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Assessment of Polycyclic Aromatic Hydrocarbons in Crude Oil Spill Sites in Emohua Local Government Area of Rivers State, Nigeria

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ABSTRACT
This study examined the concentration and distribution of Polycyclic Aromatic Hydrocarbons (PAHs) in three oil spill sites (A, B & C) in Emuoha Local Government Area of Rivers State, Nigeria. The area is in the Niger Delta region that is known for petroleum exploration and the consequent environmental degradation. The research involved collection of 20 top/surface soil, 5 sub-surface soil, 5 groundwater and 3 surface water samples from each site. A total of 100 samples were collected from the four environmental media. The samples were analyzed for the 16 priority PAHs identified by the USEPA. The results indicate mean PAHs in the surface soil was 98.096, 64.770 and 16.261 mg/kg for site A, B and C respectively. The mean PAHs found in the sub-surface soil was 3.450, 1.207 and 0.144 mg/kg for site A, B and C respectively. For surface water the PAHs found on the three sites were all less than 0.01mg/l and for ground water significant PAHs was only found at site A with mean concentration of 27.57mg/l while PAHs found in the ground water of sites B and C were less than 0.01mg/l. The mean PAHs concentrations recorded in the surface soil at sites A and B were significantly greater that the permissible limit of 40mg/kg set by Department of Petroleum Resources (DPR) for oil spill sites. The Kruskal Wallis test showed that there was significant difference in the mean total PAHs concentration in the surface and subsurface soils for the three sites. However, the test showed no significant difference in the mean total PAH concentration in surface and ground waters for the three sites. The result from this study showed the surface soil had higher percentage of Heavy Molecular Weight (HMW) PAHs than Light Molecular Weight (LMW) PAHs indicating possible pyrogenic source, but this is also attributable to the age of the spill sites. The research found that Site A had highest level of PAHs and that surface soil contributed the highest PAH concentration in all three sites. It was also found that HMWP were the predominant PAHs in all the three sites and for all the four environmental media studied. It is recommended that immediate intervention at the sites be carried out given that some PAHs are known carcinogens.

KEYWORDS: *Polycyclic Aromatic Hydrocarbon, Heavy Molecular Weight, Light Molecular Weight, Mean Concentration, Kruskal Wallis, Niger Delta*

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I. INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are a group of naturally unsubstituted organic compounds consisting of two or more fused aromatic rings (Fetzer, 2000). PAHs are persistent organic pollutants known as organic micro-pollutants, which are generally recalcitrant to biodegradation and environmentally harmful (Boisa et al., 2019). According to Gao et al. (2019) PAHs are a group of ubiquitous persistent organic pollutants, which are composed of two or more fused aromatic rings in linear, angular, or cluster arrangement. Anthropogenic processes like incomplete combustion of organic fuels are the principal sources of PAHs. Naturally PAHs occur in crude oil, gasoline, and coal. Natural contributors of PAHs into the environment include volcanic eruptions, forest fires, oil seeps, decaying organic matters while oil spills, gas flaring, use of fossil fuels for power generation and vehicles are some anthropogenic sources (Boisa et al, 2019). They are a group of several hundred individual organic compounds that contain two or more aromatic rings and occur more as complex mixtures rather than single compounds (Lee and Vu, 2010). PAHs are generally classified by their melting and boiling points, vapour pressure and solubility depending on their structure.

The presence of PAHs in crude oil is well established and according to Gao et al. (2019) are considered the main toxic components of crude oil as many are known to be carcinogenic and/or mutagenic and have been marked as priority pollutants by both the European Union and the United States Environmental Protection Agency (US EPA). The PAHs can be grouped into two main categories – the Light Molecular Weight PAHs (LMWP) which have two or three aromatic rings and the High Molecular Weight PAHs (HMWP) that have four or more rings. Boisa et al. (2019) stated that HMWP are of significant concern because they are highly toxic and lipophilic, thereby easily bioaccumulate in tissues. As earlier mentioned, one of the natural sources of PAHs in the environment is through crude oil spills and the Niger Delta is popular for the devastating environmental pollution from oil exploration and production activities including oil spills. In the last decade, 2008 to 2018 a total of 7581 oil spill incidents were reported to have occurred in the Nigerian Oil Spill Monitor (NOSDRA) website. The density of these incidents can be seen in the Figure 1. The red points indicate oil spill sites, and all are located within the Niger Delta of Nigeria. This figure represents incidents reported to the Agency and of course some incidents could have gone unreported. This figure therefore represents the minimum number of oil spill incidents in the area over the last decade (January 2008 to December 2018). This assumption agrees with the Amnesty International (2013) that all oil spill reporting in Nigeria is likely to suffer from limitations and that the NOSDRA data may not reflect all oil spills.

