST 3(Ugboroke)		ST 4 (Okotie)		Control (Agbarho)	
	D	R	D	R	D	R	D	R	D	R
Naphthalene	0.09	0	0.484	0	0	0.017	0.584	0.012	0.195	0
2-methyl naphthalene	0	0.016	0.045	0.033	0.561	0	0.04	0.192	0.007	0.411
1-methyl naphthalene	0.082	0	0.041	0.049	0.168	0	0	0.038	0.009	0
Acenaphthylene	0.01	0	0.069	0.027	0	0.0003	0.025	0	0	0
Acenaphthene	0.096	0	0	0.018	0	0.0004	0.1	0.0005	0.007	0
Fluorene	0	0	0	0.066	0	0	0.082	0.0001	0.071	0
Phenanthrene	0.022	0	0.027	0.094	0.239	0	0.139	0.003	0	0
Anthracene	0	0.011	0.142	0.255	0.292	0	0.113	0	0.035	0
Pyrene	0.17	0	0.244	0	0	0.024	0.174	0.022	0.088	0.036
Chrysene	0.11	0	0.102	0	0.033	0.028	0	0	0	0
Benzo(a)anthracene	0.142	0	0	0	1.134	0.0964	0.159	0	0	0
Benzo(b)fluoranthrene&Benzo(k) fluoranthrene	0.286	0	0.11	0.275	0.076	0	0.042	0.0682	0.514	0.053
Benzo(a)pyrene	0.484	0	0.362	0.1	0.318	0	2.138	0.166	0	0.066
Indeno(1,2,3-cd)pyrene & dibenzo(a,h)anthracene	0	0	1.11	0.01	0	0	0	0.011	0	0
Benzo(g,h,i)perylene	0.66	0	0.479	0.223	0.309	0.07	0.226	0	1.039	0.127
Fluoranthrene	0.074	0	0	0.181	0	0	0	0.033	0	0.046
Total	2.226	0.027	3.215	1.331	3.130	0.2361	3.822	0.546	1.965	0.739
Mean	0.139	0.002	0.201	0.083	0.196	0.015	0.239	0.034	0.123	0.046
Standard deviation	0.189	0.005	0.294	0.097	0.301	0.029	0.527	0.060	0.277	0.104

*D = Dry Season; R = Rainy Season

Table 3: Mean Seasonal Concentrations of PAHs in Marshy Soil samples for Warri City in mg/kg

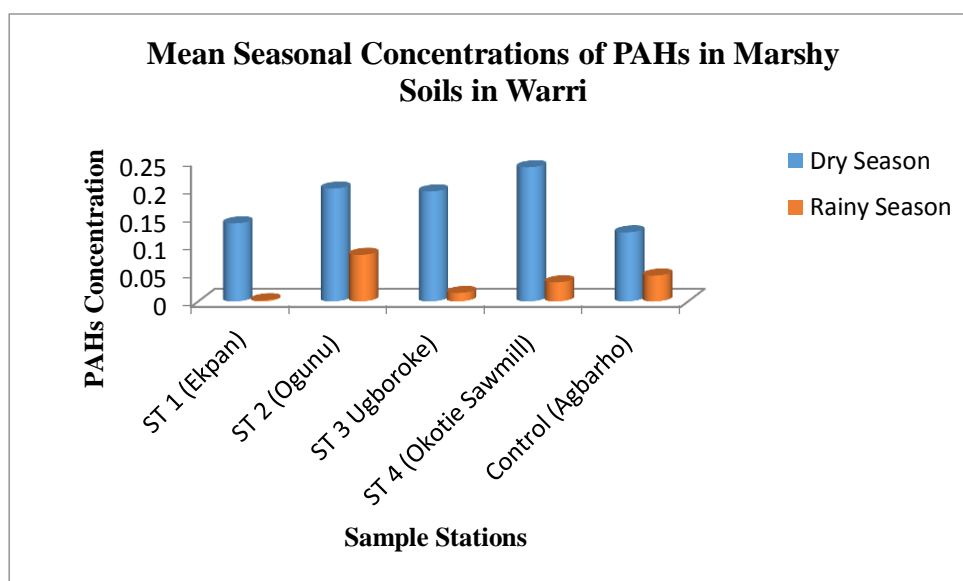| STATION	SEASON	
	Dry(mg/kg)	Rainy(mg/kg)
ST 1 (Ekpan)	0.139	0.002
ST 2 (Ogunu)	0.201	0.083
ST 3 Ugboroke)	0.196	0.015
ST 4 (Okotie Sawmill)	0.239	0.034
Control (Agbarho)	0.123	0.046

