



Critical Analysis of Polycyclic Aromatic Hydrocarbons Ring Size Distribution in Marshy Soils and Sediments in Warri City and Its Environs, Southern Nigeria

I. E. Agbozu^{1*}, A. V. Bayowa² and O. E. Oghama¹

¹Department of Environmental Management and Toxicology, Federal University of Petroleum Resources Effurun, P.M.B. 1221, Effurun, Delta State, Nigeria.

²College of Agriculture and Environmental Science, University of South Africa, Pretoria, South Africa.

Authors' contributions

This work was carried out in collaboration between all authors. Author IEA designed and supervised the study and wrote the protocol. Author AVB carried out and managed the analyses of the study. Authors IEA and AVB managed the literature searches while author OEO performed the statistical analyses. Authors IEA and OEO wrote the first draft of the manuscript. All authors read and approved the final manuscript.

Article Information

DOI: 10.9734/BJAST/2017/32126

Editor(s):

(1) Klaas Metselaar, Department of Environmental Sciences, Wageningen University, Netherlands.

Reviewers:

(1) Ayona Jayadev, All Saints' College, Thiruvananthapuram, Kerala, India.

(2) Carmen Stavarache, Institute of Organic Chemistry, Bucharest, Romania.

(3) Mahmood M. Barbooti, University of Technology, Baghdad, Iraq.

(4) Imeh Joseph Okop, Akwa Ibom State University, Nigeria.

Complete Peer review History: <http://www.sciencedomain.org/review-history/18964>

Original Research Article

Received 9th February 2017

Accepted 28th April 2017

Published 8th May 2017

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

*Corresponding author: E-mail: iwekumo@yahoo.co.uk;

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 Ogonu 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 Ogonu 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.

Keywords: PAHs; sediments; benzo(a)pyrene; gas chromatography; flame ionization detector.

1. INTRODUCTION

Industrialization and urbanization have advanced socio-economic development. As a consequence, A myriad of environmental problems have become prevalent in urban areas, including contamination by polycyclic aromatic hydrocarbons (PAHs) via various pathways [1]. 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 generally result from the incomplete combustion of fossil fuels and burning of vegetation and other organic materials [5]. The derivatives from diagenesis of organic matter in anoxic sediments and crude oil seepage are also important PAHs' sources [6]. PAHs are ubiquitous environmental pollutants and are released into the environments via various routes. They have been largely detected in various environmental media, such as organism [7], atmosphere [8], water [9], soils [10] and sediments [11]. Being potentially hazardous, persistent and prevalent in the environment, efforts have been made to reduce their emission in many countries; for example, 16 of PAHs have been listed as priority control pollutants by USEPA (United States Environmental Protection Agency) [12].

PAHs are resistant to degradation over a long period in different environmental compartments [13,14]. However, studies have shown that transformation by microorganisms is the major neutralization process of PAHs [15,16]. Microbial degradation rates vary and generally reduce with increasing temperature, oxygen concentration, number of aromatic rings, and light intensity [14]. Also important in determining the fate and transport of PAHs are the characteristics of the soil environment particularly the soil organic matter (SOM) content, and the competence of

the soil microbial community needed to degrade these compounds.

PAHs have been an issue of public concern due to their demonstrated carcinogenic, mutagenic and toxicity properties [17-19]. The prevalent mechanism of PAHs toxicity to invertebrates is narcosis (additive), which results in the degradation of cell membrane [20]. This degradation can result in mild toxic effects or mortality depending upon the quantity and duration of exposure [21]. 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.

The properties of the individual PAHs depend on the number of hydrocarbon rings: PAHs are generally lipophilic, which means they have low solubility in water but highly solubility in fats and oils. Lipophilicity increases with increasing number of rings, i.e. the more rings are present, the more fat-soluble the substance is and the better it accumulates in the fatty tissue of organisms [22]. Also, with increasing number of rings, the water-solubility of the substance decreases. As a result, higher molecular weight (HML) PAHs are generally insoluble in water which limits their mobility in the environment, while some PAHs are soluble and known contaminants in drinking water [23]. Therefore, aqueous solubility of PAHs decreases with increasing molecular mass [24].