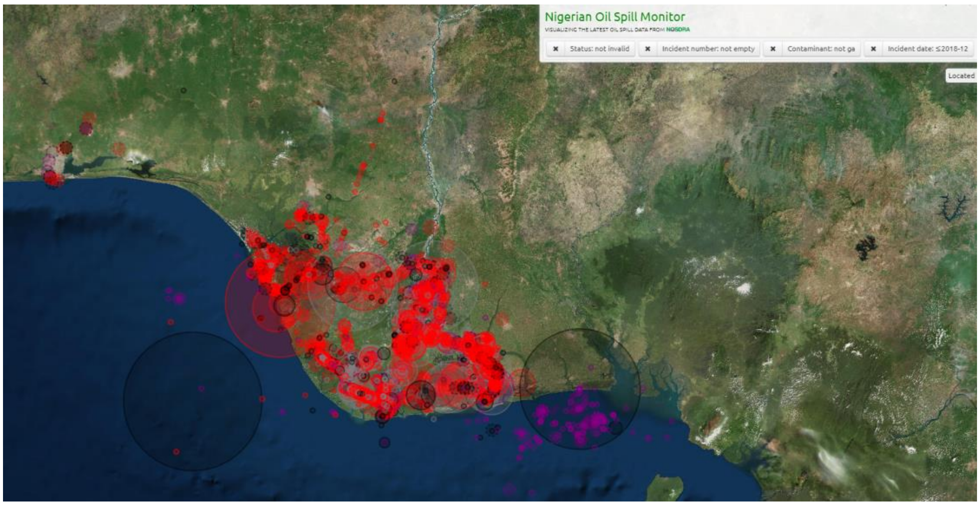

Figure 1: Oil Spills in Nigeria from 2008 to 2018 (NOSDRA online oil spill monitor)

The data indicated that about 418,414.57 barrels of crude oil were spilled in this period, though 31.66% of the total number of incidents (2, 400 incidents) had missing volume of oil spilled. The aggregate reported volume for over 5000 crude oil spill incidents maybe really conservative as Amnesty International (2013) noted that there are systemic flaws in the system adopted in investing oil spills in the Niger Delta, hence the outcome of these investigations lacks credibility and that the crude oil volumes declared during Joint Investigation Visits (JIV) of crude oil spills is deeply flawed as it was based basically on rough estimates of area and depth, which were not adequately explained. Therefore, these data from the NOSDRA Spill Monitor Website may have suffered such flaws and have been used to show the magnitude of the issue related to crude oil spills in the Niger Delta. These incidents arguably contribute to the addition of PAHs into the environment. This research, therefore, assesses the concentration and distribution of PAHs in three oil spill sites in Emuoha Local Government Area of Rivers.

II. MATERIALS AND METHODS

2.1 Study Area

The three sites used for this study are in Emohua Local Government Area (EMOLGA) of Rivers State, Nigeria. EMOLGA has a land area of 837.21 km^2 and a population of approximately 201,901 as at 2006 population census (Nigeria Population Commission, 2006). The study area lies within the tropical rainforest of the Niger Delta and is characterized by eight months and four months of the wet and dry seasons, respectively. The average temperature of the area is between 22ºC and 29ºC with high humidity and rainfall. The major occupation of the people is farming with a few others engaging in trading and public service (Ugbomeh, Goodhead, Green and Onwuteaka, 2018). EMOLGA hosts a few oil processing facilities and an array of crude oil pipelines. Several oil spill incidents have been reported generally in this area due to pipeline vandalism and illegal activities of oil thieves/militants. The site is in the Niger Delta of Nigeria with the land elevation generally below 20m above sea level. The area is gentle sloping and transversed by a seasonal swamp running from northeast to southwest joining the Sombriero River.

The Niger Delta is a tropical rain forest with swamps and seasonally waterlogged low-lying areas, so is our study site with distinct natural vegetation. UNDP (2006) reported the Niger Delta rain forest as structurally complex and floristically diverse. The sites have vegetation made up of grasses and shrubs with few scattered trees indicative of a secondary jungle forest (TEPNG, 2012). The major land use of the sites is for subsistence agriculture involving the cultivation of local crops mainly cassava, yam, cocoyam, maize, and native vegetables. The agricultural practice is bush fallowing, which involves cultivating a piece of land in one farming season and allowing same uncultivated for a period (5 to 6 years) so that the fertility of the land will be restored before returning to cultivate the same land. Bush burning is common practice in this area (TEPNG, 2012). The site lies in a humid sub-equatorial climate characterized by wet and dry seasons. The wet season is longer and extends from March/April to October while the dry season extends from November to February. The mean annual temperature of the area is 27 (±3) degrees Celsius and the annual average rainfall is about 3000mm with average evapotranspiration of about 1000mm/year, leaving an effective rainfall of 2000mm/year. (Dehez, 2014)

