

CRITICAL ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS RING SIZE DISTRIBUTION IN MARSHY SOILS AND SEDIMENTS IN WARRI CITY AND ITS ENVIRONS, SOUTHERN NIGERIA

Abstract

This study was carried out to analyze the ring size distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in marshy soils and sediment 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. It was observed that PAHs concentration was generally higher in dry than rainy seasons for soil and sediment samples. Furthermore, ring size analysis revealed that for soils, two to three-ringed as well as four-ringed PAHs were more predominant in Ugboroke location, five-ringed PAHs in Okotie and six-ringed PAHs in Ogunu location. Overall, five-ringed PAHs were more predominant in Okotie location in the dry season. However, for sediments, two to three-ringed as well as four-ringed PAHs were more predominant in Okotie location, five-ringed PAHs in Ogunu and six-ringed PAHs in Ugboroke location. Overall, two to three-ringed PAHs were more predominant in Okotie location in the dry season for sediment samples.

Key Words: PAHs; Sediments; Benzo(a)pyrene; Gas Chromatography; Flame Ionization detector

INTRODUCTION

Industrialization and urbanization have promoted socio-economic development. This has, however, led to variety of environmental problems in urban areas, including contamination by polycyclic aromatic hydrocarbons (PAHs) via various pathways [1]. Polycyclic Aromatic Hydrocarbons (PAHs) are a large class of persistent toxic substances (PTS) or persistent organic compounds (POPs) which are emitted as by-products of virtually every type of combustion technology or biomass burning [2-4].

They are primarily derived from incomplete combustion of fossil fuels and burning of vegetation and other organic materials [5]. The derivatives from crude oil seepage and diagenesis of organic matter in anoxic sediments are also important PAHs' sources [6]. PAHs are introduced into the environments via various routes and are ubiquitous environmental pollutants. They have been detected extensively in various environmental media, such as organism [7], atmosphere [8], water [9], soils [10], and sediments [11]. Because of their

potentially hazardous properties, persistence and prevalence in the environment, efforts have been made to reduce PAHs emission in many countries; for example, 16 of PAHs have been listed as priority control pollutants by the Environmental Protection Agency of the USA [12].

PAHs are resistant to degradation over a long period in different environmental compartments [13, 14]. However, the rates of degradation vary and generally decrease with increasing number of aromatic rings, oxygen concentration, temperature and light intensity [14]. Also, the characteristics of the soil environment particularly the soil organic matter (SOM) content, and the competence of the soil microbial community to degrade these compounds is of importance in determining their fate and transport.

PAHs have been an issue of public concern due to their demonstrated carcinogenic, mutagenic and toxicity properties [15-17]. The prevalent mechanism of PAHs toxicity to invertebrates is narcosis (additive), which results in the degradation of cell membrane [18]. This degradation can result in mild toxic effects or mortality depending upon the quantity and duration of exposure [19]. Photo-activated toxicity, carcinogenicity and teratogenicity have also been reported to occur due to exposure to certain PAHs, (eg, B[a]p). Though soil and sediments act as a major sink for these PTS in the environment, these compounds are soluble in soil and river waters depending on their individual and/or combined physicochemical properties.

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 [20, 21], 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 soil and sediments in Warri City. This study, therefore, is essential not only to determine the ring-size distribution of PAHs in soil 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