Two-ring PAHs, and to a lesser extent three-ring PAHs, are soluble in water, making them more available for biological uptake and degradation [25,24,26]. Furthermore, two- to four-ring PAHs volatilize adequately to appear in the atmosphere in gaseous form, although the physical state of four-ring PAHs can depend on

temperature [27,28]. In contrast, compounds with five or more rings have low solubility in water and low volatility; They are therefore predominantly in solid form, bound to particulate air pollution, soils, or sediments [29]. In solid form, these compounds are less accessible for biological uptake or degradation, increasing their persistence in the environment [24,29]. With increased environmental persistence, is increased toxicity with the most significant endpoint being cancer [30]. The low-molecular-weight PAHs (containing two or three rings) are acutely toxic while the high-molecular-weight PAHs (containing four or more rings) are largely considered as genotoxic [16]. Furthermore, low molecular weight PAHs (two- to four-rings) thrive as co-carcinogens during the promotional stage of cancer [31]; And because these PAHs are prevalent in the environment, they pose a significant risk to human health at the promotional phases of cancer. Higher molecular weight PAHs such as chrysenes, benzo(a)anthracene, dibenzo(a,h)anthracene, benzo(a)pyrene, benzo(b)fluoranthrene, benzo(k)fluoranthrene and indeno(1,2,3-cd)pyrene have been reported as potential human carcinogens by the International Agency for Research on Cancer (IARC) and the United State Environment Protection Agency (USEPA) [32].

Therefore, the persistence, stability, resistance toward biodegradation and carcinogenic index of PAHs generally increase as the number of aromatic rings increases, while volatility tends to decrease as molecular weight increases [33].

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 [34,35] 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 to determine the ring-size distribution of PAHs in soil and sediments in the city taking cognizance of the relationship between PAH ring-sizes and solubility or toxicity. As PAH ring-

size increases, the solubility decreases and toxicity increases. Higher molecular weight PAHs are hydrophobic and have less solubility in water hence they tend to settle in soil and sediments. In addition, this study is also necessary to provide PAHs 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.

2. MATERIALS AND METHODS

2.1 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 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 [36].

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

2.2 Sample Locations

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

2.2.1 Ekpan –NNPC complex area

This site is along the Ekpan bridge express, after the NNPC staff quarters. It is located between longitude 05°33'13.5"N and latitude 005°44'35.8"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.

2.2.2 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

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" |
| Ogonu (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" |