Fig 2: Mean Seasonal Concentrations of PAHs in Marshy Soils in Warri

Table 4: PAHs Concentrations in Marshy Sediment Samples in Warri City in mg/kg

PAHs	Sampling Stations (ST)									
	ST 1 (Ekpan)		ST 2 (Ogunu)		ST 3 (Ugboroke)		ST 4 (Okotie)		Control (Agbarho)	
	D	R	D	R	D	R	D	R	D	R
Naphthalene	0.041	0	0.211	0	0.0349	0	1.091	0	0.421	0.017
2-methyl naphthalene	0.039	0	0.041	0	0.0353	0	0.05	0	0	0.21
1-methyl naphthalene	0.01	0	0.001	0	0	0.209	0.18	0.073	0.37	0.033
Acenaphthylene	0.007	0.005	0.006	0	0.076	0	0.046	0.007	0.154	0
Acenaphthene	0	0.006	0.01	0	0.004	0.008	0.0216	0.02	0	0
Fluorene	0.011	0	0.057	0.13	0.013	0	0.09	0.131	0.038	0.017
Phenanthrene	0.191	0	0.07	0	0.0235	0	0.245	0.228	0.577	0.046
Anthracene	0.244	0.071	0.093	0.751	0.147	0	0.338	0.693	0.075	0
Pyrene	0.209	0	0.214	0	0.187	0	0.513	0.361	0.186	0
Chrysene	0.507	0.617	0.49	0	0.083	0	0	0.285	0	0.186
Benzo(a)anthracene	0.144	0.452	0.255	0	0.205	0	0.572	0	0.18	0
Benzo(b)fluoranthrene&Benzo(k)fluoranthrene	0.413	0.52	0.193	0	0.388	0	0	0.245	0.104	0.109
Benzo(a)pyrene	0	0	1.342	0	0.216	0	0.823	0.422	0.779	0.068

Indeno(1,2,3-cd)pyrene & dibenzo(a,h)anthracene	0	0	0.196	0	0.267	0	0.334	0	1.092	0
Benzo(g,h,i)perylene	0.218	0.112	0.753	0	1.067	0.147	0.139	0.346	0.202	0.282
Fluoranthrene	0	0.01	0.04	0	0	0	0.097	0.218	0	0.087
Total	2.034	1.793	3.972	0.881	2.747	0.364	4.540	3.029	4.179	1.055
Mean	0.127	0.112	0.248	0.055	0.172	0.023	0.284	0.189	0.261	0.066
Standard deviation	0.159	0.212	0.353	0.188	0.265	0.062	0.319	0.200	0.317	0.088

*D = Dry Season; R = Rainy Season

Table 5: Mean Seasonal Concentrations of PAHs in Marshy Sediment samples in Warri City in mg/kg

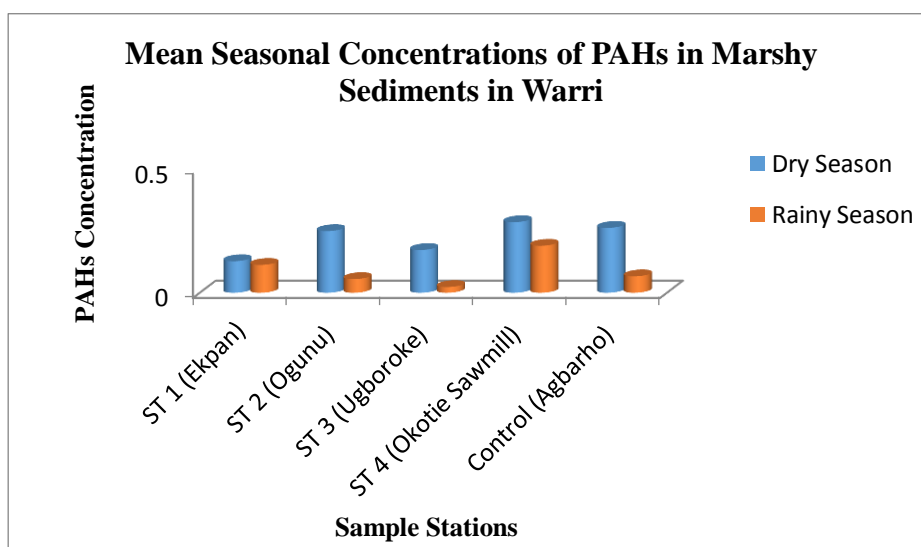| STATION	SEASON	
	Dry(mg/kg)	Rainy(mg/kg)
ST 1 (Ekpan)	0.127	0.112
ST 2 (Ogunu)	0.248	0.055
ST 3 (Ugboroke)	0.172	0.023
ST 4 (Okotie Sawmill)	0.284	0.189
Control (Agbarho)	0.261	0.066

