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paper text:

1 CRITICAL ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS RING 2 SIZE DISTRIBUTION

1 IN MARSHY SOILS AND SEDIMENTS IN WARRI CITY 3 AND ITS ENVIRONS, SOUTHERN

NIGERIA

4 I.E. AGBOZU1+, A.V. BAYOWA2, O.E. OGHAMA1 5 1Department of Environmental

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66Federal University of 6 Petroleum Resources Effurun, PMB 1221,

Effurun, Delta State, Nigeria

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South Africa

56Abstract 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

1samples were collected during dry and rainy seasons from four

locations within Warri and

a control location in Agbarho, 20km away. Levels of

7016 priority

PAHs listed in United States Environmental Protection Agency (USEPA)

were determined

using

64Gas 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

1PAHs 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. 25 Key Words: PAHs; Sediments; Benzo(a)pyrene; Gas

Chromatography; Flame Ionization 26 Detector 27 28

26INTRODUCTION 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, studies have shown that

transformation by microorganisms is the major neutralization process of PAHs [15; 16]. The

rates of microbial 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 [17-19]. The

33prevalent

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

16act 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

7properties of the individual PAHs depend on the number of

hydrocarbon rings: PAHs are generally lipophilic, which means they dissolve poorly in water

but well in fats and oils. This tendency increases with a growing 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, the

7more rings are present, the less water -

soluble the substance

is. As a result, higher molecular weight (HML)

2PAHs are generally

insoluble in water which limits their mobility in the environment,

while some PAHs

2are

soluble and known contaminants in drinking water

[22]. Therefore,

2aqueous solubility

of PAHs decreases as molecular mass increases [24]. Two-ring PAHs, and to a lesser extent

three-ring PAHs, dissolve in water, making them more available for biological uptake and

degradation[25; 24; 26]. Furthermore, 2two- to four-ring PAHs volatilize sufficiently to

appear in the atmosphere predominantly 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 state, bound to particulateair pollution, soils, or sediments[29]. In solid state, these

compounds are less accessible for biological uptake or degradation, increasing their

persistence in the environment [24; 29].With increased 77 environmental persistence, is

increased toxicity with the most significant endpoint being 78 cancer [30]. The 5low-molecular-

weight PAHs (containing two or three aromatic rings) are 79 acutely toxic while the high-

molecular-weight PAHs (containing four or more rings) are 80 largely considered as

genotoxic [16]. Furthermore, low molecular weightPAHs (two- to four- 81 ring PAHs) 2are

more potent as co-carcinogens during the promotional stage of cancer [31]; 82 and because

these 2PAHs are prevalent in the environment, they pose a significant risk to 83 human health

at the promotional phases of cancer.72Higher molecular weight PAHs such as 84 chrysene,

benzo(a) anthracene, dibenzo (a,h) anthracene, 8benzo(a)pyrene, 85 benzo(b)

fluoroanthrene, benzo(k) fluoroanthrene and indeno(1,2,3-cd)pyrene have been 86 reported as

potential 68 human carcinogens by the International Agency for Research on Cancer 87

(IARC) and the United State Environment Protection Agency (USEPA) [32]. 88 Therefore, the

stability, persistence, 5 resistance toward biodegradation and carcinogenic index 89 of PAHs

generally increase with an increase in the number of aromatic rings, 5 while volatility 90 tends

to decrease with increasing molecular weight [33] Warri 11 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 1 levels of PAHs in soils and sediments of the

city must be quantified to evaluate their ecological impacts. 11 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, 11 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 71 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. 1 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. 106

4 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

natural vegetation is a rainforest with swamp forest in some areas. The forest is rich in

timber 117 trees, palm trees, as well as fruit trees.¹ 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.¹ 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]. MAP TITLE: SAMPLE LOCATION MAP B I

R 5.590610 O S U Agbarho River I(RcOoAnDtrol) 5.590610 WARRI-PATAN Nigeria E F F U 5.570923

