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Seasonal variation of PAHs in marshy sediments from Warri City, Nigeria

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ABSTRACT

Seasonal variation was used to analyse the levels of Polycyclic Aromatic Hydrocarbons (PAHs) in marshy sediments in Warri city, Niger Delta region in Southern Nigeria. Sediment samples were collected from four locations in the city and labelled ST 1, ST 2, ST 3 and ST 4. Control samples were also collected 20 km away from the city and labelled ST 5. The objective of this study is to compare the level of PAHs in dry and rainy season and examine their variation base on the type of PAHs detected in relation to the characteristics of the different locations. The samples were collected from January to March for dry season and June to August for rainy/wet season. Levels of 16 USEPA priority PAHs were determined using GC-FID. Five-ringed benzo(a) pyrene had highest total concentration of 1.342 mg/kg for individual PAHs and it was detected at ST 2 in the dry season. PAHs concentration was higher in dry season than rainy season at all the study sampling stations and the control. ST 4 of the study location had total PAH value of 4.540 mg/kg in dry season. And the control station, ST 5 had total PAH value of 4.18 mg/kg in the same period. In the rainy season, ST 4 had highest total PAH value of 3.029 mg/kg. At ST 5, the highest total value for PAH in rainy season was 1.056 mg/kg. Total PAHs concentration within Warri city was higher than at the control.

Keywords: Benzo(a) pyrene; concentration; dry season; Niger Delta; rainy season.

INTRODUCTION

Our environment is a large sink that takes in all we give in and gives them back to us in another form which could be beneficial or harmful. The reactions that are responsible for these transformations could be physical, chemical, biological or integration of any or all of these (Botkin and Keller, 2005). Several exchanges or reactions go on all the time from as simple as flow of one river to the other or ponds to lakes to the complex decomposition processes of dead organisms. The environment naturally has a way of cycling substances around it in such a way that every part is affected directly or indirectly by the consequence of the usage of another (Botkin and Keller, 2005). The characteristics of the environmental media in which the substance is being expressed greatly determine it behaviour. If the substance being cycled is a contaminant, other parts of the environment could also be affected. These effects could reduce or increase due to the presence or absence of other substances or factors (Obayori and Salam, 2010). Sediment is an

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environmental medium with the possibility of being an integral basin of the air, soil and water media. This is explained by the inter-relationship that exists amongst every living part (flora and fauna) of the physical environment and the chemical reactions constantly going on around them. There is usually no disparity among the different type of media and soil pollutants are usually found as a result of fallout from the air or carried by water into soil and could be deposited at the bottom or river banks as sediments. Sediment is a complex aqueous formation usually at the bottom part of an aquatic environment containing substrates and other compounds that characterise the type of activities in the surrounding aquatic or terrestrial environment in which the sediment is found. Polycyclic aromatic hydrocarbons (PAHs) which are one of the many compounds that could concentrate in sediments have been found to reflect the history of fossil fuel combustion in the environment (Ekonomiuk et al., 2006). PAHs are neutral nonpolar compounds with at least two aromatic rings and carbon and hydrogen atoms only (Kouakou et al., 2015). There are several known PAHs and related compounds and the fused rings are the ones responsible for their aromatic behaviour and their classification as lower molecular weight or higher molecular weight compounds (World Health Organisation (WHO), 2003). Higher molecular weight PAHs which are hydrophobic compounds tend to settle in sediments and may be dissolved in any oily contaminant found there or attached to substrates, be degraded by microbes or bio concentrate in aquatic organisms (Nikolaou et al., 2009). Different studies done by Xiao Jun et al. (2006) and corroborated by Agbozu and Opuene (2008) affirm that a measure of PAHs in soils and sediments could give an indication of the extent of the pollutant in the environment. However, PAHs are ubiquitous and therefore present in the atmosphere, water column, biota, as well as sediment and soil (Kouakou et al., 2015).