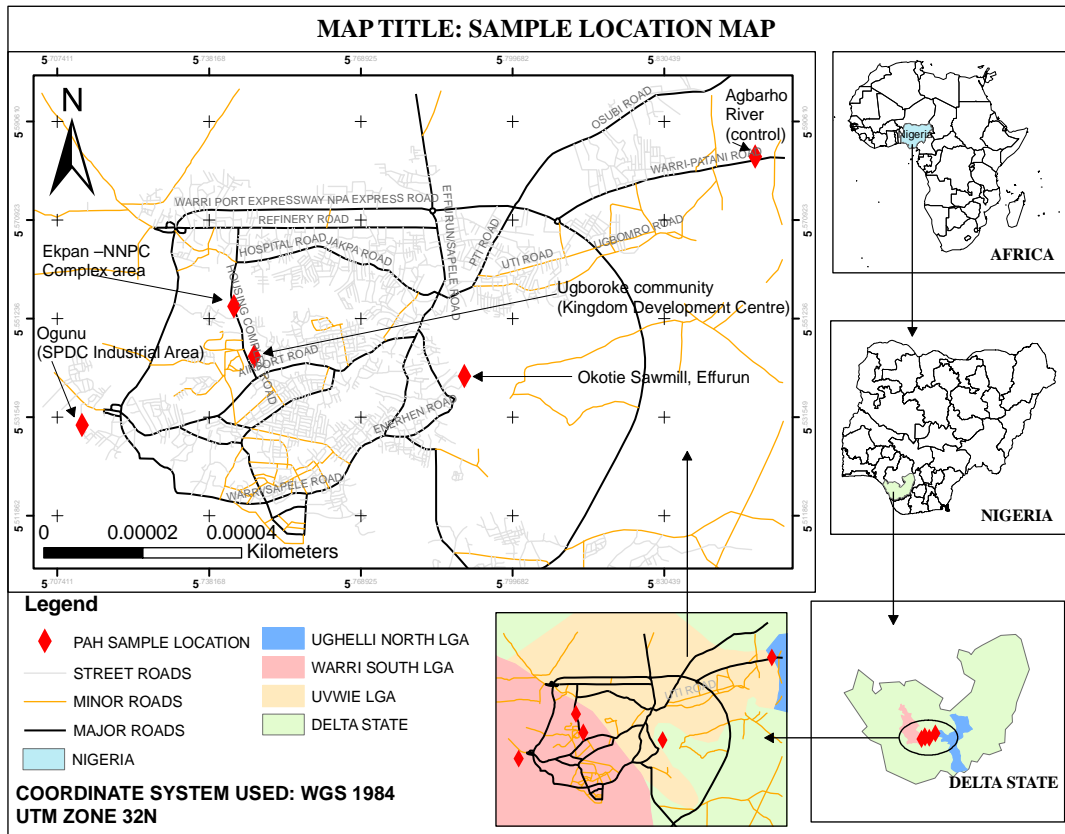


Fig. 1. GIS based map of study area

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 05°32'37.6"N and latitude 005°44'50.5"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.

2.2.3 Ogonu (SPDC industrial area)

This site is located between longitude 05°31'48.1"N and latitude 005°42'44.9"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, Ogonu 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 Ogonu 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.

2.2.4 Okotie Sawmill, Effurun

This site is located between longitude 05°32'23.3"N and latitude 005°47'24.0"E, in the outskirts 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, Effurun 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.

2.2.5 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.

2.3 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 (0-15 cm) and bottom (15-30 cm) 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. Extraction was done according to the standard reference method employed in PAH analysis, USEPA 8240. 10 g of sample was carefully weighed into a dried organic free and chromic acid pre-cleaned extraction bottle. 10 g of anhydrous Sodium Sulphate was then added and mixed with a glass rod. 20 ml of Hexane: Dichloromethane in the ratio 3:1 (90 ml of Hexane and 30ml of Dichloromethane were mixed and prepared in a standard flask) was added to the sample. The sample was then placed in an organic flask shaker at 500 osc/min for 30 mins. The extract was filtered. The sample was then left in the extraction bottle at laboratory room temperature to concentrate for a minimum of 24 hours until about 2 ml of concentrated sample was left in the extraction bottle. This was followed by fractionation in activated alumina (neutral) column to separate into aliphatic and aromatic fractions using n-Hexane and Dichloromethane respectively. The aromatic fraction was concentrated to approximately 1.0 ml using rotary evaporator. The aromatic extract was stored in a dried organic free and chromic acid pre-cleaned glass vials with Teflon rubber caps for analysis. It was refrigerated at -4°C until analysis. Analysis was carried out using Gas Chromatography (GC) with Flame Ionization Detector (FID). 1 µl of the concentrated sample



Plate 1. Ugboroke community showing the Swampy forest of Warri; Plate 2: Kingdom Development Centre Ugboroke; Plate 3: Ogonu River; Plate 4: Agbarho Cow Market

was injected by means of exmire micro syringe through rubber septum into the column. Separation occurs as the vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column by a Flame Ionisation Detector (FID). The column used was Rester, 30 m X 0.25 mm X 0.25 mm. Helium (14psi) was used as carrier gas. The column was kept at 45°C for 2 minutes. It was programmed to 280°C at the rate of 15°C/min. The column temperature was further programmed to a final hold at 300°C at the rate of 10°C/min. Temperature of the FID and T_{ij} were kept at 340°C. PAH quantification was carried out by CLARITY-GC interfaced software.

3. RESULTS AND DISCUSSION

3.1 Results

The results of analyses of the sediment and soil samples from the study area are as presented in Tables 2-5 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.

3.2 Discussion

3.2.1 Occurrence of individual PAHs for soils and sediments

Highest total concentration of individual PAHs within Warri was recorded for BaP - benzo(a)pyrene at 3.302 mg/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 2.138 mg/kg total concentration was detected there in the dry season soil samples. This is similar to the work done by Ana et al. [37] 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.