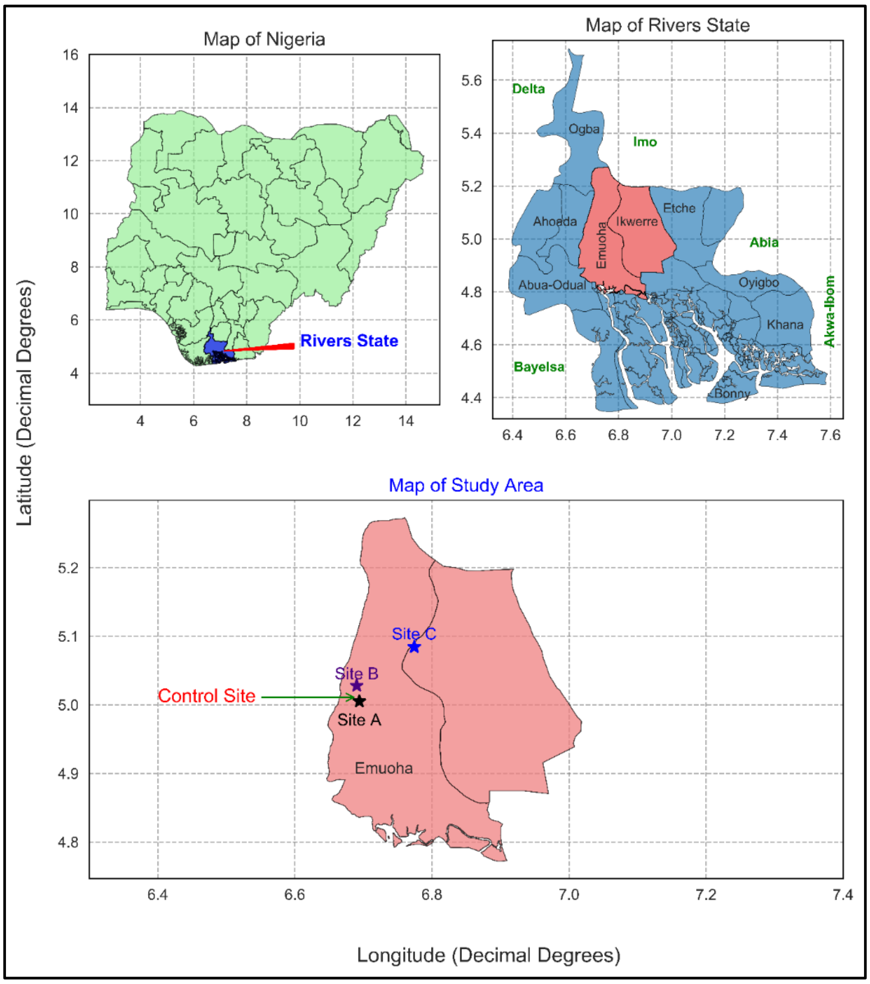

Figure 2: Map of the Study Area, EMOLGA

2.2 Sample Collection

On each of the study sites (A, B and C); 20 top/surface soil and sediment samples, 5 sub-surface soil samples, 3 surface water samples and 5 ground water samples were randomly collected from each site into air-tight containers. Surface soil and sediment samples were collected at two horizons (0 – 15cm and 15cm to 30cm) using graduated hand auger. The samples collected from the two horizons were composited for analysis. About 0.5kg of surface soil and sediment were collected and transferred into a wide mouth amber bottle. A total of 3 surface water samples each were collected from Sites A, B and C including community local fishponds and river. For ground water and sub-surface sample, 5 wells were drilled at each site, and 5 sub-surface soil samples and 5 ground water samples were collected at various depths in the well.

2.3 Extraction of PAHs

For the surface and sub-surface soil, 10g of the soil sample was dried using anhydrous sodium sulphate and 1ml of 30ug/ml Pyrene D10 surrogate standard added and mixed thoroughly with the sample. Thirty (30) ml of methylene chloride was then added, and the sample extracted. The sample extract was subsequently filtered through glass wool containing anhydrous sodium sulphate in a glass funnel. About 2g of silica gel was added and allowed to stand for a while. The extract was then decanted and allowed to concentrate at room temperature to 1ml volume and thereafter analyzed using Agilent 6890N GC/MS previously calibrated with PAH standards.

For the surface and ground water, a known volume of sample was poured into the separator funnel. Forty (40) ml of dichloromethane was added and shaken vigorously for about 2mins to allow organic layer to separate with occasional venting to release pressure. The extracted mixture was filtered through a filter paper containing 5g of activated silica gel and 5g of sodium sulphate into the vial and ready for injection. Agilent 6890N GC/MS gas chromatography was used in identifying the various PAH components.

2.4 Data Analysis

The results obtained from the laboratory analysis were subjected to both descriptive and inferential statistical analysis to determine the mean, standard deviation, skewness, and level of significance of the PAHs concentrations and distributions. Microsoft XLSTAT 2016 and SPSS were used in performing all statistical analyses.