WARRI PORT EXPRESSWAY NPA EXPRESS ROAD R

HOSRPEITFAINLERROYARDOJAADKPHAUSROAD A D U ROAD I R O UGN/BSOMRO Ekpan –

NNPC T A 5.570923 I P N P E Complex area G UTI ROAD L AFRICA C E O M 5.551236 P UgboroOake
 community R L E Ogunu X (KingdoDm Development Centre) AIRPORT ROAD R O 5.551236 (SPDC
 Industrial Area) A D R O A D Okotie Sawmill, Effurun 5.531549 E N ERHEN 5.531549 WARRI/SAPEL E
 ROAD 5.511862 O 0.00002 0.00004 5.511862 NIGERIA Kilometers 5.707411 5.738168 5.768925
 5.799682 5.830439 A D O 5.707411 5.738168 5.768925 5.799682 5.830439 Legend PAH SAMPLE
 LOCATION UGHELLI NORTH LGA STREET ROADS WARRI SOUTH LGA MINOR ROADS UVWIE LGA
 MAJOR ROADS DELTA STATE NIGERIA COORDINATE SYSTEM USED: WGS 1984 UTM ZONE 32N
 UTI ROAD DELTA STATE

Fig. 1: GIS based Map of Study Area The coordinates of the

locations of the sample in the study area are as shown in Table 1 below: 128 Table 1:

Showing Sample Locations and their GPS Coordinates Sampling Location Coordinates

Northings Eastings 1Ekpan – NNPC Complex Area 05° 33'13. 5" 005° 44'35. 8"

1Ugboroke community (Kingdom Development Centre) 05° 32'37. 6" 005° 44' 50.5"

1Ogunu (SPDC Industrial Area) 05° 31'48. 1" 005° 42'44. 9" 1Okotie Sawmill, Effurun 05°

32'23. 3" 005° 47'24. 0" Agbarho River (Control) 05° 35'01.1" 005° 50'56.0" Sample Locations

Five (5) 1areas were strategically chosen, four within Warri and one outside Warri; the one

outside Warri was chosen as the control. 132 1. Ekpan –NNPC Complex area 1This 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. 1There 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. 139 2. Ugboroke

community (Kingdom Development Centre)¹This 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 ¹community is a densely

populated area, made up of local indigenous people as well as others that have come to live

within the community. One thing peculiar to this location is that, there are clusters of old,

native houses, modern/semi-modern residential houses, small and medium scale

businesses, factories, and companies, agricultural activities (poultry, fishing amongst

others). The ¹sampling 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. ¹This

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. 153 3. Ogonu (SPDC Industrial Area)

This site is located between longitude 05°31'48.1"N and latitude 005°42'44.9"E, ¹outside 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. 162 4. Okotie Sawmill,

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

1the 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. 172

5. Agbarho River (Control)1Agbarho Community is a town outside Warri; it is1along 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. 1Just 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.

177 178 179 1 2 3 4 Plate

11: 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

1 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

80 taken to the laboratory for

analysis. Extraction was done according to

the

1 standard reference method employed in

PAH analysis, USEPA 8240. 10g of sample was carefully weighed into a dried organic free

and chromic acid pre-cleaned extraction bottle. 10g of anhydrous Sodium Sulphate was then

added and mixed with a glass rod. 20ml of Hexane: Dichloromethane in the ratio 3:1 (90ml 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 500osc/min for 30mins. The extract was filtered. The sample was then left in the extraction bottle at laboratory room temperature to concentrate for a minimum of 24hours until about 2ml 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 1.0ml 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). 11µl of the concentrated sample 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 58m 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 30was 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

Tijwere kept at 340°C.

1PAH

quantification was carried out by CLARITY-GC interfaced software.

219

1RESULTS AND

DISCUSSION 220 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

1results 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.

228 Table 2: PAHs Concentrations in

Marshy Soil Samples in Warri City in mg/kg PAHs No. Ring Sampling Stations

52(ST) ST 1 (Ekpan)

ST 2 (Ogunu) ST 3 (Ugboro) ST 4 (Okotie) Control (Agbar ho)

49D 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

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 20Indeno(1,2,3-cd)pyrene & 6dibenzo(a,h)anthracene 6 0 0

1.11 0. 01 0 0 0 0.