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 (Ogonu) | | ST 3 (Ugboroike) | | 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 |

Table 3. PAHs ring size distribution in Marshy soil samples in Warri city in mg/kg

| Ring size | ST 1 (Ekpan) | | ST 2 (Ogonu) | | ST 3 (Ugboroike) | | 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 |

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 (Ogonu) | | 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 |

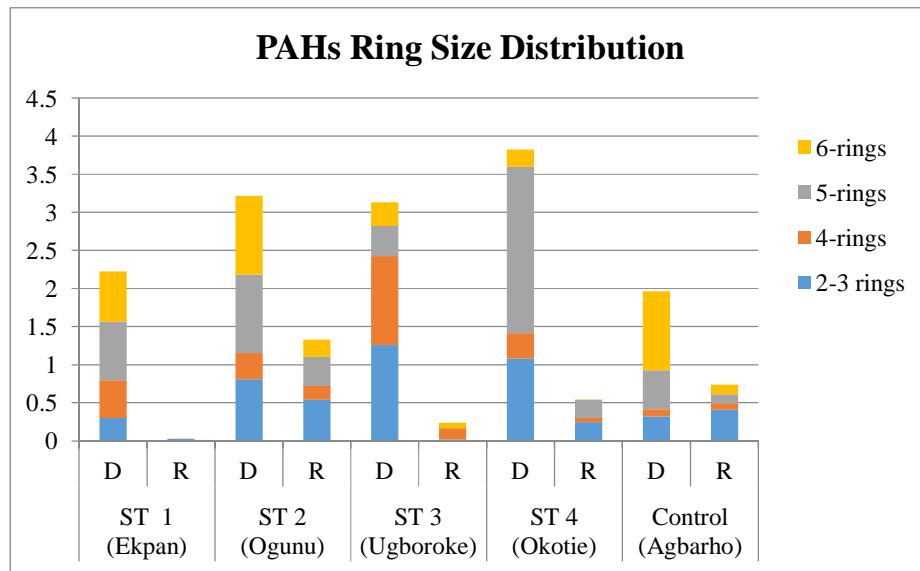


Fig. 2. The distribution pattern of 2–6-ring PAHs in Marshy Soil at the different sampling locations

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 |

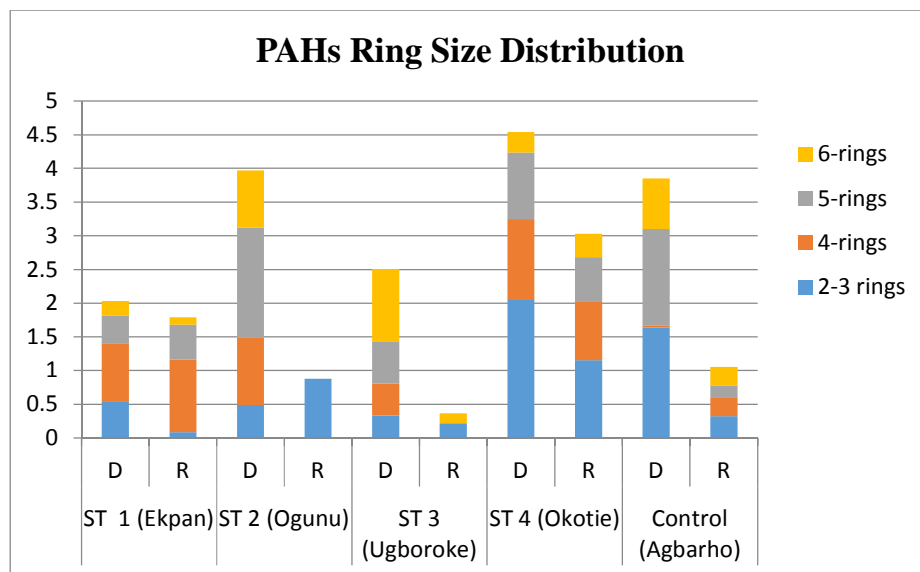


Fig. 3. The distribution pattern of 2–6-ring PAHs in Marshy Sediments at the different sampling locations

The PAH with lowest concentration in soil in Warri environs is acenaphthalene with a total concentration of 0.018 mg/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 1.039 mg/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. [38] 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, Acenaphthalene, 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&Bk F>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 and DbahA.

At the control point, highest total concentration of PAHs found in sediment was 1.092mg/kg and the mean was 0.364 mg/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. 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 3.302 mg/kg in the dry season while the lowest was Fluoranthrene with 0.074 mg/kg. In the rainy season, highest total concentration of individual PAH was recorded for benzo(b)fluoranthene and benzo(k)fluoranthene at 0.343 mg/kg while the lowest was Acenaphthene with 0.019 mg/kg.

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

3.2.2 Ring size analysis

3.2.2.1 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 [39]. 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 [40]. It has also been found that methylated form of certain organic compounds could be more harmful than the parent compound [40], 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 [39]. This is similar to an earlier work done by Inengite et al. [38]. 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 [38]. Their submission is corroborated by the work done by Karlsson and Viklander [41] 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 Ugboroke 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 predominant in Okotie sample location in the dry season while Ogonu had the least concentration in the rainy season.

