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Research Article

Source Prediction of Polycyclic Aromatic Hydrocarbons in Marshy Soils and Sediments in Warri City, Southern Nigeria

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Abstract

This study was carried out to predict the sources 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, representing the dry and wet seasons respectively. Analyses of the PAH diagnostic ratios and cross plots of the diagnostic ratios were used as veritable instruments to predict the sources of PAHs in the city. Source prediction analysis revealed that PAHs in sediments for dry season were of pyrolytic while the rainy seasons were petrogenic sources. However, for soils, PAHs in the dry season samples were from mixed sources while the rainy seasons were petrogenic.

Keywords: PAHs, Marshy Soil, Source Prediction, Benzo(a)pyrene, Gas Chromatography, Flame Ionization detector

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Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) as an important class of persistent organic pollutants with carcinogenic, mutagenic and degradation-resistant properties are of particular concern. They are widely found in the environment because they can be transported over long distances and deposited in remote areas [1-4]. For example, Laender *et al*. [5] found that PAHs had become the dominant persistent organic pollutants in the Arctic ecosystem (replacing polychlorinated biphenyls (PCBs), which dominated until relatively recently). PAHs can be derived from both petrogenic and pyrogenic sources, such as the burning of fossil fuels, biomass, the diagenesis of organic matter and crude oil leakage [6-8]. Once PAHs are released into the environment, they preferentially accumulate in sediments and organisms because of their hydrophobic natures [9, 10].

On one hand, some zoobenthos may directly ingest dissolved and particulate PAHs when exposed to sediments contaminated with PAHs [11]. On the other hand, when the environmental conditions (such as pH and salinity) change, PAHs adsorbed on the sediments could be desorbed into water and taken up by organisms [12]. This means that PAHs in sediments may enter into the food web and be a source of potential risks to organisms. The contamination of sediments with pollutants such as PAHs is, therefore, of great concern. Many studies of the distributions, transfers, and sources of PAHs have been performed in the last 50 years [13, 14].

Marshes are often found at the edges of lakes and streams and so often exposed to numerous sources of pollutants because of intensive industrial activities and high population densities in the neighbouring areas. PAHs mainly enter marshy environments by direct discharges (e.g., from wastewater treatment plants), atmospheric deposition and oil spills and accumulate in the sediments [15]. Moreover, marshes are transitional zone between aquatic and terrestrial ecosystems, having both aquatic and land influences, including tides, changes in river flow, and dry–wet cycles. The physical and chemical changes are, therefore, more extreme in marshes environments than in many other environments [16]. When marshy soil and sediments are exposed to these aquatic and land processes, PAHs adsorbed on the soil and sediments could be released into water, which thus caused a secondary pollution and then affected population health and ecological environment [12]. Thus, it has been shown in a number of previous studies focused on the organic pollutant in estuary sediments [17, 18]. These marshy soil and sediments may contain PAHs and cause

ecological risks in marshy environments. Therefore, determining PAH concentration levels in marshy environments is necessary for risk assessment and evaluation of ecosystem health.

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, 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 [9, 19], and the importance of this region to fisheries stock and other edible aquatic lives, 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 sediments in Warri City. This study, therefore, is essential not only to determine the sources of PAHs in 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^{0}C and annual rainfall amount of 2673.8 mm. There are high temperatures of 36^{0}C and 37^{0}C. 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 [20].

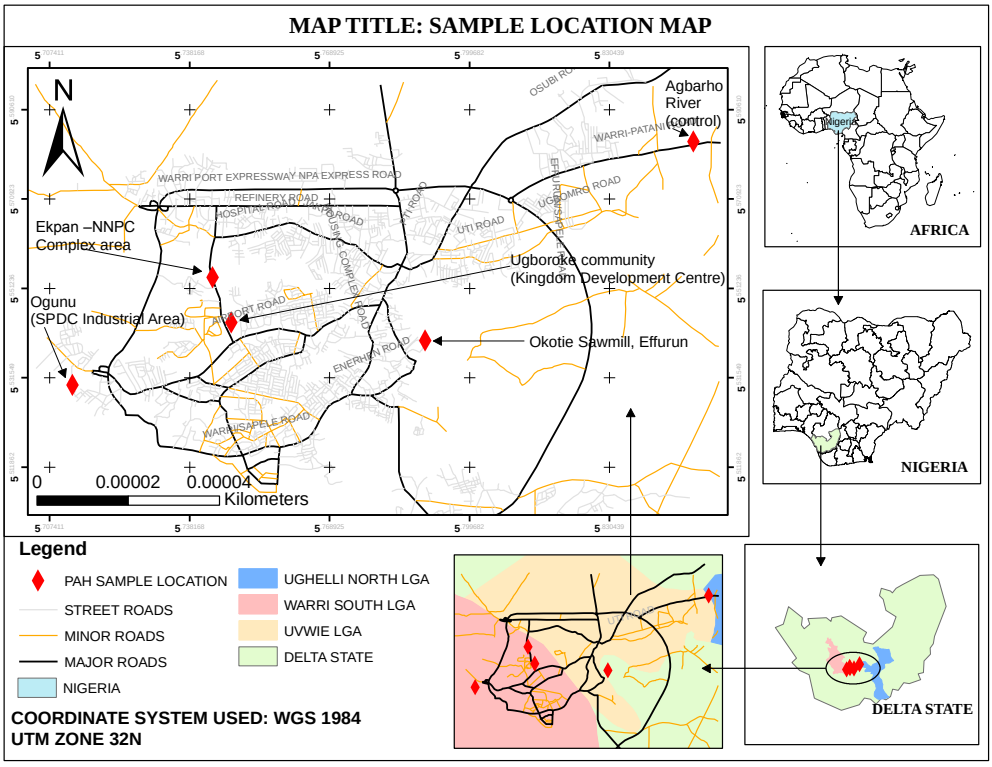

Figure 1 GIS based Map of Study Area

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.