011 0 0

6Benzo(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 57ST 1 (Ekpan) ST 2

(Ogunu) ST 3 (Ugboroke) ST 4 (Okotie) Control (Agbarho) D R 34DRDRDRDR 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 0.127 231 PAHs Ring Size Distribution 4.5 4 6-rings 3.5 3 5-
 rings 2.5 4-rings 2 2-3 rings 1.5 1 0.5 0 42DRDRDRDRDR ST 1 ST 2 ST 3 ST 4 Control 232

(Ekpan) (Ogunu) (Ugboroke) (Okotie) (Agbarho) Fig 2: The 31distribution pattern of 2–6-ring

PAHs in Marshy Soil at different sampling locations Table 4: PAHs Concentrations in Marshy

Sediment Samples in Warri City in mg/kg PAHs No. Ring Sampling Stations 52(ST) ST 1 (Ekpan)

ST 2 (Ogunu) ST 3 (Ugboro ke) ST 4 (Okotie) Control (Agbarho) 49DRDRDRDRDR

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 0.021 6 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

78Benzo(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 20Indeno(1,2,3-

cd)pyrene & 6dibenzo(a,h)anthracene 6 0 0 0.196 0 0.267 0 0.334 0 1.092 0

6Benzo(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 57ST 1 (Ekpan) ST 2

(Ogunu) ST 3 (Ugboroke) ST 4 (Okotie) Control (Agbarho) D R 34D 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 PAHs Ring Size Distribution 5 4.5 4 3.5 3 2.5

2 1.5 1 0.5 0 6-rings 5-rings 4-rings 2-3 rings 42D R D R D R D R D R ST 1 (Ekpan)ST 2 (Ogunu)

ST 3 ST 4 (Okotie) Control 242 (Ugboroke) (Agbarho) 243 31Fig 3: The distribution pattern of 2-

6-ring PAHs in Marshy Sediments at different 244 sampling locations 245 Discussion

Occurrence of 1individual PAHs for Soils and Sediments Highest total concentration of

individualPAHs within Warri was recorded for BaP - benzo(a)pyrene at 3.302mg/kg in soil

samples. The highest contributor to the bulk was at Okotie Sawmill; this location is the one

characterised with the presence of several industrial activities and about 2.138mg/kg total

concentration was detected there in the dry season soil samples. This is similar to the work

done by Ana et al.[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. The PAH

with lowest concentration in soil in Warri environs is acenaphthalene with a total

concentration of 0.018mg/kg found in the rainy season. The order for lower PAHs in soils in

Warri environs is can<Ind&DbahA<Acp<Chry. At the control point, PAHs with highest

concentration in soil sample was BghiP; it had a total concentration of 1.166mg/kg with the

larger amount of 1.039mg/kg detected in the dry season. It is important to note that the

control point location has cattle grazing ground, an abattoir and meat market. Therefore, the

high concentration of BghiP here could be attributed to the microbial production of the PAH

due to microbial activities in the abattoir area. This is similar to the study done by Inengite et

al.[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, Acenapthalene, and 1-Methyl Naph; and those detected only in rainy

season are BaP and Fluoranthene. For sediment samples within Warri environs, PAHs with

highest concentration is BaP - benzo(a) Pyrene with a total concentration of 2.803mg/kg and

the larger amount of 2.381 mg/kg being found in the dry season. The decreasing order for

total PAHs in sediment sample for dry and rainy season is:

BaP>BgHiP>Ant>Naph>BaA>Pyr>Chyr>BbF&BkF>BaA>Pyr>Naph. The lowest concentration

for PAHs in sediments was recorded for acenaphtylene – 0.012mg/kg in rainy season and for

total PAHs in dry and rainy season of 0.070mg /kg for acenaphthalene. Some PAHs that were

below detection level in the rainy season are: naphthalene, 2 methyl naphthalene and Ind

&DbahA. At the control point, highest total concentration of PAHs found in sediment was

1.092mg/kg and the mean was 0.364mg/kg for Indeno(1,2,3-

cd)Pyrene&Dibenz(a,h)Anthracene; all this amount was found only in the dry season as the

rainy season record was below detection level. The decreasing order for PAHs in sediments

here is: Ind&DbahA>BaP>Phe. The PAHs with lowest concentration was fluorene, followed

by 1methyl naphthalene, naphthalene and phenanthrene. 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

Acenaphtylene were below detection level in the rainy season.