3.2.2.2 Four -ringed PAHs

The most persistent four-ringed within Warri for both soil and sediment is pyrene. It occurred most in the dry season and more in the sediments than soil samples at Okotie Sawmill. Also, it was found in the dry season in both soil and sediment samples at every location except at Ugboroke where it was not found in the soil sample throughout the dry season though it was found once in early rainy season (June) at a value of 0.024 mg/kg. The highest mean value found for Pyrene was in sediments in dry season at Okotie sawmill, Warri and it was 0.171 mg/kg. The least persistent four-ringed is fluoranthene and it was found more in the rainy season. However, it was not found at all in Ugboroke, though all the other four-ringed – chrysene, pyrene and benz(a)anthracene were found with benz(a)anthracene occurring most. At the control point, Pyrene was also the most persistent four-ringed and a mean value of 0.062mg/kg was found in sediments samples in dry season and it was below detection limits in the rainy season [39].

The order of persistence of four-ringed PAHs within Warri for soil and sediment is:

Pyrene>Benz(a)anthracene>Chrysene>Fluoranthene; while the order outside Warri is Pyrene>Benz(a)anthracene>Fluoranthene>Chrysene.

In the marshy soil samples (Fig 2), 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 while in the marshy sediment samples (Fig 3), they were more predominant in Okotie sample location in the dry season with minimum concentrations in both Ogonu and Ugboroke locations in the rainy season.

3.2.2.3 Five-ringed PAHs

Five-ringed benzo(b)fluoranthene was the most persistent five-ringed and overall most persistent PAHs within Warri. It occurred most in Ekpan and it was more in the sediments at a mean value of 0.137 mg/kg in the dry season and 0.173mg/kg in rainy season, than soils sample which was 0.143 mg/kg in dry season. However, it was found below detection limits in soils samples at this location in the rainy season. Five-ringed benzo(a)pyrene was found only once in soil sample in the dry season at Ekpan, but a total of 2.138mg/kg and mean value 1.069 mg/kg was found in soil samples at Okotie sawmill in dry season. This was the highest value for single PAHs compound at a particular location in this study. At the control point, benzo(b)fluoranthene was also more persistent, despite this, benzo(a)pyrene had the highest total concentration of 0.779mg/kg and mean value of 0.259mg/kg for five-ringed in the dry season for sediment samples [39].

In the marshy soil samples (Fig. 2), 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 while in the marshy sediment samples (Fig. 3), they were more predominant in Ogonu location in the dry season with Ogonu and Ugboroke locations having the least concentrations in the rainy seasons.

3.2.2.4 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 1.110 mg/kg and mean value of 0.555 mg/kg in soils in the dry season. And only total of 0.010 mg/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 0.065 mg/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 1.092 mg/kg and mean value of 0.364 mg/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 [39].

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 1.067 mg/kg and mean value of 0.355 mg/kg in its sediments for BghiP, in the dry season. This is followed by a total value of 0.753 mg/kg and mean level of 0.251 mg/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 0.070 mg/kg and mean 0.023 mg/kg was found in Ugboroke soil. At the control point, BghiP was also the most persistent and had its highest total concentration of 1.039 mg/kg and mean 0.519 mg/kg in soil in dry season, but was present in low total concentration of approximately 0.202 mg/kg and mean 0.067 mg/kg in sediments [39].

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.

In summary, the composition pattern of PAHs by ring size in marshy soil in the study areas is shown in Fig. 2. As shown in Fig. 2, 5-ring PAHs are most abundant. 2-3 ring PAHs take second place followed by 6-ring PAHs and lastly 4-ring PAHs. In the study carried out by Li et al. [42],

the PAHs with 4–6 rings composed the majority of PAHs in soil samples while PAHs with 2–3 rings only accounted for 24% of the total PAHs on average. Furthermore, Vane et al. [43] observed that soils in Greater London, UK were dominated by 4–6 ring PAHs.

In the same vein, the composition pattern of PAHs by ring size in the marshy sediments in the study areas is shown in Fig. 3. As shown in Fig. 3, 2-3-ring PAHs are most abundant, which is similar to the study carried out by Wang et al. [44] who observed that 2-ring PAHs was the most dominant of the total PAH concentrations in the river plume sediment samples in Yangtze River Estuary, China. However, these results are inconsistent with some other observations [45,46]. 5-ring PAHs take second place followed by 4-ring PAHs and lastly 6-ring PAHs. This is dissimilar to the work done by Yan et al. [47] who observed 4-ring PAHs to be most abundant in the sediments of Daya Bay, South China.