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.

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.

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.

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.

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

The results of analyses of the sediment and soil samples from the study area are as presented in **Tables 2** and **3**, the PAHs diagnostic ratios are presented in **Tables 4** and **5** while the PAHs cross plots are highlighted in **Figures 2-9**. 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

Table 3 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

Table 4 PAHs Diagnostic Ratios for Sediment Samples

Stations	**PAHs Diagnostic Ratios for Sediment Samples**							
	Ant/Ant+Phe		**Fluo/Fluo+Pyr**		**BaA/BaA+Chry**		**Ind/Ind+BghiP**	
	Dry	**Rainy**	**Dry**	**Rainy**	**Dry**	**Rainy**	**Dry**	**Rainy**
ST1-Ekpan	0.56	1	0	1	0.22	0.42	0	0
ST2-Ogunu	0.57	1	0.16	0	0.34	0	0.21	0
ST3-Ugboroke	0.86	0	0	0	0.71	0	0.2	0
ST4-Okotie	0.58	0.75	0.16	0.38	1	0	0.71	0
ST5-Agbarho	0.12	0	0	1	1	0	0.84	0

Table 5 PAHs Diagnostic Ratios for Soil Samples

Stations	**PAHs Diagnostic Ratios for Soil Samples**							
	Ant/Ant+Phe		**Fluo/Fluo+Pyr**		**BaA/BaA+Chry**		**Ind/Ind+BghiP**	
	Dry	**Rainy**	**Dry**	**Rainy**	**Dry**	**Rainy**	**Dry**	**Rainy**
ST1-Ekpan	0	1	0.3	0	0.56	0	0	0
ST2-Ogunu	0.84	0.21	0	1	0	0	0.69	0.04
ST3-Ugboroke	0.55	0	0	0	0.97	0.78	0	0
ST4-Okotie	0.45	0	0	0.6	1	0	0	1
ST5-Agbarho	1	0	0	0.56	0	0	0	0

Discussion

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.* [21] 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.* [22] 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.

Source Prediction Analysis

PAHs have adverse health risks; despite these, they were not included in the environmental audit of the Niger Delta Survey [23]; it is therefore important to identify and apportion PAHs sources for effective pollution control and environmental risk management.

PAHs Diagnostic Ratios

PAH sources have been predicted using diagnostic ratios conventionally and reported in several studies such as: [24-26]. PAHs of molecular mass 178 and 202 are commonly used to distinguish between combustion and petroleum sources [26]. These ratios include but not limited to Ant/Ant + Phe; Fluo/Fluo+Pyr; BaA/BaA+Chry and Ind/Ind+BghiP. The Ant/Ant+Phe ratio presumes that ratios < 0.1 indicate PAHs source to be of petroleum origin while ratios > 0.1 indicate PAHs source to be of combustion origin. The Fluo/Fluo+Pyr ratio presumes that ratios in the range ≥ 0.4 and ≤ 0.5 indicate petroleum combustion, ratios < 0.4 indicate petroleum sources while ratios > 0.5 indicate grass, wood and coal combustion; however, mean ratio for Australian crude oils is> 0.4, and a few oils have very high proportions of Fluoranthene [22]. BaA/BaA+Chry presume that ratios < 0.2 are of petroleum origin, ratios in the range ≥ 0.2 and ≤ 0.35 as mixed sources and > 0.35 as combustion sources. And, Ind/Ind+BghiP presumes that PAHs ratios < 0.2 indicate petroleum sources, ratios in the range ≥ 0.2 and ≤ 0.5 as petroleum combustion sources and

>0.5 as grass, wood and coal combustion sources [24-26]. PAHs diagnostic ratio was calculated from the readings and the result is shown below in Tables 4 and 5

From Tables 4 and 5 above, diagnosis of the PAHs ratios showed that Ant/Ant+Phe for sediment samples within Warri in the dry season ranged from 0.56 to 0.86 and it was 0.12 at the control point. This shows PAHs from here to be of combustion origin. While the Fluo/Fluo+Pyr ranged from 0 to 0.16 within Warri and it was 0 at the control point; the values shown in this ratios are too low to make valuable judgment. The BaA/BaA+Chry ratio ranged from 0.22 to 1.0 within Warri and it was 1.0 at the control point; this indicates that within Warri PAHs are of mixed sources and combustion sources and the control point to be of combustion sources. The Ind/Ind+BghiP ratio ranged from 0 to 0.74 within Warri and 0.84 for the control point. This also shows PAHs from Warri to be of mixed sources which are petroleum sources, petroleum combustion sources and grass wood and coal combustion sources while at the control point it could be said to be of grass, wood and coal combustion sources. From this analysis it could be said that PAHs in sediment samples within Warri in the dry season were majorly of combustion sources from mixed origin which could be petroleum or grass wood and coal origin; also at the control point the PAHs were of combustion origin.

In the rainy season, the Ant/Ant+Phe ratio for sediment within Warri ranged from 0 to 1.0 while at the control point it was 0; this indicates that PAHs are of petroleum origin and petroleum combustion. The Fluo/Fluo+Pyr showed ratio 0 to 1.0 within Warri and 1.0 at the control point; this shows PAHs to be of petroleum sources and grass, wood and coal combustion within Warri and at the control point to be of grass, wood and coal combustion. The BaA/BaA+Chry ratio ranged from 0 to 0.42 and 0 at the control point; this presumes that PAH are of petroleum origin, mixed sources and combustion sources within Warri while at the control point, it is of petroleum origin. The Ind/Ind +BghiP ratio was 0 both within Warri and at the control point; this ratio tells us that ratios < 0.2 are of petroleum source and this indicate that the PAHs in the two locations are likely of petroleum sources.