Fig 3: Seasonal Variation of PAHs in Marshy Sediments in Warri

Table 6: Mean Seasonal Concentrations of PAHs in Marshy Soils and Sediment samples for Warri City in mg/kg

STATION	Dry Season (mg/kg)		Rainy Season (mg/kg)	
	Soil	Sediment	Soil	Sediment
ST 1 (Ekpan)	0.139	0.127	0.002	0.112
ST 2 (Ogunu)	0.201	0.248	0.083	0.055
ST 3 (Ugboroke)	0.196	0.172	0.015	0.023
ST 4 (Okotie Sawmill)	0.239	0.284	0.034	0.189
Control (Agbarho)	0.123	0.261	0.046	0.066

Discussion

Seasonal variation across the sample locations

During the dry season, the soil PAHs concentration at the different sample locations ranged from 0.123 to 0.239mg/kg (Table 6). Okotie Sawmill had the highest concentration of 0.239mg/kg while the lowest concentration with a value of 0.123mg/kg was obtained at the control location. For sediments, the PAHs concentration ranged from 0.127 to 0.284mg/kg, the highest concentration (0.284mg/kg) was also recorded at Okotie Sawmill while the lowest concentration (a value of 0.127mg/kg) was obtained at Ekpan. The control station (Agbarho) had 0.261mg/kg.

During the rainy season, the soil PAHs concentration at the different sample locations ranged from 0.002 to 0.083mg/kg. Ogunu had the highest concentration of 0.083mg/kg while the lowest concentration with a value of 0.002mg/kg was obtained at Ekpan. For sediments, the PAHs concentration ranged from 0.023 to 0.189mg/kg, the highest concentration (0.189mg/kg) was also recorded at Okotie Sawmill while the lowest concentration (a value of 0.023mg/kg) was obtained at Ugboroke. The control station (Agbarho) had 0.066mg/kg.

Overall, for both soil and sediments, the PAHs concentration during the dry season ranged from 0.123 to 0.284mg/kg; with the lowest concentration of 0.123mg/kg recorded at the control location and the highest concentration of 0.284mg/kg recorded at Okotie Sawmill. During the rainy season (for both soil and sediments), the concentration ranged from 0.002 to 0.189mg/kg, with the lowest concentration of 0.002mg/kg recorded at Ekpan and the highest concentration (0.189mg/kg) recorded at Okotie Sawmill.

Occurrence of individual PAHs for Soils and Sediments

Highest total concentration of PAHs within Warri was recorded for BaP - benzo(a)pyrene at 3.302mg/kg in soil samples. The highest contributor to the bulk was at Okotie Sawmill; this location is the one characterised with the presence of several industrial activities and about 2.138mg/kg total concentration was detected there in the dry season soil samples. This is similar to the work done by Ana et al. [13] on PAHs contamination of surface waters in Nigeria Coastal Areas. They reported that the concentration of total PAHs in industrialised areas was three times higher than in the less industrialised area. The order of PAHs concentration in soil within Warri is: BaP>BghiP>BaA>Naph>Ind&DbahA>2-M.Naph>BbF>Ant>Pyr>Phenan.

The PAH with lowest concentration in soil in Warri environs is acenaphthalene with a total concentration of 0.018mg/kg found in the rainy season. The order for lower PAHs in soils in Warri environs is can<Ind&DbahA<Acp<Chry.