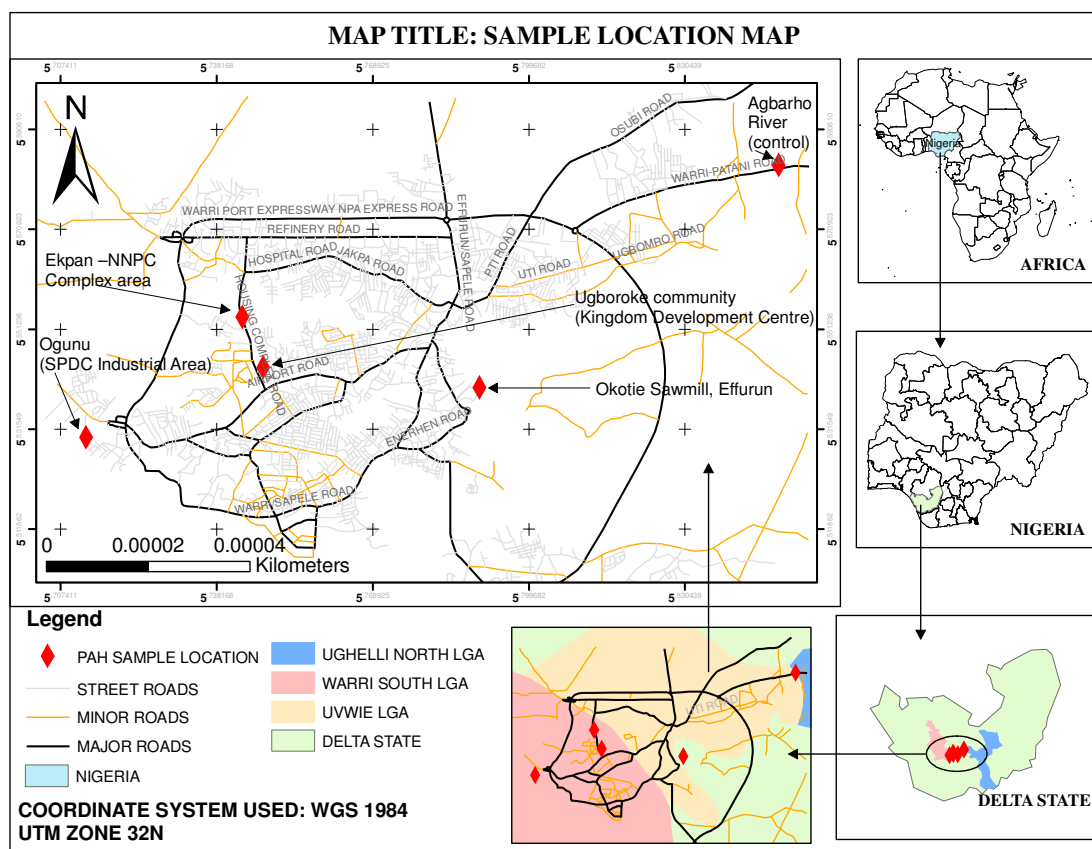
Study Area

This study was carried out in Warri located between latitude 5°31'N and longitude 5°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 humidity for most parts of the year. The area is characterized by tropical equatorial climate with mean annual temperature of 32.8°C and annual rainfall amount of 2673.8 mm. There are high temperatures of 36°C and 37°C. The

76 natural vegetation is a rainforest with swamp forest in some areas. The forest is rich in timber
77 trees, palm trees, as well as fruit trees.

78 As a result of the unique location of Warri at the bank of the Niger Delta, there are rivers,
79 creeks, ponds and wetland areas around the city hence most places in the city are swampy
80 areas and marshes. Majority of the people especially those living close to the waters are either
81 fishermen/women or take fishing as a hobby. Warri River which is one of the most important
82 coastal rivers of the Niger Delta distributed in various tributaries around the city and beyond
83 is responsible for the marshy soil and swampy area that characterise the city [22].



84
85 **Fig. 1: GIS based Map of Study Area**

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

88 **Table 1: Showing Sample Locations and their GPS Coordinates**

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

89 **Sample Locations**

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

92 **1. Ekpan –NNPC Complex area**

93 This site is along the Ekpan bridge express, after the NNPC staff quarters. It is located
94 between longitude 05°33'13.5''N and latitude 005°44'35.8''E. There is a company opposite
95 the sampling point and a church beside it. The exact sampling point is a river under the
96 bridge. One major characteristics of this location is that there are not much human population
97 here but the place is close to NNPC/Ekpan highway a major busy highway. The river could
98 be a drain receiving waste water from neighbouring residential areas and industry.

99 **2. Ugboroke community (Kingdom Development Centre)**

100 This location can be said to describe the natural vegetation of Warri which is of rainforest
101 with swamp forest in some areas; the forest in Warri is rich in timber trees, palm trees, as
102 well as fruit trees. Ugboroke community is however one of the emerging areas in Warri and
103 developmental features such as roads, modern building structures are taking over the forest.
104 The community is a densely populated area, made up of local indigenous people as well as
105 others that have come to live within the community. One thing peculiar to this location is
106 that, there are clusters of old, native houses, modern/semi-modern residential houses, small
107 and medium scale businesses, factories, and companies, agricultural activities (poultry,
108 fishing amongst others).

109 The sampling point is a pond at the back of a church (kingdom Development Centre). It is
110 located between longitude 05°32'37.6''N and latitude 005°44'50.5''E. This point is actually
111 like a wetland that is flooded most part of the year. Plantain trees, other trees, shrubs and
112 plants are typical of this environment.

113 **3. Ogunu (SPDC Industrial Area)**

114 This site is located between longitude 05°31'48.1''N and latitude 005°42'44.9''E, outside
115 Shell Petroleum Development Company SPDC residential, recreational and mild
116 administrative area. It is a local community that has been upgraded by virtue of the presence
117 of the multinational companies in the area. Apart from SPDC, Ogunu community play host
118 to, Pan Ocean Oil Company. The people in this community are majorly indigenes with few
119 other non-indigenes. Their occupations are majorly petty trading, fishing, farming or idling.
120 The exact sampling point is Ogunu River. There are residential houses around and even in or
121 on the river; there is also a local public toilet and a refuse dump close by.