For soil samples in the dry season, the Ant/Ant +Phe ratio ranged from 0 to 0.84 and it was 1.0 at the control point; this indicates that PAH source within Warri is of petroleum origin and petroleum combustion while at the control point it is of petroleum combustion. For the Fluo/Fluo+Pyr ratio, it ranged from 0 to 0.3 within Warri and 0 at the control point; since these ratios are less than 0.4, they are presumed to be of petroleum sources. The BaA/BaA+Chry ratio ranged from 0 to 0.97 within Warri and it was 0 outside Warri at the control point; this shows that PAH within Warri are of petroleum sources, mixed sources and combustion origin while outside Warri is of petroleum origin. Ind/Ind+BghiP ratio for Warri environs ranged from 0 to 0.69 and it was 0 at the control point; this shows PAH to be of petroleum sources, petroleum combustion and grass wood and coal combustion within Warri while at the control point, it was of petroleum origin.

In the rainy season, soil sample ratio for Ant/Ant+Phe within Warri ranged from 0 to 1.0 and at the control point it was 0. Similarly, the Ind/Ind+BghiP ratio in Warri ranged from 0 to 1.0 and at the control point it was 0. These show PAHs to be of petroleum origin and combustion origin within Warri and at the control point to be of petroleum origin. Fluo/Fluo+Pyr ratio ranged from 0 to 1.0 in Warri and 0.56 at the control point; this shows PAH within Warri to be of petroleum combustion and grass, wood and coal combustion while outside Warri it is of grass, wood and coal combustion. BaA/BaA+Chry ratio within Warri ranged from 0 to 0.78 and it was 0 at the control point; this indicates that PAH sources within Warri are of petroleum sources, mixed sources and combustion sources while at the control point is of petroleum sources.

PAH Cross Plots

Another valuable tool for detecting PAHs source is the PAHs cross plots of the diagnostic ratios, especially when there are several locations; this shows the specific point for the source prediction. PAHs cross plots of the diagnostic ratios above are shown below for sediment and soil samples in the dry and rainy season: N.B: Stations ST 1 to 4 are locations within Warri while ST 5 is outside Warri, control point – Agbarho;

- ST1- Ekpan Location
- ST2 – Ogunu Location
- ST3 – Ugboroke Location
- ST4 – Okotie Sawmill Location
- ST5 – Agbarho Location (Control).

PAH Cross Plots for Various Ratios in Sediment in the Dry Season

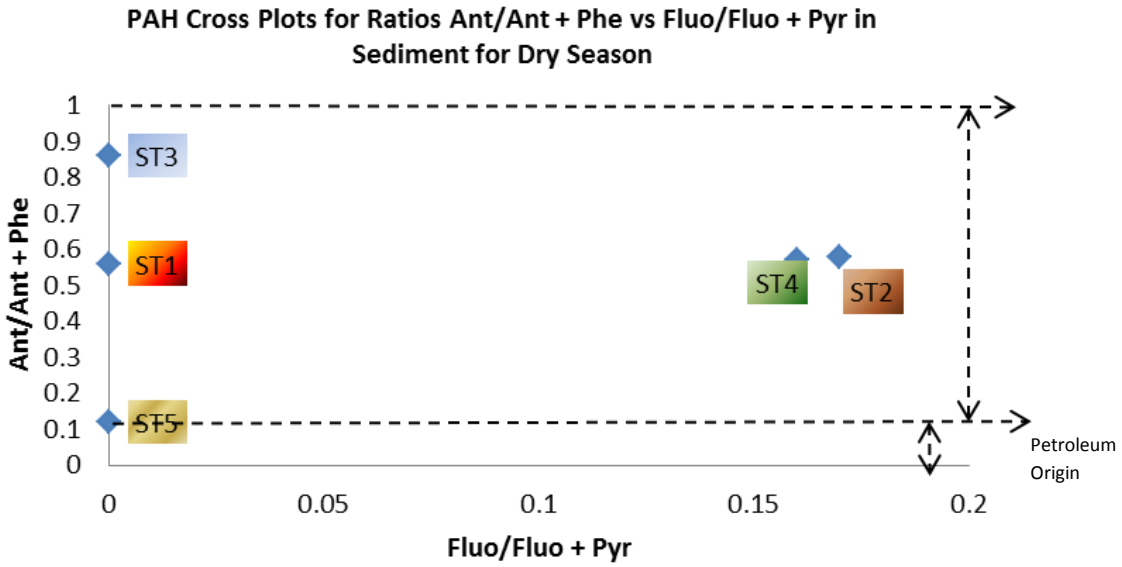

Figure 2 PAH Cross Plots for Ratios Ant/Ant + Phe vs Fluo/Fluo + Pyr in Sediment for Dry Season

From Figure 2 above, it can be seen that PAHs sources in sediment for dry season at the control point ST5 are from petroleum origin while the study area ST1-4 are from combustion origin.