3.2.3 Evaluation of the effects of PAHs on man

Although this study is majorly to 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 [48] 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 [49]. When man consumes these aquatic organisms as food, they become at risk to the negative effects of these harmful pollutants. According to WHO [48], 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 (3.634 mg/kg) in the study area was however

lower than the WHO critical level of 4 mg/kg; yet even 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 [50].

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 [51], 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 [52].

4. CONCLUSION

The ring size distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in marshy soils and sediment samples in Warri City, Southern Nigeria was 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 ring size distribution is as follows; 5-ring PAHs > 2-3 ring PAHs > 6-ring PAHs > 4-ring PAHs. Considering the dominance of 5-ring PAHs; High lipophilicity, low water solubility and low volatility PAHs are prevalent in the study area. As a result, they are predominantly in solid state, decreasing their mobility and increasing their persistence in the environment. They are also more toxic with increased carcinogenic, mutagenic and teratogenic potentials.

In the marshy sediment samples, the ring size distribution is as follows; 2 to 3-ring PAHs > 5-ring PAHs > 4-ring PAHs > 6-ring PAHs. The

dominance of 2 to 3-ring PAHs indicates that the PAHs found in the study area may have low lipophilicity, high water solubility and high volatility. As a consequence of their high volatility, they may readily appear in the atmosphere predominantly in gaseous form. Furthermore, being highly soluble in water, they are readily available for biological uptake and degradation. Hence, they are less toxic with decreased carcinogenic, mutagenic and teratogenic potential.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Flowers L, Rieth SH, Cogliano VJ, Foreman GL, Hertzler R, Hofmann EL, Mirphy DL, Nesnow. Health Assessment of Polycyclic Aromatic Hydrocarbon Mixtures: Current Practices and Future Direction. Polycyclic Aromatic Compound. 2002;22(3-4):811-821.
2. Venkataraman C, Friedlander SK. Size Distribution of Polycyclic Aromatic Hydrocarbons and Elemental Carbon.2. Ambient Measurements and Effects of Atmospheric Process. Environmental Science and Technology. 1994;28:563-572.
3. Barra R, Popp P, Quiroz R, Bauer C, Cid H, Von Wolf T. Persistent toxic substances in soils and waters along an altitudinal gradient in the Laja river basin, Central Southern Chile. Chemosphere. 2004;58:905-915.
4. Hien TT, Thanh LT, Kameda T, Takenaka N, Bandow H. Distribution characteristics of polycyclic aromatic hydrocarbons with particle size in urban aerosols at the roadside in Ho Chi City, Vietnam. Atmospheric Environment. 2007;41:1575-1586.
5. Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S. PAHs in the Fraser River Basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 2002;33:489-515.
6. Lima AL, Farrington JW, Reddy CM. Combustion-derived polycyclic aromatic hydrocarbons in the environment – a review. Environmental Forensics. 2005;6:109-131.