122 **4. Okotie Sawmill, Effurun**

123 This site is located between longitude 05°32'23.3''N and latitude 005°47'24.0''E, in the
124 outskirts of Warri, in a place called Effurun. To many people, Effurun is not part of the Warri
125 town ship but by geographical and political description, Effurun is part of the larger Warri
126 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 05°35'01.1''N and latitude 005°50'56.0''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 (4°C) 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 2-5 below with their ring size distribution highlighted in Fig 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

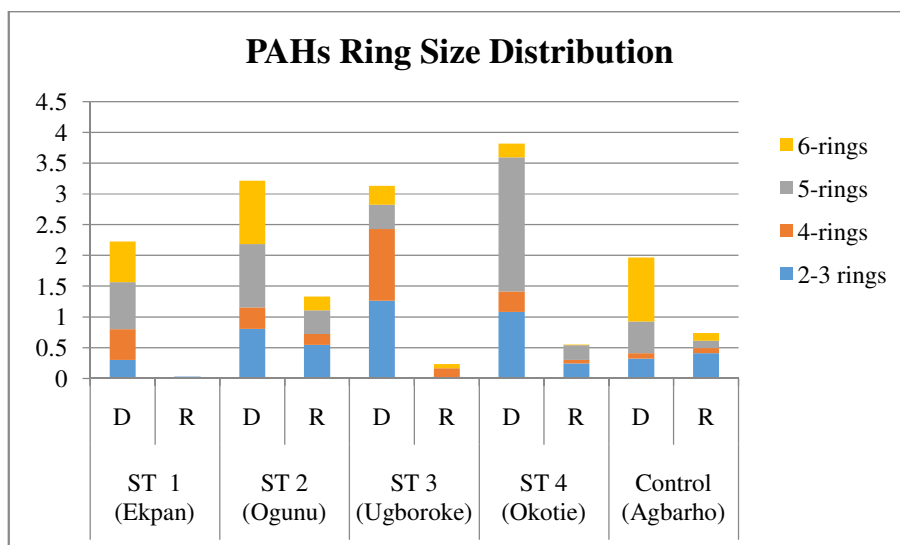
PAHs	Ring No.	Sampling Stations (ST)									
		ST 1 (Ekpan)		ST 2 (Ogunu)		ST 3 (Ugboro)		ST 4 (Okotie)		Control (Agbarho)	
		D	R	D	R	D	R	D	R	D	R
Naphthalene	2	0.09	0	0.484	0	0	0.017	0.584	0.012	0.195	0
2-methyl naphthalene	2	0	0.016	0.045	0.033	0.561	0	0.04	0.192	0.007	0.411
1-methyl naphthalene	2	0.082	0	0.041	0.049	0.168	0	0	0.038	0.009	0
Acenaphthylene	3	0.01	0	0.069	0.027	0	0.0003	0.025	0	0	0
Acenaphthene	3	0.096	0	0	0.018	0	0.0004	0.1	0.0005	0.007	0
Fluorene	3	0	0	0	0.066	0	0	0.082	0.0001	0.071	0
Phenanthrene	3	0.022	0	0.027	0.094	0.239	0	0.139	0.003	0	0
Anthracene	3	0	0.011	0.142	0.255	0.292	0	0.113	0	0.035	0
Pyrene	4	0.17	0	0.244	0	0	0.024	0.174	0.022	0.088	0.036
Chrysene	4	0.11	0	0.102	0	0.033	0.028	0	0	0	0
Benzo(a)anthracene	4	0.142	0	0	0	1.134	0.0964	0.159	0	0	0
Benzo(b)fluoranthrene & Benzo(k)fluoranthrene	5	0.286	0	0.11	0.275	0.076	0	0.042	0.0682	0.514	0.053
Benzo(a)pyrene	5	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	6	0	0	1.11	0.01	0	0	0	0.011	0	0
Benzo(g,h,i)perylene	6	0.66	0	0.479	0.223	0.309	0.07	0.226	0	1.039	0.127
Fluoranthrene	4	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

170 **Table 3: PAHs Ring Size Distribution in Marshy Soil Samples in Warri City in mg/kg**

Ring Size	ST 1 (Ekpan)		ST 2 (Ogunu)		ST 3 (Ugboro)		ST 4 (Okotie)		Control (Agbarho)	
	D	R	D	R	D	R	D	R	D	R
2-3 rings	0.3	0.027	0.808	0.542	1.26	0.0177	1.083	0.2456	0.324	0.411
4-rings	0.496	0	0.346	0.181	1.167	0.1484	0.333	0.055	0.088	0.082
5-rings	0.77	0	1.027	0.38	0.394	0	2.18	0.2397	0.514	0.119
6-rings	0.66	0	1.034	0.228	0.309	0.07	0.226	0.0055	1.039	0.127