At the control point, PAHs with highest concentration in soil sample was BghiP; it had a total concentration of 1.166mg/kg with the larger amount of 1.039mg/kg detected in the dry season. It is important to note that the control point location has cattle grazing ground, an abattoir and meat market. Therefore, the high concentration of BghiP here could be attributed to the microbial production of the PAH due to microbial activities in the abattoir area. This is similar to the study done by Inengite et al. [14] on PAHs sources in Kolo Creek soil in Niger Delta area of Nigeria where it was found that concentration of BghiP was high near an abattoir. The order of PAHs concentration in soil in decreasing order is BghiP>BbF&BkF>2-Methyl.Naph. Lowest concentration of total PAHs detected at control station for soil for both dry and rainy season is 0.007mg/kg, and the order is Acn≤2Methyl.Naph≤1-Methyl.Naph. Most of the PAHs were not found at all and they include: Phe., Acnptyl.,Ind&DbahA, BaA, and Chry. Those detected only in dry season are: Ant, Fluoren, Acenapthalene, and 1-Methyl Naph; and those detected only in rainy season are BaP and Fluoranthene.

For sediment samples within Warri environs, PAHs with highest concentration is BaP - benzo(a)Pyrene with a total concentration of 2.803mg/kg and the larger amount of 2.381 mg/kg being found in the dry season. The decreasing order for total PAHs in sediment sample for dry and rainy season is: BaP>BghiP>Ant>Naph>BaA>Pyr>Chyr>BbF&BkF>BaA>Pyr>Naph. The lowest concentration for PAHs in sediments was recorded for acenaptylene – 0.012mg/kg in rainy season and for total PAHs in dry and rainy season of 0.070mg/kg for acenaphthalene. Some PAHs that were below detection level in the rainy season are: naphthalene, 2 methyl naphthalene and Ind &DbahA.

At the control point, highest total concentration of PAHs found in sediment was 1.092mg/kg and the mean was 0.364mg/kg for Indeno(1,2,3-cd)Pyrene&Dibenz(a,h)Anthracene; all this amount was found only in the dry season as the rainy season record was below detection level. The decreasing order for PAHs in sediments here is: Ind&DbahA>BaP>Phe. The PAHs with lowest concentration was fluorene, followed by 1methyl naphthalene, naphthalene and phenanthrene. Acenapthalene was below detection level in this location while fluoranthene and chrysene were only below detection level in the dry season. Also, Ind&DbahA, Benzo(a)anthracene, Pyrene Anthracene and Acenaptylene were below detection level in the rainy season.

For Soil samples, the highest total concentration of individual PAH was recorded for benzo(a)pyrene with 3.302mg/kg in the dry season while the lowest was Fluoranthrene with 0.074mg/kg. In the rainy season, highest total concentration of individual PAH was recorded for benzo(b)fluoranthene and benzo(k)fluoranthene at 0.343mg/kg while the lowest was Acenaphthene with 0.019mg/kg.

For Sediments, the highest total concentration of individual PAH was recorded for benzo(a)pyrene with 2.381mg/kg in the dry season while the lowest was Acenaphthene with 0.036mg/kg. In the rainy season, highest total concentration of individual PAH was recorded for Anthracene at 1.515mg/kg while the lowest was Acenaphthylene with 0.012mg/kg; while Naphthalene and 2-methylnaphthalene were not detected.

Seasonal Variation of PAHs in Soils and Sediments
Dry Season
Mean levels of individual PAHs for sediment samples in the dry season for Warri environs ranged from 0.001mg/kg low for Acenaphthene to 0.447mg/kg high for Benzo(a)pyrene. At the control location, mean values ranged from 0.012mg/kg low for Fluorene to 0.364mg/kg high for Indeno(1,2,3-cd)pyrene & Dibenz(a,h)anthracene in sediments. For soil samples in the dry season, mean levels of PAHs within Warri environs ranged from 0.005mg/kg low for Acenaphtylene to 1.069mg/kg high for Benzo(a)pyrene. While in the control point it ranged from 0.003mg/kg low for 2methyl- Naphthalene to

0.519mg/kg high for Benzo(g,h,i)perylene in soil samples.

It can be noticed here that individual PAH levels within Warri was low for three rings – Acenaphtylene and Acenaphthene and high for five-ringed – Benzo(a)Pyrene in soil and sediment samples in dry season. This could indicate that the activities within that environment are influencing the soil and the sediment in similar way. However, at the control point, a different trend was seen. PAH levels was low for three-ringed fluorene in soil samples and two-ringed naphthalene in sediments while it was high for Indeno (1,2,3-cd)pyrene & Dibenz(a,h) anthracene in sediments and six-ringed Benzo(g,h,i)perylene in soil samples. This is similar to a study reported in [15], in which was explained that soils and sediments have been found to be good environmental sink for PAHs thereby reflecting their levels in the environment and could contain about 90% of these compounds with longer half-life than the atmosphere or in plants.