For Soil samples, the

1 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 1for 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 1Two 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 11 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 [39]. 1It has also been

found that methylated form of certain organic compounds could be more harmful than the

parent compound [39], 1hence, 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. [38]. 1Higher 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]. 1Their submission is corroborated by the

work done by Karlsson and Viklander [40] 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 1same location in the rainy season while in

the marshy sediment samples (Fig 3), they were more predominant in Okotie sample location in

74the dry season while Ogunu had the least concentration in the rainy season.1Four -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 0.024mg/kg. The

highest mean value found for Pyrene was in sediments in dry season at Okotie sawmill,

Warri and it was 0.171mg/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. 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.

12 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

1 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 Ogunu and Ugboroke locations in the rainy season.

1Five-

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 0.137mg/kg in the dry season and 0.173mg/kg in rainy season,

than soils sample which was 0.143mg/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 1.069mg/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.

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 Ogunu location in the dry season with Ogunu and Ugboroke locations having the least concentrations in the rainy seasons.

1 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 Ogunu, 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 13 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 Ogunu in the dry

season. BghiP was absent in Ogunu 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 Ogunu location having the least concentrations in the rainy season. In summary, the

3 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. [41], the

37PAHs 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. [42] observed that soils in Greater London, UK were

81dominated by 4–6

ring PAHs. In the

same vein, the

67composition pattern of PAHs by ring size in the

marshy sediments in the

study areas

3is shown in Fig. 3. As shown in Fig. 3, 2-3 -ring

PAHs are most abundant, which is65similar to the study carried out by Wang et al. [43] who

observed that

2-ring PAHs was the most dominant of the total

59PAH concentrations in the

river plume sediment samples in Yangtze River Estuary,

China. However, these results are

inconsistent with some other observations [44; 45]. 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. [46] who observed 4-ring PAHs to be most abundant in the sediments of Daya Bay, South China. 409

1Evaluation of the

Effects of PAHs on Man Although this study is majorly to determine

the analyse the ring size

distribution of

1PAHs 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,

1most 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 [47]. 1for soils and sediments. PAHs in aquatic environment have been found to be

capable of attaching or bioconcentrating in 14 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 [48]. When man

consumes these aquatic organisms as food, they become at risk to the negative effects of

these harmful pollutants. According to WHO [47], 1man 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 [49]. 1When 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 [50], 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

[51]. 435 CONCLUSION The ring size distribution of

1Polycyclic 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

1naphthalene, 2-methyl

naphthalene and 1-methyl naphthalene while the three -ringed PAHs

were acenaphthylene,

acenaphthene, fluorine, anthracene and phenanthrene. The four

77-tinged PAHs were

fluoranthene, chrysene, pyrene and benzo(a)anthracene. The

five-tinged PAHs were

73benzo(a)pyrene, benzo(b)fluoranthene and benzo(k)

fluoranthene while the

1six-

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 79benzo(g,h,i)perylene. In the marshy soil

samples, the ring size distribution is as follows; 5-ring

3PAHs > 2-3 ring PAHs > 6 -ring PAHs > 4 -

ring PAHs.

Considering the dominance of 5-ring PAHs;high lipophilicity,

76low water

solubility and low volatility PAHs are prevalent in the

study area. As a result,

54they are

predominantly in solid state,

decreasing their mobility and

54increasing 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

69-6 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 15

are readily available for biological uptake and degradation. Hence, they are less toxic with

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