171

172



173

174 **Fig 2: The distribution pattern of 2–6-ring PAHs in Marshy Soil at different sampling**
 175 **locations**

176

177

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

PAHs	Ring No.	Sampling Stations (ST)									
		ST 1 (Ekpan)		ST 2 (Ogunu)		ST 3 (Ugboro)		ST 4 (Okotie)		Control (Agbarho)	
		D	R	D	R	D	R	D	R	D	R
Naphthalene	2	0.041	0	0.211	0	0.0349	0	1.091	0	0.421	0.017
2-methyl naphthalene	2	0.039	0	0.041	0	0.0353	0	0.05	0	0	0.21
1-methyl naphthalene	2	0.01	0	0.001	0	0	0.209	0.18	0.073	0.37	0.033
Acenaphthylene	3	0.007	0.005	0.006	0	0.076	0	0.046	0.007	0.154	0
Acenaphthene	3	0	0.006	0.01	0	0.004	0.008	0.0216	0.02	0	0
Fluorene	3	0.011	0	0.057	0.13	0.013	0	0.09	0.131	0.038	0.017
Phenanthrene	3	0.191	0	0.07	0	0.0235	0	0.245	0.228	0.577	0.046
Anthracene	3	0.244	0.071	0.093	0.751	0.147	0	0.338	0.693	0.075	0
Pyrene	4	0.209	0	0.214	0	0.187	0	0.513	0.361	0.186	0

Chrysene	4	0.507	0.617	0.49	0	0.083	0	0	0.285	0	0.186
Benzo(a)anthracene	4	0.144	0.452	0.255	0	0.205	0	0.572	0	0.18	0
Benzo(b)fluoranthrene & Benzo(k) fluoranthrene	5	0.413	0.52	0.193	0	0.388	0	0	0.245	0.104	0.109
Benzo(a)pyrene	5	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	6	0	0	0.196	0	0.267	0	0.334	0	1.092	0
Benzo(g,h,i)perylene	6	0.218	0.112	0.753	0	1.067	0.147	0.139	0.346	0.202	0.282
Fluoranthrene	4	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 5: PAHs Ring Size Distribution in Marshy Sediment Samples in Warri City in mg/kg

Ring Size	ST 1 (Ekpan)		ST 2 (Ogunu)		ST 3 (Ugboroke)		ST 4 (Okotie)		Control (Agbarho)	
	D	R	D	R	D	R	D	R	D	R
2-3 rings	0.543	0.082	0.489	0.881	0.3337	0.217	2.0616	1.152	1.635	0.323
4-rings	0.86	1.079	0.999	0	0.475	0	1.182	0.864	0.0366	0.273
5-rings	0.413	0.52	1.633	0	0.6174	0	0.99	0.667	1.429	0.177
6-rings	0.218	0.112	0.851	0	1.0804	0.147	0.306	0.346	0.748	0.282

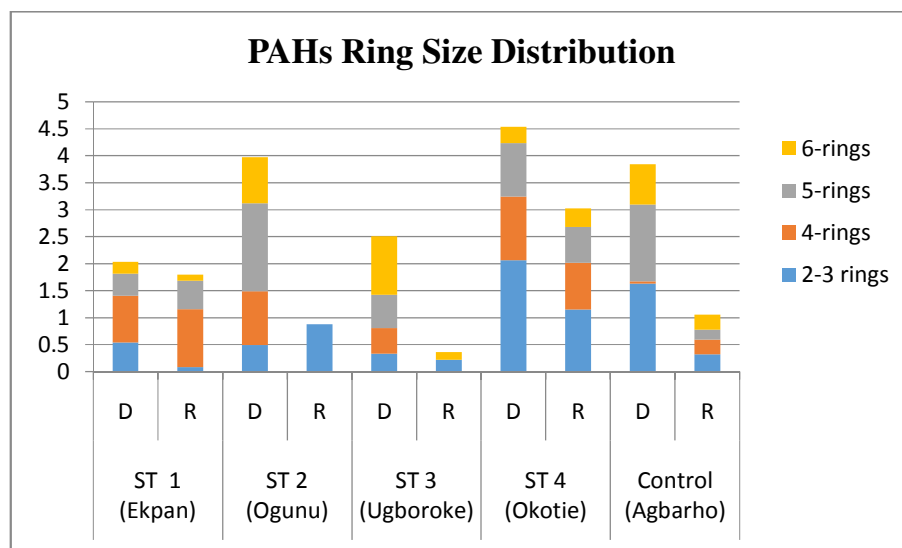


Fig 3: The distribution pattern of 2–6-ring PAHs in Marshy Sediments at different sampling locations