Furthermore, studies done by a parliament set up by the European Union (EU) revealed that, though natural events cannot be controlled, yet they have notable local impact and are important contributor to understanding the background of PAHs sources (EU, 2003). Atmospheric conditions are natural every day event and they vary in different geographical location. The southern part of Nigeria and specifically the Niger Delta area where this study was conducted has majorly two atmospheric weather season – dry season and rainy/wet season. The dry season usually runs from December to March while the rainy season is from April to November (Egborge and Olomukoro, 2004). Dry season is the period of the year characterised by high temperature, low humidity and little or no rainfall. There is also harmattan in this period which is characterised by early morning dry windy but cold weather and characteristic hot sunny afternoons (Egborge and Olomukoro, 2004). The rainy season is the period of the year when it rains regularly and almost every day. In this season, there is also a period of high rainfall and that of low rainfall, humidity is high and there is little sunshine (Egborge and Olomukoro, 2004). However, different part of the country experience varying amount of the atmospheric weather condition every year. The Niger Delta area is characterised by a longer period of rainy season and a short period of dry season (Egborge and Olomukoro, 2004). This study is set out to compare how rainy and dry season could impact on PAHs distribution in the study location and the control.

In the early 1950s, crude oil was discovered in the Niger Delta and this increased the influx of people into the area. There are quite a number of petroleum exploration and production investors, crude oil refining, and related activities with subsequent establishment of many industries in the area. This led to urbanisation, and as it is in many industrialised cities the unavoidable menace- environmental pollution. Polycyclic Aromatic Hydrocarbons (PAHs) is one of the several pollutants released into the environment during crude oil exploring and production activities by sources termed as petrogenic (Teaf, 2008). However, studies have revealed that there are also natural sources of PAHs (Delgado, 2000). Other sources of PAHs are from pyrolytic activities involving industrial and commercial burning of fuel or hydrocarbons in oil, certain cooking practices such as broiling of food over charcoal frying and smoking (Teaf, 2008). PAHs from pyrolytic sources are produced due to incomplete combustion and have been shown to be a major source of PAHs intake by humans (European Food Safety Authority - EFSA, 2008). Several other studies also revealed that PAHs have carcinogenic, mutagenic and teratogenicity tendencies on human following exposure through ingestion, inhalation or skin contact (Public Health England (PHE), 2008; Padmini et al., 2009). The people of Warri (this study location) feed largely on fish and most other aquatic organisms obviously due to their proximity to the river. They trade on the rest and most times distribute to neighbouring cities and possibly across the world. They are therefore prone to likely exposure from PAHs pollutants and hence a need for various studies on this topic. This study was undertaken to compare the level of PAHs in dry and rainy season in the study location and control. In a view to examine the variations of the different types detected in the two atmospheric seasons and establish a relationship base on the characteristics of the different locations from which the samples were collected. The results will no doubt increase understanding of behaviour of PAHs and serve as valuable literature for future research.

MATERIALS AND METHODS

Description of study location

Warri also known as 'Oil City' is a small commercial city in Delta state southern Nigeria in the oil rich Niger Delta region. It is located at an elevation of about 1meter above sea level and the coordinate is as indicated: 5°31′N 5°45′E5.517°N 5.75°E. Warri is one of the wettest locations in the region with rainfall of about eight to ten months which runs majorly from May to October. The dry season only last for about three to four month in November to March (Egborge and Olomukoro, 2004). This season is significantly marked by the cool "harmattan" dusty haze from the north-east winds. However, it rains frequently in the dry season. The area is characterized by tropical equatorial climate with mean annual temperature of 32.8 °C and annual rainfall amount of 2673.8 mm. Some recent data has also shown high temperatures of 36 °C and 37 °C (Egborge and Olomukoro, 2004).

The land area in Warri and its environs are majorly marshy. There is usually a need to sand fill or compost the land before erecting most structures especially a building. Warri River which is one of the most important coastal rivers of the Niger Delta is distributed in various tributaries around the city and beyond. This together with high level of rainfall is belief to be responsible for the marshy soil and swamp that characterise the city (Egborge and Olomukoro, 2004).

Sampling sites

Five areas were strategically chosen, four within Warri and one outside Warri-Agbarho. The one outside Warri was chosen to serve the control.

1. Ekpan –NNPC Complex area Co-ordinates: 05º 33′ 13.5sN 005º 44′ 35.8sE
2. Ogunu (SPDC Industrial Area) 05º 31′ 48.1sN 005º 42′ 44.9sE
3. Ugboroke community (Kingdom Development Centre) 05º 32′ 37.6sN 005º 44′ 50.5sE
4. Okotie Sawmill, Effunrun 05º 32′ 23.3sN 005º 47′ 24.0sE
5. Agbarho river (control) 05º 35′ 01.1sN 005º 50′ 56.0sE

The sample location map is shown in Figure 1.