7. Liang Y, Tse MF, Young L, Wong MH. Distribution patterns of polycyclic aromatic hydrocarbons (PAHs) in the sediments and fish at Mai Po Marshes Nature Reserve, Hong Kong. *Water Research*. 2007;41: 1303–1311.
8. Qi S, Yan J, Zhang G, Fu J, Sheng G, Wang Z, Tong SM, Tang UW, Min Y. Distribution of polycyclic aromatic hydrocarbons aerosols and dustfall in Macao. *Environmental Monitoring and Assessment*. 2001;72:115–127.
9. Zhou JL, Maskaoui K. Distribution of polycyclic aromatic hydrocarbons in water and surface sediments from Daya Bay, China. *Environmental Pollution* 2003;121: 269–281.
10. Mielke HW, Wang G, Gonzales CR, Le B, Quach VN, Mielke PW. PAH and metal mixtures in New Orleans soils and sediments. *The Science of the Total Environment*. 2001;281:217–227.
11. McCready S, Slee DJ, Birch GF, Taylor S. The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Marine Pollution Bulletin*. 2000;40:999–1006.
12. Manoli E, Samara C, Konstantinou I, Albanis T. Polycyclic aromatic hydrocarbons in the bulk precipitation and surface waters of Northern Greece. *Chemosphere*. 2000;41:1845–1855.
13. Maliszewska-Kordybach B. Sources, concentrations, fate and effects of polycyclic aromatic hydrocarbons (PAHs) in the Environment. Part A: PAHs in Air. *Polish Journal of Environmental Studies*. 1999;8(3):131-136.
14. Canadian Council of Ministers of the Environment (CCME). Canadian soil quality guidelines for the protection of environmental and human health: Benzo [a] pyrene. In: *Canadian Environmental Quality Guidelines*, Winnipeg, Canada. 2008;235.
15. Ghosal D, Ghosh S, Dutta TK, Ahn Y. Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): A review. *Front. Microbiol*. 2016;7:1369.
DOI: ORG/10.3389/FMICB.2016.01369
16. Abdel-Shafy HI, Mansour MSM. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. *Egypt. J. Petrol*. 2016;25:107–123.
17. World Health Organization (WHO), Health risk of persistent organics pollutants from long-range transboundary air pollution. European Centre for Environment and Health. Bonn; 2002.
18. Sehili AM, Lammel G. Global fate and distribution of polycyclic aromatic hydrocarbons emitted from Europe and Russia. *Atmospheric Environment*. 2007;41:8301-8315.
19. Hervy RG. Polycyclic aromatic hydrocarbons. Cambridge Uni. Press. Illustrated Edn. 2011;412.
20. Di Toro DM, McGrath JA, Hansen DJ. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. water and tissue. *Environmental Toxicological Chemistry*. 2000;19(8):1951-1970.
21. Burgess RM. Evaluating ecological risk to invertebrate receptors from PAHs in sediments at hazardous waste sites. national health and environmental effects Research Laboratory Atlantic Ecology Division Narragansett, RI 02882. 2009;19.
22. German Federal Environment Agency (GFEA) (). Polycyclic aromatic hydrocarbons: Harmful to the environment! toxic! inevitable? German Federal Environment Agency, Press Office, Germany. 2012;4.
23. Feng X, Pisula W, Müllen K. Large polycyclic aromatic hydrocarbons: Synthesis and discotic organization. *Pure Appl. Chem*. 2009;81(12):2203–2224.
24. Johnsen AR, Wick LY, Harms H. Principles of microbial PAH-degradation in soil. *Environmental Pollution*. 2005;133(1):71–84.
25. Choi H, Harrison R, Komulainen H, Delgado Saborit J. Polycyclic aromatic hydrocarbons. WHO Guidelines for Indoor Air Quality: Selected pollutants. Geneva: World Health Organization; 2010.
26. Mackay D, Callcott D. Partitioning and physical chemical properties of PAHs. In A. Neilson (ed.). PAHs and related compounds. The handbook of environmental chemistry. Springer Berlin Heidelberg. 1998;325–345.
27. Atkinson R, Arey J. Atmospheric chemistry of gas-phase polycyclic aromatic hydrocarbons: formation of atmospheric mutagens. *Environmental Health Perspectives*. 1994;102:117–126.
28. Srogi K. Monitoring of environmental exposure to polycyclic aromatic