Rainy Season
In the rainy season, individual PAH in sediments ranged from 0.001mg/kg low in acenaphthylene to 0.231mg/kg high for anthracene. While at the control, it was 0.005mg/kg low in Fluorene to 0.094mg/kg high for Benzo(g,h,i)perylene in sediment samples. In soil samples within Warri, mean levels of individual PAHs for rainy season ranged from 0.001mg/kg low in phenanthrene to 0.090mg/kg high for Benzo(b)Fluoranthene & Benzo(k)Fluoranthene. At the control point, it was 0.012mg/kg low for pyrene to 0.130mg/kg high for 2-Methyl-Naphthalene in soil samples. A general observation from PAH levels result in the rainy season, at the study location and the control is that, lower amounts were detected in the rainy season compared to the dry season. It was also observed that mean levels in sediment samples were higher than in soils for this study period. A similar trend was observed in a related study in the Niger Delta area of Nigeria [14]. According to them, during rainy season, it is expected that dissolution and washing-off of the PAHs from the soil matrix could occur into the rivers thereby increasing their levels in sediment. Furthermore, the type of individual PAH detected reflected the activities going on in the environment as three-ringed acenaphthylene and phenanthrene were still relatively low in soils and sediments in Warri environs in rainy season as observed in the dry season. And Benzo(b)fluoranthene & Benzo(k)fluoranthene, which is the five-ringed detected high in soil samples within Warri environs in rainy season has been observed according to the work done by Aubin & Farant [16], to be more stable and a much better

marker of PAH source than Benzo(a)pyrene, which was detected high in soil samples in dry season. At the control station, Benzo(g,h,i)perylene which was detected high in soil samples in dry season was found to be high in sediments in rainy season, a likely indication of washing off as observed in [14].

The results from this study show that the type of PAH and their levels in soils and sediments vary for each season under consideration and in this case, dry and rainy season. For soil samples, four ringed pyrene occurred most in the dry season and it was found in the dry season at all the locations for both soil and sediment samples. Also, values for two to three ringed PAHs such as naphthalene and acenaphthene in soils during rainy season were mostly below detection limit of <0.001mg/kg. For sediments, the two to three rings were found majorly in the dry season and almost absent in the rainy season. Four ringed PAHs such as chrysene were also found more in the dry season than rainy season for both soil and sediment samples. The five ringed PAHs such as benzo(a)pyrene were found more in the dry season than the rainy season. However, their values vary at different locations in the soil and sediment samples. Six ringed indeno(1,2,3-cd)pyrene was found high in the dry season in control station sediment samples and absent in the rainy season. More different PAHs were detected in the dry season than in the rainy season and overall concentration of PAHs was also higher in the dry season than in the rainy season for soils and sediments samples.

Factors that could be responsible for the Seasonal Variation of PAHs levels

PAH in soil is usually from atmospheric deposition due to pyrolytic sources [17]; and the other sources are petrogenic due to petroleum or crude oil activities and spillage. While PAHs in sediments have been found to reflect the history of fossil fuel combustion in the environment [15], and higher molecular weight PAHs which are hydrophobic compounds and have less solubility in water tend to settle in sediments.

Dry season in the Niger Delta which is the area for this study is marked with dust and cool "harmattan" haze and there could be high temperature of 36ºC and 37ºC. These conditions are favourable for high PAH levels in soil and could be considered to be one of the responsible factors for high PAHs levels in soil samples in dry season for the areas under this study.

According to Adejuwon [18], annual rainfall amount in the study area- Warri, could get to 2807mm. Apart from usual rainfall in rainy season- May to October, it frequently even rains in the dry season (November to April). Most of the areas in Warri (and mostly the

Niger Delta) are as a result more swampy and marshy with bottom sediments. It was mentioned earlier that PAHs could be washed off (from the atmosphere and soil) during rainy season and are most likely to have undergone reactions that could either increase or decrease their level [14]. According to Brooks [19], when PAHs enter aquatic environment, their fate is determined by the type of compound and the characteristics of the substrate to which they are attached; this is because PAHs are complex compounds and they are hardly found as a single substance. Consequently, PAHs in an aquatic environment could evaporate, disperse into the water column, become incorporated into bottom sediments, and concentrate in aquatic biota or experience oxidation – including photo-oxidation and biodegradation [19]. These factors could be some of the responsible reasons for PAHs high and low levels in sediment in different seasons.