Sampling

Sediment samples from the five sampling points were collected every month 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 grab sampler when the river was full into an aluminium foil. Top (0-15 cm) and bottom (15-30 cm) samples were collected at each point to form one composite sample. A total of five sediment samples for each month in the dry season (January-March) and in the wet season (June-August) were collected.

The samples were wrapped in aluminium foil and properly preserved by cooling in a refrigerator at 4 ºc pending further treatment in the laboratory.

Sample treatment

The standard reference method employed in the PAH analysis is USEPA 8240. 10 g of sample was carefully weighed into a dried organic free and chromic acid pre-cleaned extraction bottle and 10 g of anhydrous Sodium Sulphate was added and mixed with a glass rod. Thereafter, 20 ml of Hexane:Dichloromethane in the ratio 3:1 (90 ml of Hexane and 30 ml 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 oscillations per minute for 30 minutes and 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 and the extract, stored in a dried organic free and chromic acid pre-cleaned glass vials with Teflon rubber caps for analysis. It was then refrigerated at 4 ºC after treatment until analysis.

Sample analysis

Analysis was done using Gas Chromatography (GC). 1µl 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. PAH quantification was carried out by CLARITY-GC interfaced software.

RESULTS AND DISCUSSION

The results of analysis of the sediment samples from the study area and control for dry (D) and rainy/wet (R) seasons of sampling are as presented in Table 1. The four sampling stations within Warri City are represented as ST 1- ST 4 (ST 1-Ekpan NNPC complex area, ST 2 – Ogunu SPDC Industrial area, ST 3 Ugboroke Kingdom Development area and ST 4 Okotie Sawmill). The control station Agbarho is represented as ST 5. 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 or mg/kg. The minimum detection limit is 1 x 10^{-3} mg/kg. The result was analysed for individual PAHs based on the table values (Tables 1 and 2). The PAHs analysed in this study are: Naphthalene(Naph.), 2-methyl naphthalene, 1-methyl naphthalene, Acenaphtylene(Acp) Acenaphthene(Acn), Fluorene(Fluo), Phenathrene(Phe), Antracene(Ant.), Pyrene(Pyr), Chrysene(Chr),), Fluoranthene(Fluoran), Benzo(a)anthracene(B(a)A), Benzo(b)fluoranthene(B(b)F), Benzo(k)fluoranthene(B(k)F, Benzo(a)Pyrene(B(a)P), Dibenzo(a,h)Anthracene(Db(ah)A and Indeno(1,2,3-cd)Pyrene(Ind). The mean level of the total PAHs at each location of the study and control was analysed in a chart to show their distribution at the different locations in dry and rainy season. This is shown in Figure 2.