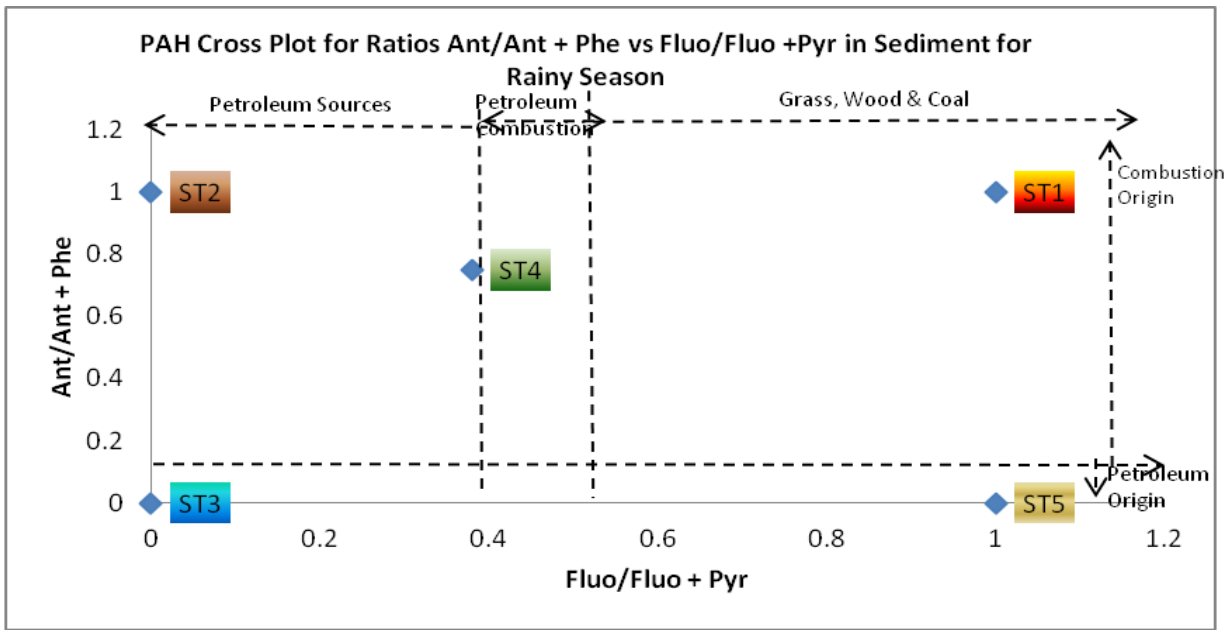

Figure 3 PAH Cross Plot for Ratios Ant/Ant+Phe vs Fluo/Fluo+Pyr in Sediment for Rainy Season

This Figure 3 shows PAHs to be from many sources such as: petroleum origin, combustion origin, petroleum combustion, as well as grass, wood and coal in the rainy season both at the study area and control locations. From the Figure 4, it can be seen that PAHs sources in the dry season are just from petroleum sources/origin and combustion origins. Figure 5 shows PAHs source to be from petroleum origin, combustion origin, grass, wood and coal sources, petroleum combustion and petroleum sources. The ratio BaA/BaA+Chry vs Ind/Ind+BghiP used for analysing PAHs in sediments at different locations in the dry season in Figure 6 was able to give more details about other sources not detected by the Ant/Ant+Phe vs Fluo/Fluo+Pyr and therefore enabling better analyses.

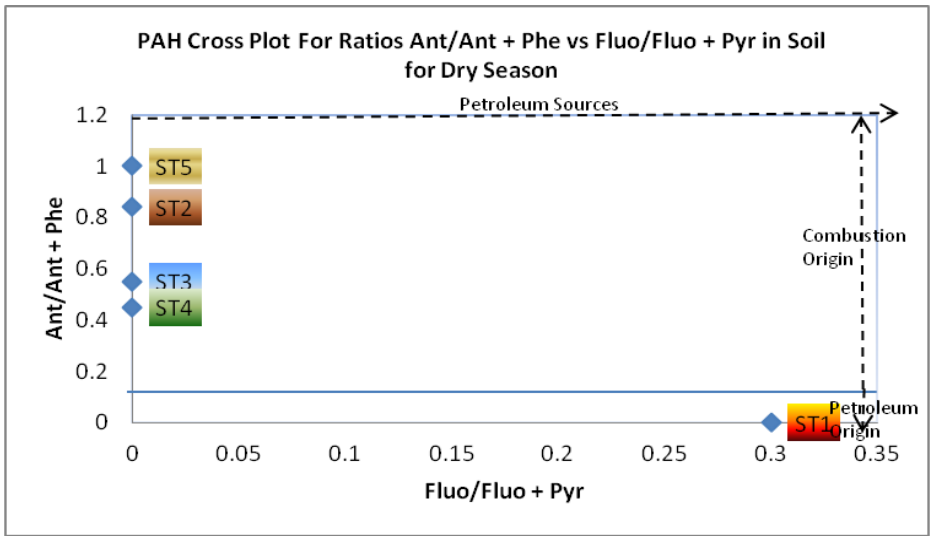

Figure 4 PAH Cross Plot for Ratios Ant/Ant+Phe vs Fluo/Fluo +Pyr in Soil for Dry Season

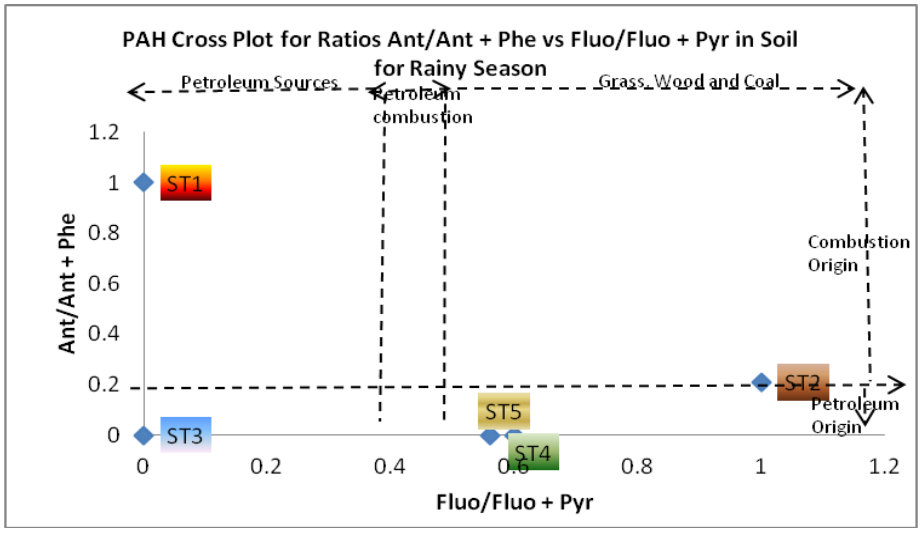

Figure 5 PAH Cross Plot for Ratios Ant/Ant+Phe vs Fluo/Fluo+Pyr in Soil for Rainy Season