III. RESULTS AND DISCUSSION

3.1 Results

3.1.1 Polycyclic Aromatic Hydrocarbon (PAH) Concentrations

The sixteen priority PAHs identified by the United State Environmental Protection Agency (USEPA) were measured in surface soil, sub-surface soil, surface water and groundwater for all three sites. Figures 1-6 show the Individual components (a total of16) and mean total PAH concentrations partitioned into low and high molecular weight PAHs for surface and sub-surface soil, and surface and groundwater for the sites. The mean PAHs found in the surface soil was 98.096, 64.770 and 16.261 mg/kg for sites A, B and C, respectively. The mean PAHs found in the sub-surface soil was 3.450, 1.554 and 0.144 mg/kg for sites A, B and C, respectively. For surface water the mean PAHs found on the three sites were all less than 0.1mg/l and for groundwater significant PAHs was only found at site A with mean concentration of 27.57mg/l while PAHs found in the groundwater of sites B and C were less than 0.1mg/l. Comparative analysis of the mean PAHs on the three sites was done and Kruskal Wallis non-parametric test was used to evaluate if there was significance difference in the PAHs concentrations in the three sites.

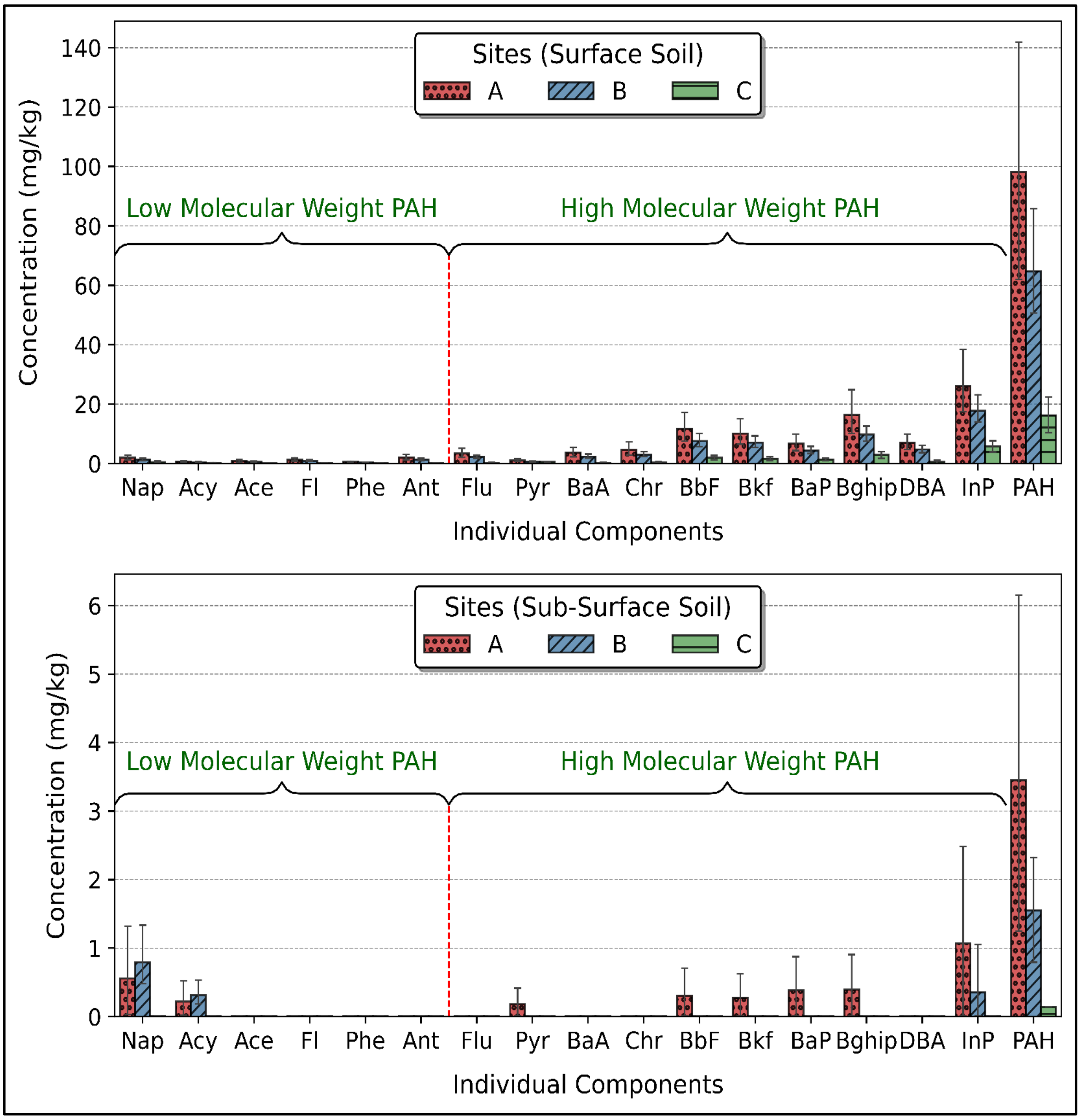

Figure 3: Individual component and mean total PAH concentration for Surface and Sub-surface Soil