Critical Analysis based on number of PAH Rings

Two to three -ringed PAHs

In Warri city and at the control point, two and three ringed PAHs were predominant in the dry season. The two-ringed PAHs which are: naphthalene, 2-methyl naphthalene and 1-methyl naphthalene ranged from ≥0.001 mg/kg to ≤1.091 mg/kg in Warri city. 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 (Botkin and Keller, 2005). It has also been found that methylated form of certain organic compounds could be more harmful than the parent compound (Botkin and Keller, 2005), hence, the need to analyse methyl forms. At the study location in dry season, naphthalene had highest concentration of 1.091 mg/kg at ST 4 and 1-methyl naphthalene was lowest with a value of 0.001 mg/kg at ST 2. At the control point, two-ringed PAHs in the dry season ranged from <0.001 mg/kg to ≤0.421 mg/kg. During rainy season, two-ringed PAHs were mostly below detection limit at study location and ranged from ≥0.017 mg/kg to ≤0.210 mg/kg at control station. At the study location and control, it was observed that only the methylated form of naphthalene (1-methyl naphthalene and 2-methyl naphthalene) was detected in the samples in rainy season, though it was in minute quantity. The three-ringed PAHs analysed in this study are: acenaptylene, acenaphthlene, fluorene, phenanthrene and anthracene. In the dry season, there value ranged from <0.001 mg/kg to ≤0.338mg/kg at the study location. Anthracene and phenanthrene were the most persistent there. At the control point, values for three-ringed PAHs ranged from <0.001 to ≤0.577. Highest concentration for three-ringed PAHs at the study location was 0.338 mg/kg anthracene at ST 4 while at the control it was 0.577 mg/kg of phenanthrene. In the rainy season, three-ringed PAHs were also mostly below detection limit at the study location and control. However at study location, anthracene had a value of 0.751 mg/kg in the rainy season which was higher than the corresponding dry season value of 0.093 mg/kg. Phenanthrene was the only three ringed found at all locations including the control and it was predominant 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 a work done on Evaluation of PAHs in Sediment of Kolo Creek in Niger Delta Nigeria. In this work, higher ringed PAHs were detected more than the lower ringed PAHs in the rainy season and the authors attributed this to heavy rain. They resolved that the solubility of the PAHs in a medium is related to the number of rings (Inengite et al., 2010). Also, Karlsson and Viklander in an earlier work in 2008 back up this finding in which they reported that PAHs with more rings are less soluble and the fewer rings were more soluble and therefore could be below detection limit in the rainy season. These findings also agree with this study work in which the two to three rings were almost undetected in the rainy season. The methylated form of naphthalene (1-methyl naphthalene and 2-methyl naphthalene) which were analysed in this study however, gave an indication that the two-ringed PAHs could be present at the locations. Other works conducted on microbial action on PAHs revealed that, microbial degradation of PAHs is rapid for the lower molecular weight compounds such as naphthalene and phenanthrene by microbes in sediment (Obayori and Salaam, 2010). In addition, several studies have revealed that volatilisation and biodegradation are the major removal processes for lower molecular weight PAHs in aquatic environment (Neff et al., 2005; Obayori and Salaam, 2010).

Four -ringed PAHs

The four-ringed PAHs analysed in this study are: fluoranthene, chrysene, benzo(a)anthracene and pyrene. Their value ranged from <0.001 mg/kg to ≤0.572 mg/kg for dry season samples at the study location. Benzo(a)anthracene had highest concentration of 0.572 mg/kg at ST 4 in the season. This is followed by pyrene with a close value of 0.513 mg/kg. At the control station, values for four-ringed PAHs in the dry season ranged from <0.001 mg/kg to ≤0.186 mg/kg. Pyrene had highest value of 0.186 mg/kg followed by benzo(a)anthracene also with a close value of 0.180 mg/kg. The other four-ringed PAHs analysed were below detection limit at the control station in this season. In the rainy season, values for four-ringed PAHs at the study location ranged from <0.001 mg/kg to ≤0.617 mg/kg. Chrysene had highest concentration of 0.617 mg/kg at ST 1 and benzo(a)anthracene was 0.452 mg/kg at same station. At the control station, the rainy season values ranged from <0.001 mg/kg to ≤0.186 mg/kg. Chrysene had highest value of 0.186 mg/kg. This result reveals that the range of values for four-ringed PAHs in the rainy season was higher than that of the dry season. Four-ringed PAHs have been classified as semi-volatile compounds and could be said to possess characteristics in between the lower molecular weight and higher molecular weight PAHs (Neff et al., 2005). Their character however is mostly determined by those of the substrates to which they are attached and the medium (Neff et al., 2005). Some earlier studies found that the quantity of PAHs found in cold season could be more than those found in hot season (Environmental Forensics Case Study (EFCS), 2010). This could probably help explain why the range of values for four-ringed PAHs in the rainy season was higher compare to the dry season at the study location. Other works also revealed that chrysene and benzo(a)anthracene are susceptible to oxidation and photo degradation in light in aqueous environment (Obayori and Salaam, 2010). This could help explain why the value for chrysene and benzo(a)anthracene was higher in the rainy season than dry season at most locations except where it was below detection limit. At the control station, a similar variation was observed for chrysene and fluoranthene. This could be related to the characteristic reduced sunlight in the study region (Niger Delta) in rainy season (that could have act to break down the PAHs by photo degradation) and thereby increasing PAHs availability in the sediment samples in the season. Other works conducted on microbial action has shown that chrysene strongly oppose biodegradation by microbes in sediment (Obayori and Salaam, 2010). As a result of this, their availability in the sediment samples could be readily detected. This observation is worthy of note, as earlier studies has found that PAHs with four rings and above are less acutely toxic but more carcinogenic and teratogenic (Obayori and Salaam, 2010).