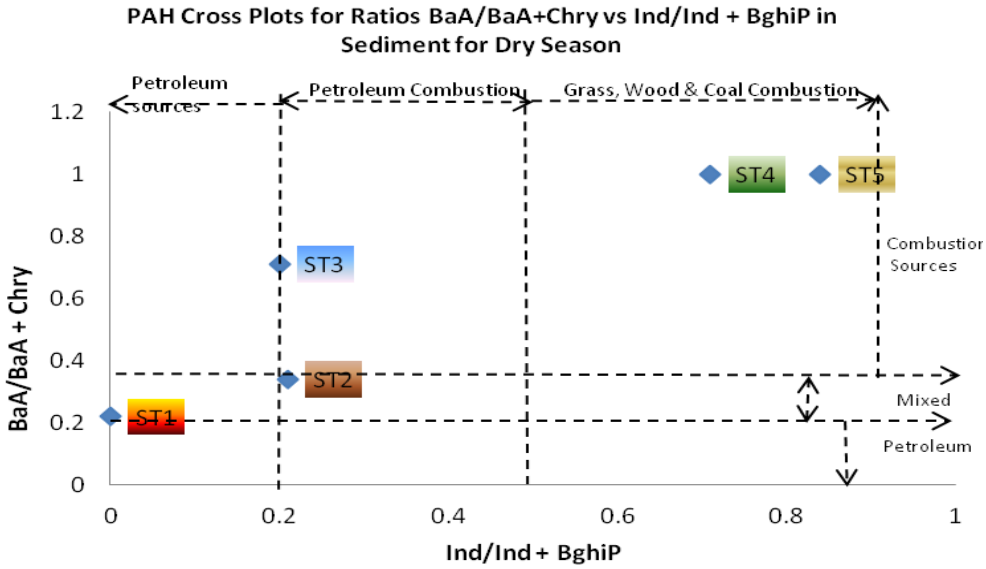

Figure 6 PAH Cross Plots for Ratios BaA/BaA+Chry vs Ind/Ind+BghiP in Sediment for Dry Season

Figure 7 shows clusters for petroleum origin and petroleum sources at Stations 2, 3 and 4 within Warri and station 5, the control point. The PAHs cross plot ratio in Figure 8 shows clusters at petroleum and combustion sources for stations 4, 3 and 1; while ST2 showed sources from petroleum origin and grass, wood and coal combustion. The control location ST5 however showed sources from petroleum origin and petroleum sources. In Figure 9, the ratios BaA/BaA+Chry vs Ind/Ind+BghiP in the rainy season shows clusters for petroleum origin and petroleum sources for ST 1,2,3 and 5; ST4 was clustered at petroleum origin and grass, wood and coal combustion.

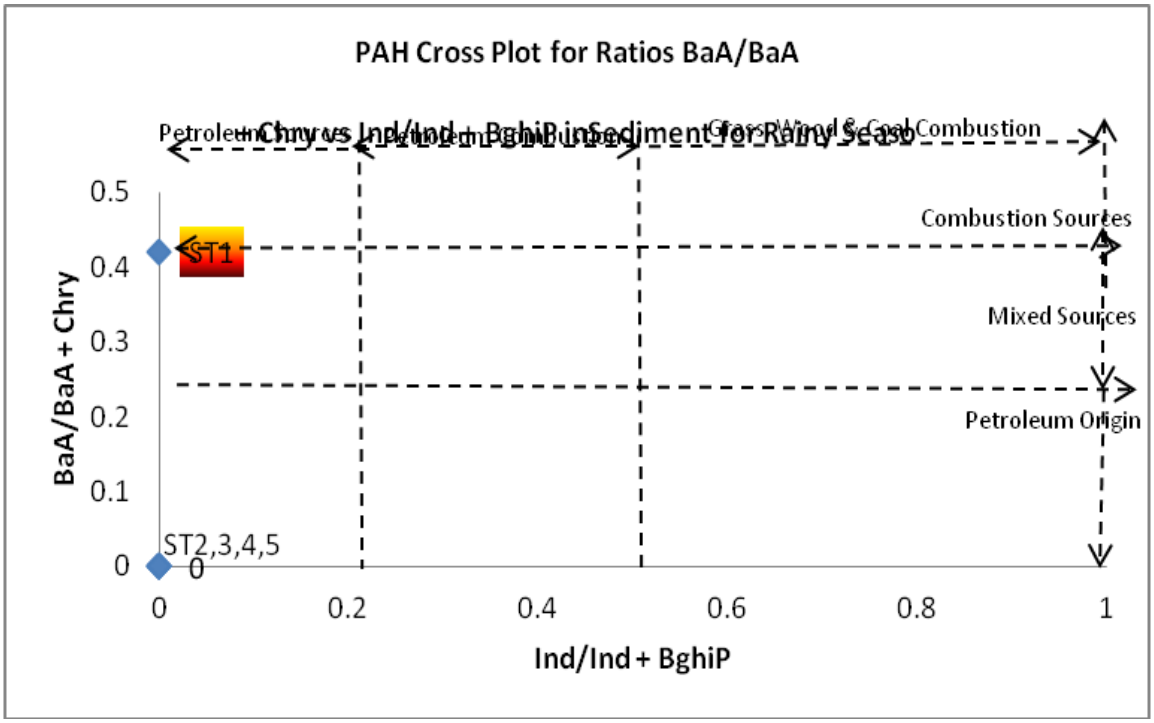

Figure 7 PAH Cross Plot for Ratios BaA/BaA+Chry vs Ind/Ind+BghiP in Sediment for Rainy Season