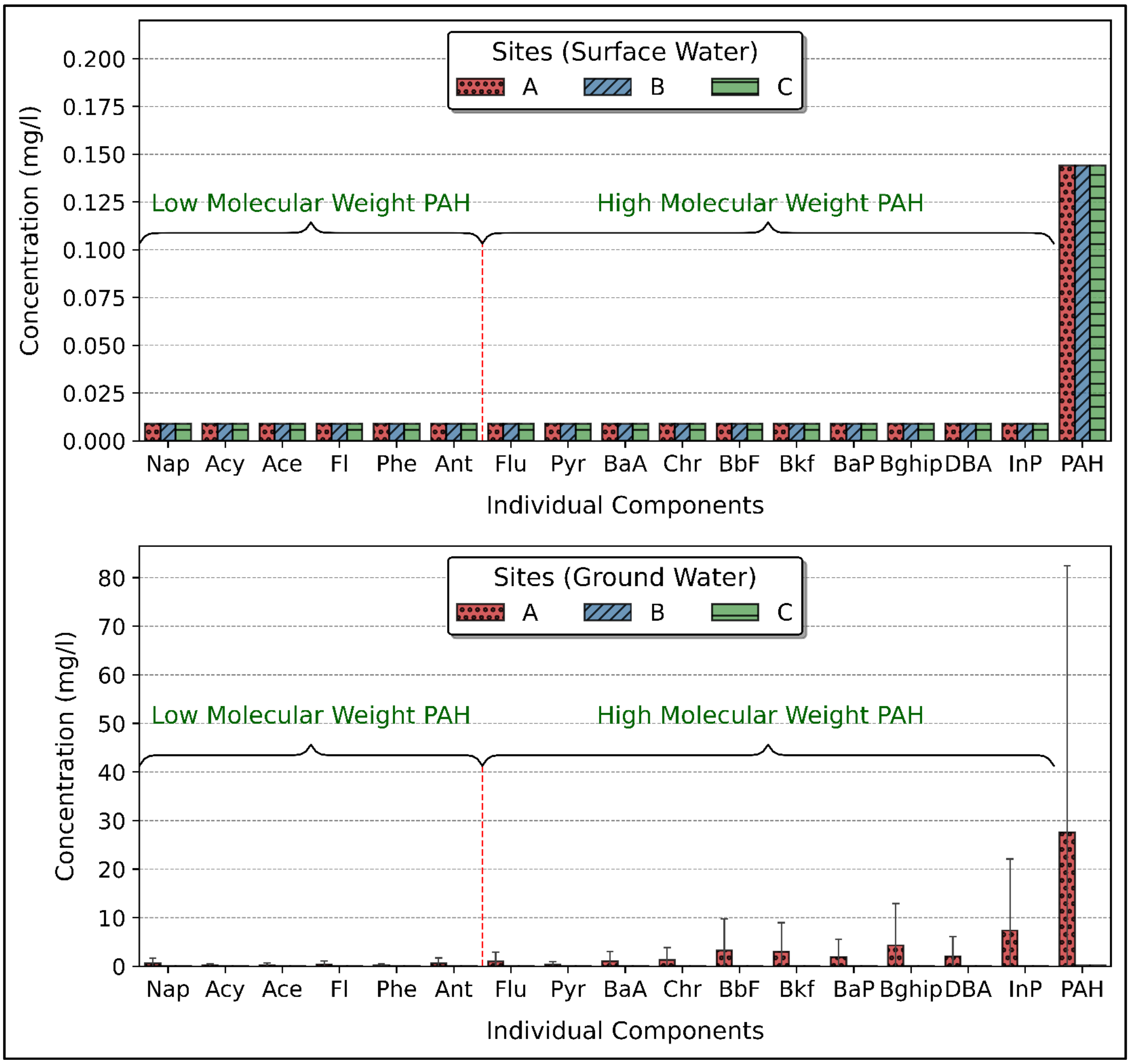

Figure 4: Individual component and mean total PAH concentration for Surface and Ground water

3.1.2 Comparative Analysis of PAH Concentrations in 3 Sites from 4 Environmental media

The result of the comparative analysis of the mean total PAHs concentrations for the four environmental media for the three sites is presented in Figure 5. It was observed from Figure 5 that, the mean total PAHs concentration for the surface soil at site C was the lowest among the three sites with a mean total PAHs of 16.26mg/kg. The mean total PAHs at site A was approximately twice the mean total PAHs concentration recorded at site B and six times the mean total PAHs recorded at site C. The results show that site A had the most polluted surface soil among the three sites used for this study. For the sub-surface soil, site A had the maximum mean total PAHs concentration of 3.45mg/kg. The mean total PAHs recorded in the sub-surface soil at site A was four times the mean total PAHs recorded at site B and twenty-four times the mean total PAHs concentration recorded at site C. For surface water, mean total PAH recorded for the three sites were generally low and the three sites had a mean total PAHs concentration of 0.144mg/kg. For the groundwater, site A had the highest recorded mean total PAHs of 27.567mg/kg. The mean total PAHs concentration recorded at site A was 191 times the mean total PAHs recorded at both sites (B and C). The result from the comparative study gave strong indication that site A was the most polluted of the three sites with PAHs and site C is the least polluted site.