Discussion

189 **Occurrence of individual PAHs for Soils and Sediments**

190 Highest total concentration of PAHs within Warri was recorded for BaP - benzo(a)pyrene at
 191 3.302mg/kg in soil samples. The highest contributor to the bulk was at Okotie Sawmill; this
 192 location is the one characterised with the presence of several industrial activities and about
 193 2.138mg/kg total concentration was detected there in the dry season soil samples. This is
 194 similar to the work done by Ana *et al.* [23] on PAHs contamination of surface waters in
 195 Nigeria Coastal Areas. They reported that the concentration of total PAHs in industrialised
 196 areas was three times higher than in the less industrialised area. The order of PAHs
 197 concentration in soil within Warri is: BaP>BghiP>BaA>Naph>Ind&DbahA>2-
 198 M.Naph>BbF>Ant>Pyr>Phenan.

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

202 At the control point, PAHs with highest concentration in soil sample was BghiP; it had a total
 203 concentration of 1.166mg/kg with the larger amount of 1.039mg/kg detected in the dry
 204 season. It is important to note that the control point location has cattle grazing ground, an
 205 abattoir and meat market. Therefore, the high concentration of BghiP here could be attributed
 206 to the microbial production of the PAH due to microbial activities in the abattoir area. This is
 207 similar to the study done by Inengite *et al.* [24] on PAHs sources in Kolo Creek soil in Niger
 208 Delta area of Nigeria where it was found that concentration of BghiP was high near an
 209 abattoir. The order of PAHs concentration in soil in decreasing order is BghiP>BbF&BkF>2-
 210 Methyl.Naph. Lowest concentration of total PAHs detected at control station for soil for both
 211 dry and rainy season is 0.007mg/kg, and the order is Acn≤2Methyl.Naph≤1-Methyl.Naph.
 212 Most of the PAHs were not found at all and they include: Phe., Acnptyl.,Ind&DbahA, BaA,
 213 and Chry. Those detected only in dry season are: Ant, Fluoren, Acenaphthalene, and 1-Methyl
 214 Naph; and those detected only in rainy season are BaP and Fluoranthene.

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

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

and phenanthrene. Acenaphthalene 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.

Ring Size Analysis

Two to three -ringed PAHs

In Warri environs and at the control point, two and three ringed PAHs were found predominantly in the dry season for both soils and sediments samples. Naphthalene, 2-methyl naphthalene and 1-methyl naphthalene were the two-ringed PAHs analysed in this study. The essence of analysing the methyl form of naphthalene is because of the ease of solubility and disintegration of fewer ringed PAHs especially in aqueous solution, which could make them converted into other forms such as methylated form and therefore not detectable as naphthalene [25]. It has also been found that methylated form of certain organic compounds could be more harmful than the parent compound [25], hence, the need to analyse methyl forms.

Within Warri environs, anthracene and phenanthrene were the most persistent of the three rings. Although anthracene was the most persistent, being more distributed in all the locations, yet phenanthrene appeared more in quantity at some locations and has overall more appearance. At the control point, phenanthrene was the most persistent three-ringed and it was found only in sediment samples predominantly in the dry season. Generally, the two to three rings were found majorly in the dry season and almost absent in the rainy season. This is similar to an earlier done by Inengite *et al.* [24]. Higher ringed PAHs were found to predominate in the rainy season. The authors attributed it to heavy rains, since the solubility of the PAHs is related to number of rings [24]. Their submission is corroborated by the work done by Karlsson and Viklander [26] in which it was reported that the more rings the less soluble; which indicates that the fewer rings were more soluble.

In the marshy soil samples (Fig 2), the two to three-ringed PAHs were more predominant in Ugboro sample location in the dry season with the least concentration recorded in same location in the rainy season while in the marshy sediment samples (Fig 3), they were more

268 predominant in Okotie sample location in the dry season while Ogunu had the least
269 concentration in the rainy season.

270 **Four -ringed PAHs**

271 The most persistent four-ringed within Warri for both soil and sediment is pyrene. It occurred
272 most in the dry season and more in the sediments than soil samples at Okotie Sawmill. Also,
273 it was found in the dry season in both soil and sediment samples at every location except at
274 Ugboroke where it was not found in the soil sample throughout the dry season though it was
275 found once in early rainy season (June) at a value of 0.024mg/kg. The highest mean value
276 found for Pyrene was in sediments in dry season at Okotie sawmill, Warri and it was
277 0.171mg/kg. The least persistent four-ringed is fluoranthene and it was found more in the
278 rainy season. However, it was not found at all in Ugboroke, though all the other four-ringed –
279 chrysene, pyrene and benz(a)anthracene were found with benz(a)anthracene occurring most.
280 At the control point, Pyrene was also the most persistent four-ringed and a mean value of
281 0.062mg/kg was found in sediments samples in dry season and it was below detection limits
282 in the rainy season.