Five to six-ringed PAHs

Five to six-ringed PAHs and above are classified as the higher molecular weight fractions. The ones analysed in this study includes: benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3)cd pyrene and benzo(g,h,i)perylene. They are the five to six ringed PAHs. Their values ranged from <0.001 mg/kg to ≤1.342 mg/kg in the dry season. Five-ringed benzo(a)pyrene had highest value of 1.342 mg/kg, followed by benzo(g,h,i)perylene with a value of 1.067 mg/kg at ST 3. The quantity detected for benzo(a)pyrene is the highest concentration for individual PAHs detected during this study in dry and rainy season. It is important to note that benzo(a)pyrene was below detection limit in rainy season at ST 2 where it highest concentration was detected in dry season. Indeno(1,2,3)cd pyrene was detected at all the stations in the study area except ST 1 in dry season. Also, six-ringed benzo(g,h,i)perylene was detected at all the sampling stations in the study area in dry season. At the control station, dry season values ranged from ≥0.104 mg/kg to ≤1.092 mg/kg. Indeno(1,2,3)cd pyrene and dibenzo(a,h)anthracene had highest concentration of 1.092 mg/kg in the season. The lowest value for higher molecular weight PAHs in dry season was detected for six-ringed benzo(g,h,i)perylene at 0.202 mg/kg. In the rainy season, the values at the study location ranged from <0.001 mg/kg to ≤0.520 mg/kg. Benzo(b)fluoranthene and benzo(k)fluoranthene had highest concentration of 0.520 mg/kg at ST 1 followed by benzo(a)pyrene with 0.422 mg/kg at ST 4. Indeno(1,2,3)cd pyrene and dibenzo(a,h)anthracene were below detection limit at all the stations in the study area in the season. Benzo(g,h,i)perylene was the most persistent also in the rainy season as it was present at all the study area stations except ST 2. At the control station, the rainy season values ranged from <0.001 mg/kg to ≤0.282 mg/kg. Benzo(g,h,i)perylene had the highest value of 0.282 mg/kg and benzo(a)pyrene was 0.068 mg/kg. Indeno(1,2,3)cd pyrene and dibenzo(a,h)anthracene which had the highest concentration here in the dry season was below detection limit in the rainy season. From this result, it can be seen that more different higher ringed PAHs were detected in the rainy season than the lower rings. This agrees with an earlier study referred to in this work in which higher ringed PAHs were detected more in the rainy season than the lower rings (Inengite et al., 2010). Due to their hydrophobic and lipophilic nature, higher molecular weights PAH are most likely to settle in sediment or be attached to substrates, depending on the medium (WHO, 2003). Such substrates could be absorbed by aquatic organisms present there and be transported up the food chain (EFSA, 2008). This reduces their availability in the medium and in this case, sediment. This character could help explain why they occurred in more quantity in sediment samples in dry season when there was less rain and less hydration in the sediment. This realisation reveals the possibility that most of the PAHs detected here in the dry season may have been adsorbed by aquatic organisms or available in substrates through which they could move up the food chain and be likely available for human consumption in rainy season. Also, benzo(a)pyrene which had the highest concentration of all PAHs analysed in this study have been found to oppose biodegradation by microbes in sediment (Obayori and Salaam, 2010). This PAH which is considered to be probably carcinogenic in human (EFSA, 2008), could possibly be available in human consumables. The findings from this study points towards the necessity of determining the level of PAHs in aquatic organisms in dry and rainy season.

Seasonal Variation of PAHs in Sediments

The mean of the total PAHs detected in this study period as observed in Figure 3 and Table 2 reveal that PAHs concentration in the dry season was higher than the rainy season at every location of the study area and the control. Most of the PAHs detected in this study were in the dry season and the highest concentration for individual PAHs at the study location and control were found in dry season. ST 4 had highest mean value of 0.283 mg/kg and ST 3 had lowest value of 0.171 mg/kg. At the control station, the mean concentration of PAHs in the dry season was 0.261 mg/kg.