- hydrocarbons: A review. *Environmental Chemistry Letters*. 2007;5(4):169–195.
29. Haritash AK, Kaushik CP. Biodegradation aspects of polycyclic aromatic hydrocarbons (PAHs): A review. *Journal of Hazardous Materials*. 2009;169(1–3):1–15.
 30. Agency for Toxic Substances and Disease Registry (ATSDR). Polycyclic aromatic hydrocarbons (pahs): what health effects are associated with pah exposure? agency for toxic substances and disease registry, 4770 Buford Hwy NE, Atlanta, GA 30341; 2013.
 31. Ramesh A, Walker SA, Hood DB, Guillén MD, Schneider K, Weyand EH. Bioavailability and risk assessment of orally ingested polycyclic aromatic hydrocarbons. *International Journal of Toxicology*. 2004;23(5):301–333.
 32. UNEP. Evaluation of urban pollution of surficial and groundwater aquifers in Africa Project; 2002.
 33. Marston CP, Pereira C, Ferguson J, Fischer K, Hedstrom O, Dashwood WM, Baird WM. Effect of a complex environmental mixture from coal tar containing polycyclic aromatic hydrocarbons (PAH) on the tumor initiation, PAH-DNA binding and metabolic activation of carcinogenic PAH in mouse epidermis. *Carcinogenesis*. 2001;22:1077–1086.
 34. Barata C, Calbet A, Saiz E, Ortiz L, Bayona JM. Predicting single and mixture toxicity of petrogenic polycyclic aromatic hydrocarbons to the copepod *Oithona davisae*. *Environ Toxicol Chem*. 2005;24:2992–2999.
 35. Vane CH, Harrison I, Kim AW. Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in sediments from the Mersey Estuary, UK. *Sci Total Environ*. 2007;374:112–126.
 36. Olomukoro JO, Egborge ABM. Hydrobiological studies on Warri River Nigeria Part II: Seasonal trend in physicochemical limnology. *Trop. Fresw. Biol*. 2004;12(1):9-23.
 37. Ana GREE, Sridhar MKC, Emerole GO. Contamination of surface waters by polycyclic aromatic hydrocarbons in two nigerian coastal communities. *Journal of Environmental Health Research*. 2011;11(2):77-85.
 38. Inengite AK, Oforika NC, Osuji LC. Evaluation of polycyclic aromatic hydrocarbons in sediment of Kolo Creek in the Niger Delta. *International Journal of Applied Environmental Sciences*. 2010;5(1):127-143.
 39. Bayowa AV. Levels of polycyclic aromatic hydrocarbons (pahs) in marshy soils and sediments within Warri environs, Nigeria. Unpublished masters thesis, College of Agriculture and Environmental Science, University of South Africa, Pretoria; 2015.
 40. Botkin B, Keller E. *Environmental Science-Earth as a Living Planet*. 5th edition. USA.: Wiley; 2005.
 41. Karlsson K., Viklander M. Polycyclic aromatic hydrocarbons (PAH) in water and sediment from gully pots. *Water, Air and Soil Pollution*. 2008;188(1-4):271-282.
 42. Li J, Shang X, Zhao Z, Tanguaya RL, Dong Q, Huang C. Polycyclic aromatic hydrocarbons in water, sediment, soil, and plants of the Aojiang River waterway in Wenzhou, China. *J. Hazard. Mater*. 2010;173(1-3):75–81. DOI: 10.1016/j.jhazmat.2009.08.050.
 43. Vane CH, Kim AW, Beriro DJ, Cave MR, Knights K, Moss-Hayes V, Nathanail PC. Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) in urban soils of Greater London, UK. *Applied Geochemistry*. 2014;51:303–314.
 44. Wang Z, Liu M, Yang Y. Characterization and sources analysis of polycyclic aromatic hydrocarbons in surface sediments in the Yangtze River Estuary. *Environ Earth Sci*; 2014. DOI: 10.1007/s12665-014-3594-x
 45. Magi E, Bianco R, Ianni C, Di Carro M. Distribution of polycyclic aromatic hydrocarbons in the sediments of the Adriatic Sea. *Environmental Pollution*. 2002;119:91–98.
 46. Guo W, He M, Yang Z, Lin C, Quan X, Wang H. Distribution of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River watershed, China. *Chemosphere*. 2007a;68:93–104.
 47. Yan W, Chi J, Wang Z, Huang W, Zhang G. Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in sediments from Daya Bay, South China. *Environmental Pollution*. 2009;157:1823–1830.
 48. World Health Organisation WHO Guidelines for Drinking water Quality. Polynuclear Aromatic Hydrocarbons in Drinking-water; 2003.

49. Brooks MK. Literature review, computer model and assessment of the potential environmental risks associated with creosote treated wood products used in aquatic environments; Aquatic environmental sciences, Port Townsend, WA 98368; 1997.
50. Malawska M, Ekonomiuk A, Wilkomirski B. (); Polycyclic aromatic hydrocarbons in Peat Cores from Southern Poland: Distribution in Stratigraphic Profiles as an indicator of PAH Sources. Mires and Peat. 2006;1:5.
51. Agency for toxic substances and disease registry ATSDR, Toxicological Profile for Total Petroleum Hydrocarbons (TPH). U.S. Department of Health and Human Services: Public Health Service; 1999.
52. Irwin RJ. Environmental contaminants encyclopedia, PAHs entry. National Park Service, Water resources division, Water Operations Branch, Colorado State University; 1997.
- Available:<http://www.mires-and-peat.net/pages/volumes/map01/map0105.php>

© 2017 Agbozu et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
<http://sciencedomain.org/review-history/18964>