Kruskal Wallis test of significance was used to evaluate if the difference observed in the three sites in the four environmental media were significantly different from site to site and the result is presented in Table 1. The Kruskal Wallis test showed that there was significant difference in the mean total PAHs concentration in the surface soil for the three sites as the test statistic (35.96) was greater than the critical value (5.99). The Multiple pairwise comparisons using Dunn's procedure test showed that the mean total PAHs in the surface soil at site C differ significantly from the mean total PAHs obtained from sites A and B. The result also showed that the mean total PAHs in the surface soil at sites A and B was not significantly different, which indicates that the source of contamination of the surface soil with PAHs at both sites was same and the extent to which both sites A and B were polluted seemed relatively similar.

Kruskal Wallis test showed that there was significant difference in the PAHs concentrations in the sub-surface soil as the test statistic (10.35) was greater than the critical value (5.99) at 0.05 level of significance (Table 1). The Multiple pairwise comparisons using Dunn's procedure test showed that the mean total PAHs in the sub-surface soil also gave the same result as obtained for the surface soil. The result showed that sites A and B had significantly higher mean total PAHs concentrations than site C. The result also showed that though the mean total PAHs concentration for sub-surface soil in site A was higher than site B, there was no significant difference. For surface water, that there was no significant difference in the mean total PAHs concentration for the three sites, as the mean total PAHs concentration of the three sites were 0.144mg/kg, respectively. For groundwater, Kruskal Wallis test showed that there was no significant difference for the three sites, though site A had a higher mean total PAHs concentration.

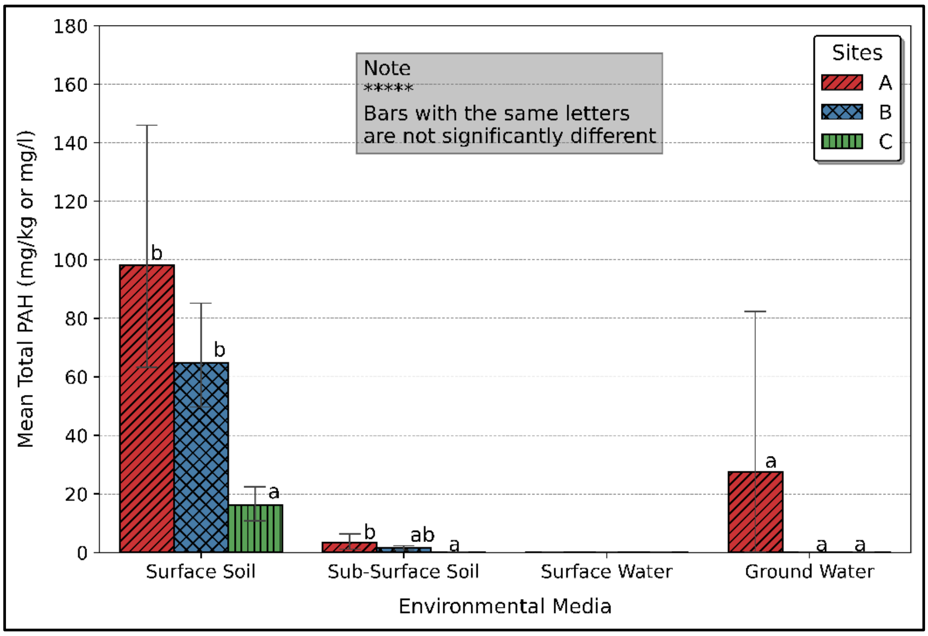

Figure 5: Comparative plot of mean total PAHs for the three sites

Table 1: Kruskal Wallis Test of significance for the three sites

	Surface Soil	Sub-Surface soil	Groundwater
K (Observed value)	35.9567	10.3496	2.0000
K (Critical value)	5.9915	5.9915	5.9915
DF	2	2	2
p-value (Two-tailed)	< 0.0001	0.0057	0.3679
alpha	0.05	0.05	0.05

3.1.3 Composition Profile of PAHs and Molecular Weights

Figures 6 and 7 show the percentage composition of low molecular weight PAHs to high molecular weight PAHs at sites A and B, respectively. Figure 6 showed that about 7% of the PAHs composition were lower molecular weight (LMW) PAHs while about 93% were higher molecular weight (HMW) for surface soil, indicating that the PAHs composition were predominately higher molecular weight PAHs. For the sub-surface soil at site A, about 52.27% of the PAHs composition were LMW while about 47.73% of the PAHs composition were HMW. For groundwater, 37.5% of the PAHs composition were LMW while 62.5% were HMW PAHs. For surface water it was observed that about 31.52% of the composition were LMW PAHs while 68.48% of the composition were HMW PAHs. From Figure 7, the average percentage composition of lower molecular weight PAHs was about 8% while the average percentage composition of higher molecular weight PAHs was about 92% for surface soil at site B. For Sub-Surface Soil in site B, the average percentage composition of LMW PAHs was 92.37% while the average percentage composition of HMW PAHs was 7.63%. For surface and groundwater, the average percentage composition for LMW PAHs was 37.5% while the average percentage composition for HMW PAHs was 62.5%.