In rainy season, the mean of total PAH detected was lower than the corresponding dry season at all stations in the study area and the control. Although individual PAHs concentration was high at some locations in the rainy season, most of the lower molecular weights PAHs were below detection limit in rainy season. This is believed to be responsible for the overall lower result in the season. ST 4 had highest mean total concentration of 0.180 mg/kg and ST 3 was the lowest with 0.022 mg/kg. These two stations (ST 4 and 3) also had highest and lowest values in the dry season respectively. At the control station, 0.065 mg/kg was the mean value recorded in the rainy season.

The seasonal variation of PAHs in this study reveals that the difference in the dry and rainy season values were determined at the different locations base on the type of commercial, industrial or other activities going on there. This realisation is backed up by the results which show that the location with highest concentration in the dry season was also the same location with highest concentration in the rainy season. And the location with the lowest concentration in the dry season was also the same with the lowest concentration in the rainy season. According to an earlier work done on evaluation of sediments in Kolo creek in Niger Delta area of Nigeria, total PAHs concentration in late dry season was found to be higher than the rainy season at most of the locations (Inengite et al., 2010). A similar trend in which the station with the highest value in the dry season was the same with the highest in the rainy season and the one with the lowest in dry season was lowest in rainy season (except for the station with values below detection limit) was also observed there (Inengite et al., 2010). On the contrary, observations from this study work are different from those obtained in surface sediments collected in a tropical coastal lagoon (Grand – Lahou Lagoon) in Côte d'Ivoire (Kouakou et al., 2015). In their study, lower concentrations of PAHs were detected in the dry season than in the rainy season (Kouakou et al., 2015). These two comparative studies (Kolo creek and Grand – Lahou Lagoon) also believe that varying level of contamination at the different locations could be responsible for the high or low concentration detected in the samples.

PAH variation base on characteristics of the different locations

The results of this study revealed that PAHs contamination in dry and rainy season is largely dependent on the characteristics of the different locations from which the samples were collected. The activities at the locations gave clearer understanding on why PAHs levels at some places are high and others low irrespective of the season (dry or rainy season).

Station one (ST 1) is in Ekpan-NNPC complex area of Warri city. This location is along a busy expressway and the sampling point is a river under the bridge. A major peculiarity of this location is the busy highway that could generate PAHs from vehicular emissions that are of pyrolytic source. Also, the river could be a drain receiving waste water from close residential area and industry. This could increase PAH quantity from garbage load. Many of the few ringed-PAHs were detected here in the dry season but mostly below detection limit in rainy season. Higher-ringed PAHs such as benzo(a)pyrene, indeno(1,2,3)cd pyrene and dibenzo(a,h)anthracene were below detection limit in dry season and rainy season. Benzo(a)pyrene is believe to be of petrogenic origin (Neff, 2005). The activities in this location can be said to be responsible for the type of PAHs detected there. Sampling location two (ST 2) Ogunu is a community close to an industrial area that is involved in oil and gas activities. The sampling point- Ogunu River is crowded with domestic activities of the local inhabitants such as: fishing, bathing, boat riding, cooking and dumping of refuse and sewage. This river is also suspected to be an avenue for illegal petroleum product marketing activities. This location has residential houses, a local public toilet and a refuse dump around it. All the PAH compounds analysed in this study were detected here in the dry season. The highest concentration of benzo(a)pyrene (1.342 mg/kg) was found here in dry season. In the rainy season, two-ringed anthracene and fluorene were the only PAH detected. The activities at this location indicate that PAHs found here could be of petrogenic and pyrolytic origin. The third sampling point (ST 3) is Ugboroke community in Warri. This location is densely populated by local inhabitants whose major source of livelihood is small scale farming (fishing, poultry and plant cropping) and other small businesses. The sampling point is a swampy forest with timber trees, palm trees and fruit trees. PAHs from this location would likely be from bush burning, home cooking and residential burning of garbage. Apart from four-ringed fluoranthene, all the other PAHs analysed in this study were found at ST 3 in varying quantity. Okotie sawmill ST 4 is a location that has several industrial activities around it. The waterside from where the sediment samples were collected has a construction company and sawmill just close by. Consequently, all the various PAHs analysed in this study were found at this location in both rainy and dry season. This is similar to the study done by Ana et al. (2011) on PAHs analysis in surface waters. They also found out that the highest number of the various PAHs analysed were detected in the highly industrialised area. This location had the highest concentration of PAHs in both dry and rainy season. The control point ST 5 is characterised with the presence of a cattle grazing ground, an abattoir and a meat market. In addition to this, it was noticed that river dredging activities were taking place within the area throughout the study period. Most of the lower-ringed and higher-ringed PAHs were detected in both dry and rainy season. Benzo(a)pyrene, indeno(1,2,3)cd pyrene and dibenzo(a,h)anthracene were present in considerable amount. PAHs from the control station could also be from various origins.