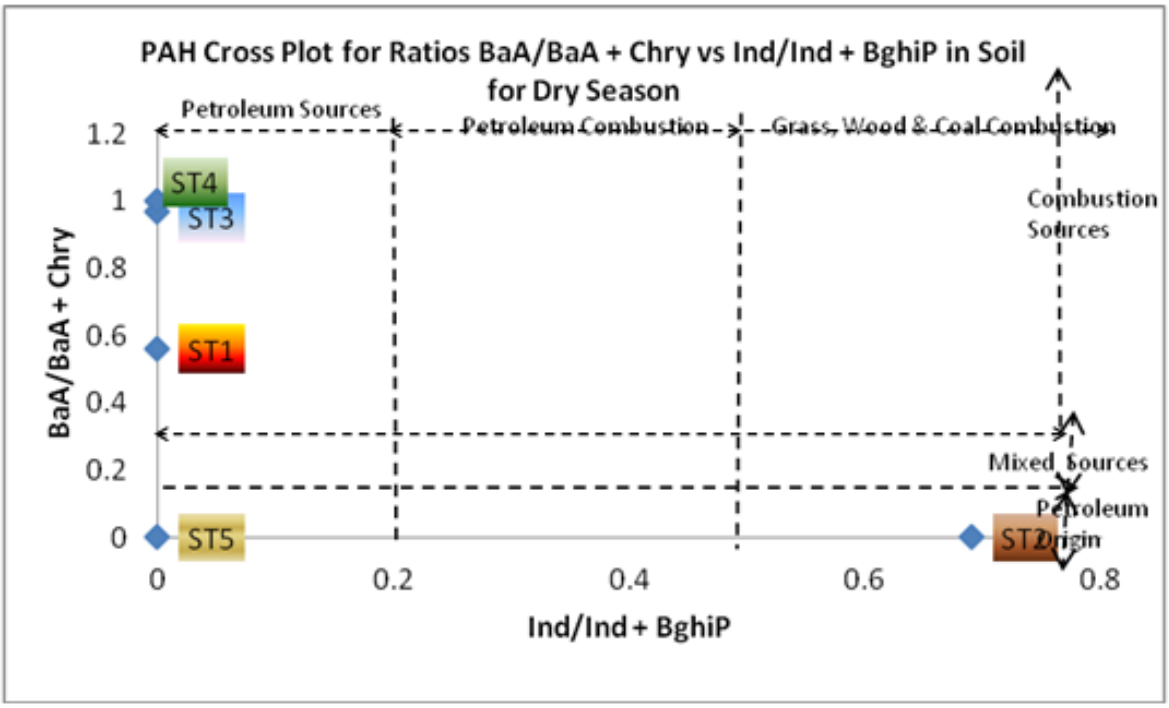

Figure 8 PAH Cross Plots for Ratios BaA/BaA+Chry vs Ind/Ind+BghiP in Soil for Dry Season

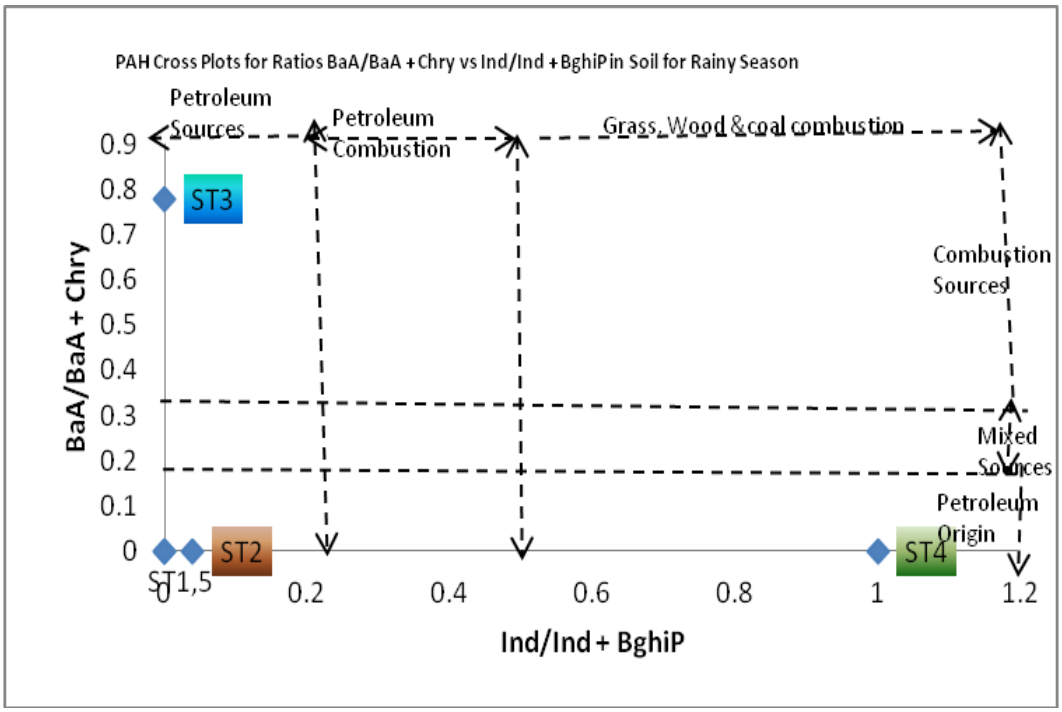

Figure 9 PAH Cross Plots for Ratios BaA/BaA+Chry vs Ind/Ind+BghiP in Soil for Rainy Season