The distribution pattern of PAHs rings and abundance of the individual PAHs are shown in Figures 8 and 9. From Figure 8, the predominant PAHs ring group found on the surface soil in Site A was composed of 6 rings (Indeno (123) preylene and Benzo (ghi) preylene) PAHs. The 6 rings PAHs found on the surface soil in Site A accounted for 43.33% of the mean total PAHs concentration. The next abundant PAHs group found on the surface soil on site A were 5 rings PAHs which accounted for 36.25% of the mean total PAHs. The result showed that 2-3 rings were the least group that made up the mean total PAHs in the surface soil in Site A. The result also showed that 6 rings was still the predominant group of PAHs found in the sub-surface soil followed by the 5 rings groups. The 6 rings group accounted for 42.33% of the total PAHs concentration followed by 5 rings group which accounted for 28.07%. For surface water, the 2-3 rings groups were the predominant ring group followed by the four-ring group.

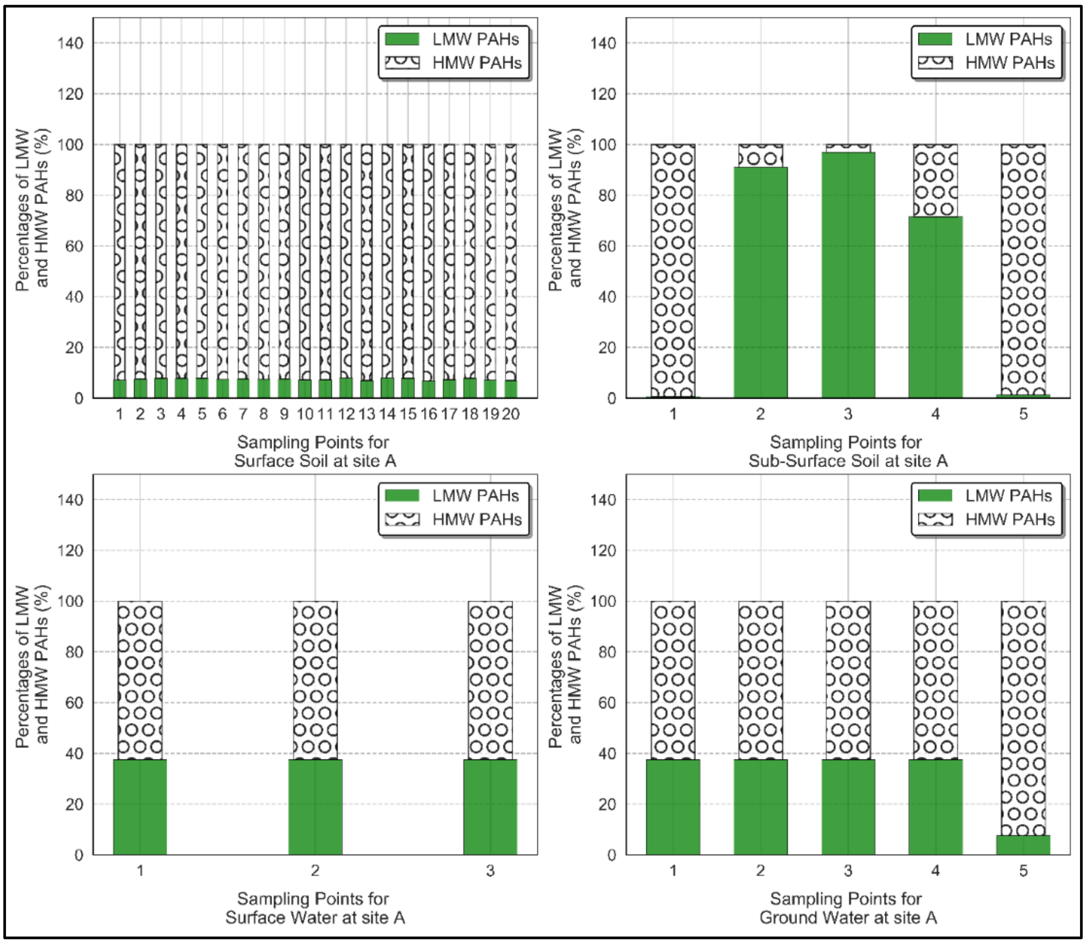

Figure 6: Percentage composition of LMW to HMW of PHAs for environmental media in site A