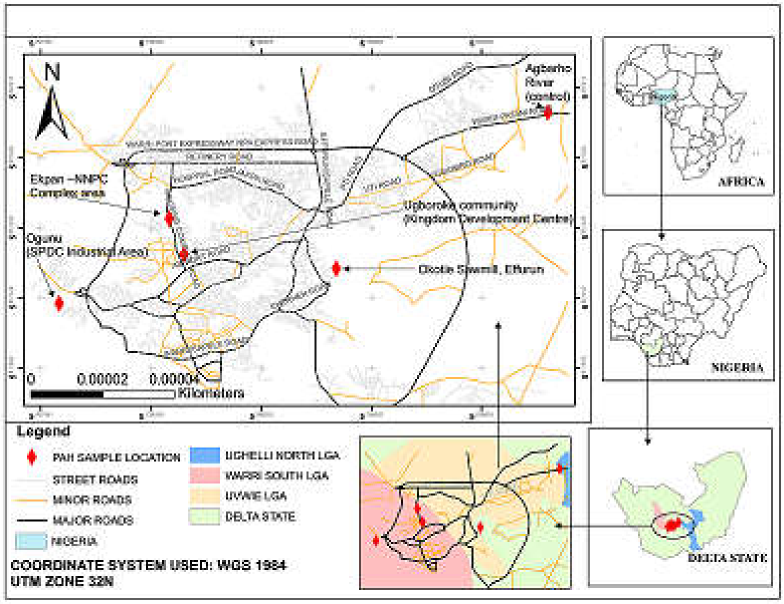

Figure 1: PAH sample location Map.

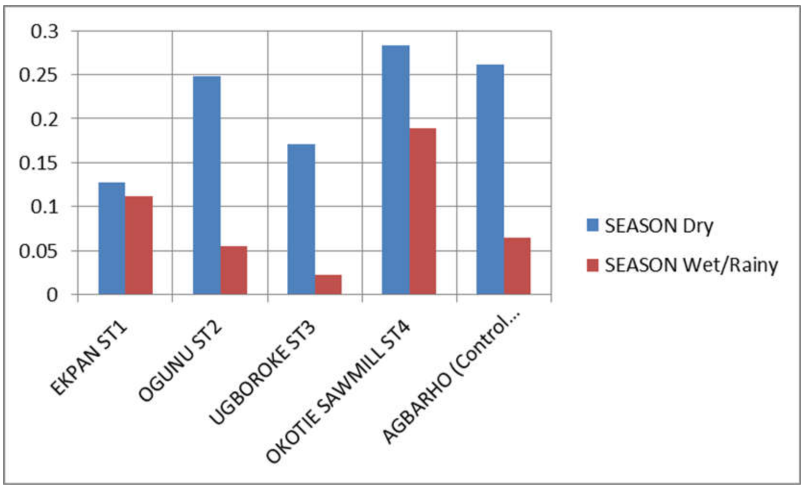

Figure 2: Chart for the mean of total PAHs value in Sediment samples for Warri city and Agbarho (control station) in dry and rainy season in mg/kg.

Table 1: Results of analysis of the sediment samples from the study area and control for dry (D) and rainy/wet (R) seasons of sampling.