Analyses of the Cross Plots

From Figure 2, the PAH cross plot for sediment in the dry season for Ant/Ant+Phe vs Fluo/Fluo+Pyr ratios showed clusters of ST1 to ST4 within Warri to be of combustion origin and the control point ST5 to be of petroleum origin; however, the same plot in Figure 3 for the rainy season reflects PAHs to be from various sources – petroleum origin, petroleum combustion, combustion origin and grass, wood and coal combustion, for both the study area (Warri) and the control (Agbarho ST5); although combustion at the control point was more of grass, wood and coal combustion.

On the other hand, from Figure 4, Ant/Ant+Phe vs Fluo/Fuo+Pyr ratio for soil in the dry season showed clusters of ST2, 3 and 4 to be of petroleum sources and combustion origin and ST1 to be majorly of petroleum origin while the control point ST 5 was of petroleum sources and combustion origin. In the rainy season, from Figure 5, the PAHs source in soil for same ratios showed ST 2 and 4 to be of petroleum origin and grass, wood and coal combustion, ST 3 to be of petroleum sources and ST 1 to be of petroleum sources and combustion origin. At the control point, it was majorly of petroleum origin and grass, wood and coal combustion.

Furthermore, in Figure 6, the cross plot BaA/BaA+Chry vs Ind/Ind+BghiP for sediment in the dry season ST 4 and 5 were of combustion sources and grass, wood and coal combustion, ST1 was of petroleum sources and mixed sources, ST2 mixed sources and petroleum combustion while ST 3 was petroleum combustion and combustion sources. And in the rainy season, same plot for sediment in Figure 7 showed ST1 as being from petroleum sources and combustion sources and ST 2, 3, and 4 from petroleum origin or sources. The control point ST5 was also from petroleum origin or sources. Meanwhile, according to Figure 8, soil samples for the same cross plot in dry season reflected that ST 4, 3 & 1 are of petroleum origin or sources and combustion sources, ST2 had clusters of petroleum origin and grass, wood & coal combustion. The control point ST 5, was clustered at petroleum origin and sources. While for soil samples, in the rainy season as reflected in Figure 9, ST1 & 2 are of petroleum sources, ST 3 is of petroleum and combustion sources and ST 4 from petroleum origin and grass, wood and coal combustion. The control point ST5 was majorly of petroleum sources.

From the cross plots analyses, it can be seen that PAHs within Warri environs are from different sources and this could be said to reflect the activities at the various sampling points from which the samples were collected, however, they altogether indicate majorly that PAHs are more from anthropogenic activities in Warri environs. Also, it was observed from the analysis that PAHs in sediment in dry season in Warri environs were majorly of combustion origin while in soil samples, they were more of petroleum origin and mixed sources. In the rainy season, PAHs in soil and sediments within Warri were majorly from petroleum and combustion sources.

At the control point, PAHs in sediment samples in dry season were majorly from combustion sources while the soil samples were more of petroleum origin. In the rainy season however, the sources in the soil and sediments were of mixed origin, petroleum source, petroleum combustion and grass, wood and coal combustion. This is similar to what happened at Kolo Creek, in Niger Delta area of Nigeria when Inengite *et al*. [22] analysed PAH source in soil samples. In another work done by same authors on sediments, PAH sources in rainy season reflected mixed sources. A condition that could be responsible for the many sources especially in sediment samples is the runoff from rainwater which could have washed several PAHs from various sources thereby giving conflicting PAHs ratios for source determination [22].

Source Prediction at Study Locations

From all these analyses, there is a clearer understanding as to the specific location that the PAHs were generated and it can be seen that anthropogenic petrogenic activities were more localised at specific locations due to activities there. For instance, Ogunu – ST 2 and Okotie Sawmill – ST 4 had several clusters for petroleum origin and petroleum combustion in soil and sediment samples in both dry and rainy season. This also agrees with the fact that Benz(a)Pyrene B(a)P which is a PAHs of petroleum origin was found unusually high at ST 4 (2.138mg/kg) in dry season in soil samples; and that was the highest value for single PAHs in a particular location in this study. The B(a)P concentration was also high at ST 2 having a total of 1.342mg/kg in sediment, following that of ST 4. As stated earlier, ST 4 has many industrial activities around it, such as: sawmill a construction company, Coca Cola Warri Depot and other small companies in it vicinity. Also, ST 2 – Ogunu, has offices of oil companies around it, although not of major drilling or exploration activities. Furthermore, B(a)P was the PAH with highest concentration within Warri and this could want to give the impression that PAHs in Warri is of petrogenic origin, however, because B(a)P was in high concentration only in two locations and was found only once in ST1 in the dry season, this conclusion need to be made with care.

Benzo(b)Fluoranthene B(b)F and Benzo(a)Pyrene B(a)P

The most persistent PAH, B(b)F was shown in a previous study to be a much better marker of PAH source than B(a)P, the usual indicator [27]. In the study conducted in a vicinity of two Soderberg aluminium Smelters in Canada, it was found that B(b)F degrades more slowly than or at the same rate as most other particulate PAHs monitored (15 PAHs were analysed). B(b)F was also found to be more stable than all other particulate PAHs investigated and was used as a potential alternative to B(a)P as an indicator of exposure to airborne PAHs [27].