283 The order of persistence of four-ringed PAHs within Warri for soil and sediment is:
284 Pyrene>Benz(a)anthracene>Chrysene>Fluoranthene; while the order outside Warri is
285 Pyrene>Benz(a)anthracene>Fluoranthene>Chrysene.

286 In the marshy soil samples (Fig 2), the four-ringed PAHs was more predominant in Ugboroke
287 sample location in the dry season with the minimum concentration recorded in Ekpan
288 location in the rainy season while in the marshy sediment samples (Fig 3), they were more
289 predominant in Okotie sample location in the dry season with minimum concentrations in
290 both Ogunu and Ugboroke locations in the rainy season.

291 **Five-ringed PAHs**

292 Five-ringed benzo(b)fluoranthene was the most persistent five-ringed and overall most
293 persistent PAHs within Warri. It occurred most in Ekpan and it was more in the sediments at
294 a mean value of 0.137mg/kg in the dry season and 0.173mg/kg in rainy season, than soils
295 sample which was 0.143mg/kg in dry season. However, it was found below detection limits
296 in soils samples at this location in the rainy season. Five-ringed benz(a)pyrene was found
297 only once in soil sample in the dry season at Ekpan, but a total of 2.138mg/kg and mean
298 value 1.069mg/kg was found in soil samples at Okotie sawmill in dry season. This was the
299 highest value for single PAHs compound at a particular location in this study. At the control
300 point, benzo(b)fluoranthene was also more persistent, despite this, benz(a)pyrene had the
301 highest total concentration of 0.779mg/kg and mean value of 0.259mg/kg for five-ringed in
302 the dry season for sediment samples.

303 In the marshy soil samples (Fig 2), the five-ringed was more predominant in Okotie location
304 in the dry season while Ekpan and Ugboroke locations had the least value in the rainy season
305 while in the marshy sediment samples (Fig 3), they were more predominant in Ogunu
306 location in the dry season with Ogunu and Ugboroke locations having the least
307 concentrations in the rainy seasons.

Six-ringed PAHs

Six-ringed PAHs Indeno 1,2,3-cd pyrene and Dibenzo (a,h)anthracene (which were analysed as one compound and to be represented in this study as ind and DbahA) was the least persistent six-ringed and overall least persistent PAHs found within Warri. It was below detection level in soil samples at Ugboroke and found only in the dry season for the sediment samples. At Ogonu, it was found unusually high with a total of 1.110mg/kg and mean value of 0.555mg/kg in soils in the dry season. And only total of 0.010mg/kg was found in the soils samples at the same location in late rainy season. While in the sediment only total of 0.196mg/kg and mean value of 0.065mg/kg of the six ringed ind and DbahA was found in the dry season and this was absent in the rainy season. Ind and DbahA was below detection limit in Ekpan soils and sediment samples throughout the sampling period. However, at the control point, a high total concentration of 1.092mg/kg and mean value of 0.364mg/kg was found in the sediment in dry season but it was not found in the wet season. The values for six ringed Ind and DbahA was below detection limit in soils samples.

However, Benzo(ghi)Perylene - BghiP which was the most persistent six-ringed recorded in the study area – Warri was found in all the locations; with highest values detected for sediment samples in the dry season. Ugboroke had the highest total concentration of 1.067mg/kg and mean value of 0.355mg/kg in its sediments for BghiP, in the dry season. This is followed by a total value of 0.753mg/kg and mean level of 0.251mg/kg in sediments samples from Ogonu in the dry season. BghiP was absent in Ogonu sediments in rainy season and the lowest detectable total value of 0.070mg/kg and mean 0.023mg/kg was found in Ugboroke soil. At the control point, BghiP was also the most persistent and had its highest total concentration of 1.039mg/kg and mean 0.519mg/kg in soil in dry season, but was present in low total concentration of approximately 0.202mg/kg and mean 0.067mg/kg in sediments.

In the marshy soil samples (Fig 2), the six-ringed PAHs had the maximum value in the control location while Ekpan had the least concentration in the rainy season while in the marshy sediment samples (Fig 3), they were more predominant in the dry season in Ugboroke location with Ogonu location having the least concentrations in the rainy season.

Evaluation of the Effects of PAHs on Man

Although this study is majorly to determine the analyse the ring size distribution 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 [27] 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 [28]. When man consumes these aquatic organisms as food, they become at risk to the negative effects of these harmful pollutants. According to WHO [27], 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 [29].

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 [30], 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 [31].