Evaluation of the Effects of PAHs on Man

Although this study is majorly to determine levels of PAHs in soils and sediments within the study area, an extension to the evaluation of the effects on man is attempted because man is the ultimate consumer in the food chain and would bear the consequences of the presence of these harmful pollutants in the environmental segments.

As earlier stated, most of the places in Warri are swampy and marshy and most of the people especially those living close to the waters are either professional fishermen/women or fish as a hobby. The observed PAHs concentration (4.840mg/kg) in sediment samples was above the critical level of 4mg/kg recommended by WHO [20] for soils and sediments. PAHs in aquatic environment have been found to be capable of attaching or bioconcentrating in aquatic organisms, mostly bivalve molluscs (such as mussels *Mytilus edulis*) and oysters of the genera (*Ostrea* and *Crassastrea*) and fish as well as other aquatic organisms with highly permeable filtering gills [19]. When man consumes these aquatic organisms as food, they become at risk to the negative effects of these harmful pollutants. According to WHO [20], man is mainly exposed to PAHs from food and ambient and indoor air that have been polluted with PAHs. The PAHs levels in soil samples (3.634mg/kg) in the study area was though lower than the WHO critical level of 4mg/kg, yet even at this concentration may be considered to be harmful since PAHs in soil is partly a deposition from the atmosphere, and soil and sediments are regarded as good environmental sink that contain about 90% of these compounds with longer half-life than the atmosphere or in plants [15].

When these harmful compounds are inhaled or ingested by man they could go through harmful metabolism. Although extensive metabolism of PAHs compounds done through animal studies have shown that food chain bio-magnification of the compounds does not appear to be significant [17], yet evidences exist that PAHs are enzymatically converted to highly reactive metabolites that bind covalently to macromolecules such as DNA and result in mutagenesis and carcinogenesis in experimental animals [21].

CONCLUSION

The seasonal Polycyclic Aromatic Hydrocarbons (PAHs) distribution in marshy soils and sediment samples in Warri City, Southern Nigeria were examined in this study. During the dry season, the soil PAHs concentration at the different sample locations ranged from 0.123 to 0.239mg/kg while for sediments, the PAHs concentration ranged from 0.127 to 0.284mg/kg. During the rainy season, the soil PAHs concentration at the different sample locations ranged from 0.002 to 0.083mg/kg while for sediments, the PAHs concentration ranged from 0.023 to 0.189mg/kg.

Mean levels of individual PAHs for sediment samples in the dry season ranged from 0.001mg/kg low for Acenaphthene to 0.447mg/kg high for Benzo(a)pyrene while for soil samples in the dry season, mean levels ranged from 0.005mg/kg low for Acenaphtylene to 1.069mg/kg high for Benzo(a)pyrene. In the rainy season, individual PAH in sediments ranged from 0.001mg/kg low in acenaphthylene to 0.231mg/kg high for anthracene while for soil samples, mean levels of individual PAHs for rainy season ranged from 0.001mg/kg low in phenanthrene to 0.090mg/kg high for Benzo(b)Fluoranthene & Benzo(k)Fluoranthene. It was also observed that mean levels in sediment samples were higher than in soils for the rainy study period because during rainy season, it is expected that dissolution and washing-off of the PAHs from the soil matrix could occur into the rivers thereby increasing their levels in sediment.

Overall, the highest total concentration of individual PAH was recorded for benzo(a)pyrene with 3.302mg/kg in soil samples in the dry season while the lowest total concentration was Acenaphthylene with 0.012mg/kg in sediments in the rainy season.

The results from this study show that the type of PAH and their levels in soils and sediments vary for each season under consideration and in this case, dry and rainy season. For soil samples, four ringed pyrene occurred most in the dry season and it was found in the dry season at all the locations for both soil and sediment samples. Also, values for two to three ringed PAHs such as naphthalene and acenaphthene in soils during rainy season were mostly below detection limit of <0.001mg/kg. For sediments, the two to three rings were found majorly in the dry season and almost absent in the rainy season. Four ringed PAHs such as chrysene were also found more in the dry season than rainy season for both soil and sediment samples. The five ringed PAHs such as benzo(a)pyrene were found more in the dry season than the rainy season. However, their values vary at different locations in the soil and sediment samples. Six ringed indeno(1,2,3-cd)pyrene was found high in the dry season in control station sediment samples and absent in the rainy season. More different PAHs were detected in the dry season than in the rainy season and overall concentration of PAHs was also higher in the dry season than in the rainy season for soils and sediments samples.

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