	PAHs Concentrations in Sediment Samples at study location and Control sampling stations ST in mg/kg									
	ST1-Ekpan		ST2-Ogunu		ST3-Ugboroke		ST4-Okotie		ST5-Agbarho	
	Seasons Dry D, Rainy R									
Parameters	D	R	D	R	D	R	D	R	D	R
Naphthalene	0.041	<0.001	0.211	<0.001	0.0349	<0.001	1.091	<0.001	0.421	0.017
2-methyl naphthalene	0.039	<0.001	0.041	<0.001	0.0353	<0.001	0.05	<0.001	<0.001	0.21
1-methylnaphthalene	0.01	<0.001	0.001	<0.001	<0.001	0.209	0.18	0.073	0.37	0.033
Acenaptylene	0.007	0.005	0.006	<0.001	0.076	<0.001	0.046	0.007	0.154	<0.001
Acenaphthlene	<0.001	0.006	0.01	<0.001	0.004	0.008	0.0216	0.02	<0.001	<0.001
Fluorene	0.011	<0.001	0.057	0.13	0.013	<0.001	0.09	0.131	0.038	0.017
Phenanthrene	0.191	<0.001	0.07	<0.001	0.0235	<0.001	0.245	0.228	0.577	0.046
Anthracene	0.244	0.071	0.093	0.751	0.147	<0.001	0.338	0.693	0.075	<0.001
Pyrene	0.209	<0.001	0.214	<0.001	0.187	<0.001	0.513	0.361	0.186	<0.001
Chrysene	0.507	0.617	0.49	<0.001	0.083	<0.001	<0.001	0.285	<0.001	0.186
Fluoranthene	<0.001	0.01	0.04	<0.001	<0.001	<0.001	0.097	0.218	<0.001	0.087
Benzo(a)anthracene	0.144	0.452	0.2554	<0.001	0.205	<0.001	0.572	<0.001	0.18	<0.001
Benzo(b)fluoranthene&Benzo(k)Fluoranthene	0.413	0.52	0.193	<0.001	0.388	<0.001	<0.001	0.245	0.104	0.109
Benzo(a)Pyrene	<0.001	<0.001	1.342	<0.001	0.216	<0.001	0.823	0.422	0.779	0.068
Indeno(1,2,3-cd)Pyrene & Dibenzo(a,h)anthracene	<0.001	<0.001	0.196	<0.001	0.267	<0.001	0.334	<0.001	1.092	<0.001
Benzo(g,h,i)Perylene	0.218	0.112	0.753	<0.001	1.067	0.147	0.139	0.346	0.202	0.282
Total	2.034	1.793	3.974	0.881	2.746	**0.364**	4.54	3.029	4.179	1.056
Mean	0.1695	0.22413	0.24828	0.4405	0.19619	0.12133	0.32426	0.25242	0.34817	0.1055
Standard Deviation	0.159	0.211	0.353	**0.188**	0.264	0.061	0.319	0.19247	0.32209	0.09115

Table 2: Mean of Total PAHs value in Sediment samples for Warri city and Control stations in dry and rainy season in mg/kg.

STATION	SEASON	
	Dry (mg/kg])	Wet/Rainy
EKPAN ST1	0.127	0.112
OGUNU ST2	0.248	0.055
UGBOROKE ST3	0.171	0.022
OKOTIE SAWMILL ST4	0.283	0.189
AGBARHO (Control Station)ST5	0.261	0.065

Conclusion

The total quantity of PAHs detected in the dry season was higher than those of the rainy season in marshy sediment samples collected in Warri city in this study period. More different higher ringed PAHs were detected in the rainy season than the lower rings. Five-ringed benzo(a)pyrene had highest concentration of 1.342 mg/kg. It was also discovered that characteristics of the different sampling stations affected the type and quantity of PAHs detected there. From all the work done in this study, the following conclusions were made:

- Overall concentration of PAHs was higher in the dry season than in the rainy season; more different PAHs of higher and lower rings were found in the dry season than in the rainy season.
- Total PAHs concentration within Warri city was higher than at the control point ST 5 (Agbarho) for the study period;
- PAHs concentrations are high in the more industrialised areas;
- Poor domestic waste management such as refuse dump, sludge water, burning, burning of refuse and incineration were also determinants of the variation of PAHs concentrations in both dry and rainy season for the study area.

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COMPETING INTERESTS

The authors declare that they have no competing interest.

AUTHORS' CONTRIBUTIONS

AVB was the principal investigator in this work and IEA the supervisor. The article was jointly written by both authors.

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