CONCLUSION

The ring size distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in marshy soils and sediment samples in Warri City, Southern Nigeria were examined in this study. The two-ringed PAHs analysed were naphthalene, 2-methyl naphthalene and 1-methyl naphthalene while the three-ringed PAHs were acenaphthylene, acenaphthene, fluorine, anthracene and phenanthrene. The four-ringed PAHs were fluoranthene, chrysene, pyrene and benzo(a)anthracene. The five-ringed PAHs were benzo(a)pyrene, benzo(b)fluoranthene and benzo(k)fluoranthrene while the six-ringed PAHs were indeno(1,2,3-c,d)pyrene and dibenzo(a,h)anthracene (which were analysed as one compound in this study), and benzo(g,h,i)perylene.

In the marshy soil samples, the two to three-ringed PAHs was more predominant in Ugboroke sample location in the dry season with the least concentration recorded in same location in the rainy season; the four-ringed PAHs was more predominant in Ugboroke sample location in the dry season with the minimum concentration recorded in Ekpan location in the rainy season; the five-ringed was more predominant in Okotie location in the dry season while Ekpan and Ugboroke locations had the least value in the rainy season; the six-ringed PAHs had the maximum value in the control location while Ekpan had the least concentration in the rainy season.

In the marshy sediment samples, the two to three-ringed PAHs was more predominant in Okotie sample location in the dry season while Ogunu had the least concentration in the rainy season; the four-ringed PAHs was more predominant in Okotie sample location in the dry season with minimum concentrations in both Ogunu and Ugboroke locations in the rainy season; the five-ringed PAHs was more predominant in Ogunu location in the dry season with Ogunu and Ugboroke locations having the least concentrations in the rainy seasons

while the six-ringed PAHs was more predominant in the dry season in Ugboroke location with Ogunu location having the least concentrations in the rainy season.

REFERENCES

- [1] Flowers, L., Rieth, S.H., Cogliano, V.J., Foreman, G.L., Hertzler, R., Hofmann, E.L., Mirphy, D.L, Nesnow (2002) Health Assessment of Polycyclic Aromatic Hydrocarbon Mixtures: Current Practices and Future Direction. *Polycyclic Aromatic Compound*, **22(3-4)**: 811-821
- [2] Venkataraman, C. and Friedlander, S.K. (1994). Size Distribution of Polycyclic Aromatic Hydrocarbons and Elemental Carbon.2. Ambient Measurements and Effects of Atmospheric Process. *Environmental Science and Technology*. **28**: 563-572.
- [3] Barra, R., Popp, P., Quiroz, R., Bauer, C., Cid, H., Von Wolf, T. (2004) Persistent Toxic Substances in Soils and Waters Along an Altitudinal Gradient in the Laja River Basin, Central Southern Chile. *Chemosphere*. **58**: 905-915.
- [4] Hien, T.T., Thanh, L.T., Kameda, T., Takenaka, N., and Bandow, H. (2007). Distribution Characteristics of Polycyclic Aromatic Hydrocarbons with Particle Size in Urban Aerosols at the Roadside in Ho Chi City, Vietnam. *Atmospheric Environment*. **41**: 1575-1586,
- [5] Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., and Sylvestre, S., (2002). PAHs in the Fraser River Basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochemistry* **33**: 489–515.
- [6] Lima, A.L., Farrington, J.W., and Reddy, C.M., (2005). Combustion-derived polycyclic aromatic hydrocarbons in the environment – a review. *Environmental Forensics* **6**: 109–131.
- [7] Liang, Y., Tse, M.F., Young, L., and Wong, M.H. (2007). Distribution patterns of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong. *Water Research* **41**: 1303–1311.
- [8] Qi, S., Yan, J., Zhang, G., Fu, J., Sheng, G., Wang, Z., Tong, S.M., Tang, U.W., and Min, Y. (2001). Distribution of polycyclic aromatic hydrocarbons aerosols and dustfall in Macao. *Environmental Monitoring and Assessment* **72**: 115–127.
- [9] Zhou, J.L., Maskaoui, K., (2003). Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. *Environmental Pollution* **121**: 269–281.
- [10] Mielke, H.W., Wang, G., Gonzales, C.R., Le, B., Quach, V.N. and Mielke, P.W. (2001). PAH and metal mixtures in New Orleans soils and sediments. *The Science of the Total Environment*, **281**:217–227.
- [11] McCready, S., Slee, D.J., Birch, G.F., and Taylor, S., (2000). The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Marine Pollution Bulletin* **40**:999–1006.