Furthermore, B(b)F source according to EPA is from petroleum, garbage or any animal or plant material burns; It is usually found in smoke and soot and combines with dust particles in the air and is carried into water and soil or deposited on plants [28]. Studies have also shown that of all estimated environmental releases of B(b)F, 97% is found in air and approximately equal amount of the remaining 3% is release to water and land [28]. Based on these findings, it could be said that B(b)F which is also a five ringed PAHs if considered as an alternative to B(a)P could indicate that there were traces or indications of petrogenic PAHs all around Warri since B(b)F is persistent around the study area, although it is not in such high concentration as to be the major source of PAHs contamination.

Benzo(ghi)Perylene B(ghi)P

In order to attempt to correctly predict the source of PAHs within Warri, the next PAH with the highest concentration, B(ghi)P was further analysed. B(ghi)P is majorly from combustion source; vehicle exhausts and domestic wood and coal fires, emissions from industrial effluents, municipal waste water treatment facilities, waste incinerators, aluminium smelting and cigarette smoke. It could also be released naturally from forest fires and volcanoes, yet, anthropogenic pyrogenic sources remain the major source of B(ghi)P in the environment [29]. B(ghi)P was found in all the locations in Warri, mostly in the dry season and mostly in sediment samples. It also has its highest concentration at Ugboroke ST 3, followed by Ogunu ST 2. These two locations have more of domestic activities that involve burning of wood and coal fires, municipal waste water and cigarette smoke. It is important to also note that all the sampling locations within Warri had a refuse dump either within them or not far away from them. According to Venkatesan [30], low levels of perylene encountered in sediments could be derived from anthropogenic sources. Also, it has been found that native microbes act on PAHs as well as other hydrocarbons in the environment in order to

remove them [31]. Furthermore, it has been found that high levels of B(ghi)P at a site could be attributed to microbial activities at the site [22, 30].

Based on all these indications, it could be suggested that PAHs in Warri is more from anthropogenic pyrogenic activities than from petrogenic sources.

Source Prediction at the Control Point

At the control point, source prediction analyses revealed that soil and sediment samples in the rainy season were from same sources which are: petroleum origin and grass, wood and coal combustion. While in the dry season sediment samples were from petroleum origin, and soil samples from petroleum source and combustion. PAH with highest concentration here is BghiP and it was also the most persistent. The next most concentrated PAH at the control is Ind & DbahA. Studies have shown that BghiP is a PAH of combustion origin [29], and Ind&DbahA are from combustion and petroleum combustion origin. Ind&DbahA were also high in sediment and this could be due to their individual ability to attach strongly to substrates and not to be easily leached but transported from one location to another [29]. The activities at the control station also reflect the results. Dredging was taking place at the riverside from which the sediment samples were collected. The engines used for this could have released PAHs from petroleum origin into the river and consequently the sediments within the area. However, the concentrations were not high enough to make it the highest source of PAHs, the source predictions showed that there was PAHs pollution from petroleum origin. There is also an abattoir and a meat market that involves burning of tyre. Other domestic activities in the market and daily activities of local dwellers could also release PAHs from combustion sources into the environment. Furthermore, this location is close to a major highway that is a trans-link to a nearby state (Bayelsa) and vehicular activities could have released PAHs from petroleum sources and combustion into the surrounding soil. As observed in the source determination analysis, the rainy season showed PAHs to be from petroleum origin and grass, wood and coal combustion for both soils and sediments. There is possibility that surface runoff to the river affected PAHs source and brought about detection of many sources.

Lastly, a major factor that could affect PAHs as well as other contaminants source anywhere is that, they could have been carried from other places, and since PAHs are found everywhere, it cannot really be said altogether that a particular action was totally responsible. However, PAHs source determination is highly important and has been adequately used as a useful tool to get clues to pollutant source and make valuable decision in environmental pollution management.

Evaluation of the Effects of PAHs on Man

Although this study is majorly to predict the sources 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 [32] 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 [33]. When man consumes these aquatic organisms as food, they become at risk to the negative effects of these harmful pollutants. According to WHO [32], 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 [34].

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 [35], 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 [28].

Conclusion

The sources of Polycyclic Aromatic Hydrocarbons (PAHs) in marshy soils and sediment samples in Warri City, Southern Nigeria were examined in this study. Analyses of the PAH diagnostic ratios and cross plots of the diagnostic ratios were used as veritable instruments to predict the sources of PAHs in the city.

From the analyses of the PAHs diagnostic ratios, it was observed that PAHs in sediment samples within Warri in the dry season were majorly of combustion sources from mixed origin which could be petroleum or grass wood and coal origin; at the control point the PAHs were of combustion origin. In the rainy season, PAHs were of petroleum origin, mixed sources and combustion sources while at the control point, it was of petroleum origin. For soil samples, in the dry season, PAHs were observed to be of petroleum sources, petroleum combustion and grass wood and coal combustion within Warri while at the control point, it was of petroleum origin. In the rainy season, PAHs were observed to be of petroleum, mixed and combustion sources while at the control point, it was of petroleum sources.

Furthermore, analyses of the cross plots showed that PAHs within Warri are from different sources and this could be said to reflect the activities at the various sampling points from which the samples were collected; however, they altogether indicate majorly that PAHs are more from anthropogenic activities in Warri. Also, it was observed from the analyses that PAHs in sediment in dry season in Warri were majorly of combustion origin while in soil samples, they were more of petroleum origin and mixed sources. In the rainy season, PAHs in soil and sediments within Warri were majorly from petroleum and combustion sources.

Based on all the analyses of the PAHs diagnostic rations and the cross plots, it could be suggested that PAHs in Warri is more from anthropogenic pyrogenic activities than from petrogenic sources.

Finally, it is important to note that PAHs source determination is highly important and has been adequately used as a useful tool to get clues to pollutant source and make valuable decision in environmental pollution management.

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