- 422 [12] Manoli, E., Samara, C., Konstantinou, I., Albanis, T., (2000). Polycyclic aromatic
423 hydrocarbons in the bulk precipitation and surface waters of Northern Greece. *Chemosphere*
424 41: 1845–1855.
- 425 [13] Maliszewska-Kordybach, B. (1999) Sources, Concentrations, Fate and Effects of
426 Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment. Part A: PAHs in Air. *Polish*
427 *Journal of Environmental Studies*. 8(3): 131-136.
- 428 [14] Canadian Council of Ministers of the Environment (CCME) (2008), Canadian Soil
429 Quality Guidelines for the Protection of Environmental and Human Health: Benzo [a]
430 Pyrene. In: Canadian Environmental Quality Guidelines, Winnipeg, Canada. 235.
- 431 [15] World Health Organization (WHO) (2002), Health Risk of Persistent Organics Pollutants
432 from Long-Range Transboundary Air Pollution. European Centre for Environment and
433 Health. Bonn. 200
- 434 [16] Sehili, A.M. and Lammel, G. (2007). Global Fate and Distribution of Polycyclic
435 Aromatic Hydrocarbons Emitted from Europe and Russia. *Atmospheric Environment*. 41:
436 8301-8315.
- 437 [17] Hery, R.G. (2011) Polycyclic Aromatic Hydrocarbons. Cambridge Uni. Press.
438 Illustrated Edn., 412.
- 439 [18] Di Toro, D.M., McGrath, J.A. and Hansen, D.J. (2000) Technical Basis for Narcotic
440 Chemicals and Polycyclic Aromatic Hydrocarbon Criteria. I. Water and Tissue. *Environmental*
441 *Toxicological Chemistry*. **19**(8): 1951-1970.
- 442 [19] Burgess, R.M., (2009) Evaluating Ecological Risk to Invertebrate Receptors from PAHs
443 in Sediments at Hazardous Waste Sites. National Health and Environmental effects Research
444 Laboratory Atlantic Ecology Division Narragansett, RI 02882, 19.
- 445 [20] Barata, C., Calbet, A., Saiz, E., Ortiz, L., and Bayona, J.M. (2005). Predicting single and
446 mixture toxicity of petrogenic polycyclic aromatic hydrocarbons to the copepod *Oithona*
447 *davisae*. *Environ Toxicol Chem*, **24**:2992–2999
- 448 [21] Vane, C.H., Harrison, I., and Kim, A.W. (2007). Polycyclic aromatic hydrocarbons
449 (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, UK.
450 *Sci Total Environ*, **374**:112–126
- 451 [22] Olomukoro, J.O. and Egborge, A.B.M. (2004). Hydrobiological studies on Warri River
452 Nigeria Part II: Seasonal trend in physicochemical limnology. *Trop. Fresw. Biol.* **12**(1):9-23
- 453 [23] Ana, G.R.E.E, Sridhar, M.K.C and Emerole, G.O (2011). Contamination of Surface
454 waters by Polycyclic Aromatic Hydrocarbons in two Nigerian Coastal Communities. *Journal*
455 *of Environmental Health Research*, **11**(2): 77-85.

- 456 [24] Inengite, A.K., Oforka, N.C., Osuji, L.C. (2010). Evaluation of Polycyclic Aromatic
457 Hydrocarbons in Sediment of Kolo Creek in the Niger Delta. *International Journal of*
458 *Applied Environmental Sciences*. **5**(1): 127-143
- 459 [25] Botkin, B., Keller E., (2005). *Environmental Science-Earth as a Living Planet*. 5th
460 edition. U.S.A.: Wiley.
- 461 [26] Karlsson, K., and Viklander, M. (2008). Polycyclic aromatic hydrocarbons (PAH) in
462 water and sediment from gully pots. *Water, Air and Soil Pollution*, **188**(1-4), 271-282.
- 463 [27] World Health Organisation WHO Guidelines for Drinking water Quality. (2003).
464 Polynuclear Aromatic Hydrocarbons in Drinking-water.
- 465 [28] Brooks, M.K., (1997). Literature review, computer model and assessment of the
466 potential environmental risks associated with creosote treated wood products used in aquatic
467 environments; Aquatic environmental sciences, Port Townsend, WA 98368.
- 468 [29] Malawska, M., Ekonomiuk, A., Wilkomirski, B. (2006); Polycyclic aromatic
469 hydrocarbons in Peat Cores from Southern Poland: Distribution in Stratigraphic Profiles as an
470 indicator of PAH Sources. *Mires and Peat* 1: Art. 5. (Online: <http://www.mires-and-peat.net/pages/volumes/map01/map0105.php>)
471
- 472 [30] Agency for Toxic Substances and Disease Registry ATSDR (1999), Toxicological
473 Profile for Total Petroleum Hydrocarbons (TPH). U.S. Department of Health and Human
474 Services: Public Health Service.
- 475 [31] Irwin, R.J. (1997). Environmental Contaminants Encyclopedia, PAHs Entry. National
476 Park Service, Water Resources Division, Water Operations Branch, Colorado State
477 University