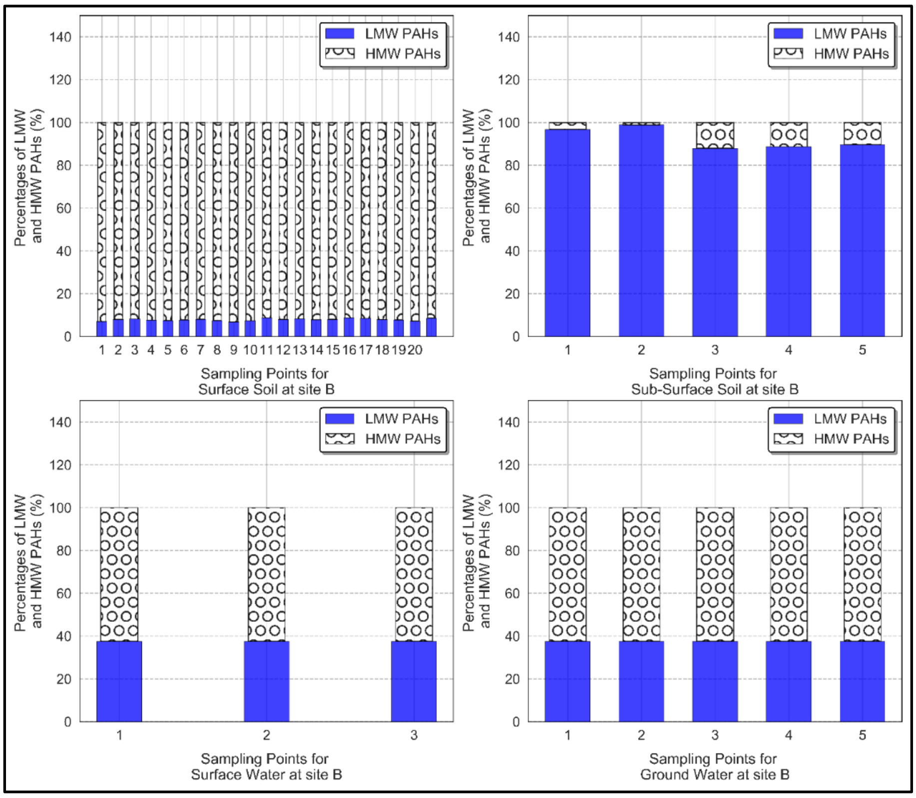

Figure 7: Percentage composition of LMW to HMW of PHAs for environmental media at site B

Figure 9, showed that the PAHs composition in the surface soil were made up of more of 6 fused benzene rings. About 43% of the entire PAHs composition were 6 fused benzene rings structure while about 37% of the entire PAHs composition were made up of 5 fused benzene rings. The 2-3 fused benzene rings had the least percentage composition, accounting for just about 8% of the entire PAHs composition. For the sub-surface soil, it was observed that 2-3 fused benzene rings made up majority of the PAHs composition. The 2-3 fused benzene rings accounted for about 94% of the PAHs composition. The next most abundant ring group found in the sub-surface soil for site B were 4 and 5 fused benzene rings. Both group of rings accounted for 2.39% each of the total PAHs composition. For the surface and ground water, both had the same distribution pattern for the fused benzene rings. The 2-3 fused benzene rings were the most abundant, accounting for 37.5% of the total PAHs composition. The least ring was the 6 fused benzene rings, just accounting for about 13% of the total PAHs concentration.

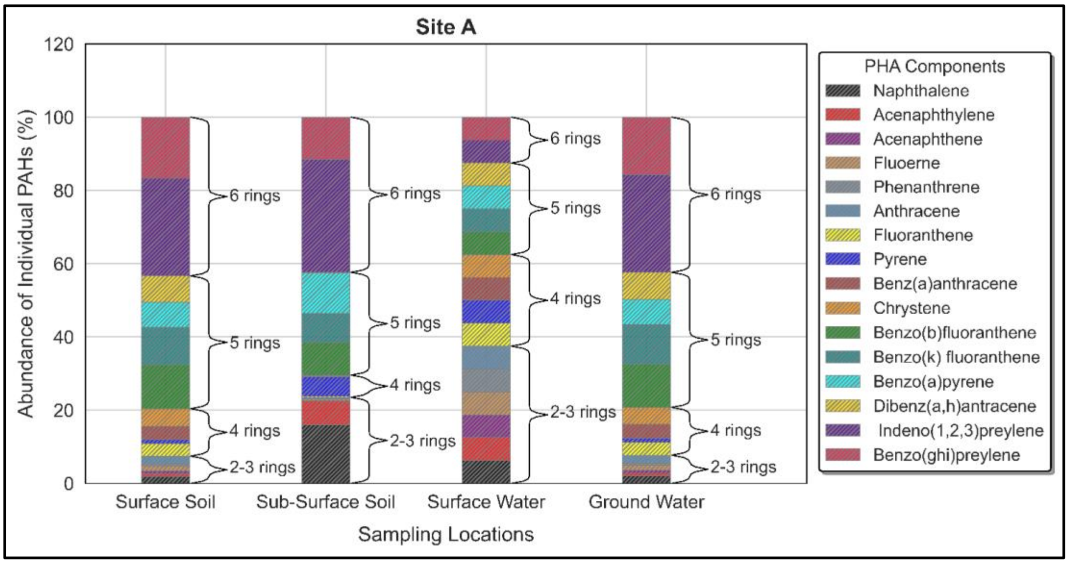

Figure 8: Distribution of PAHs rings for site A

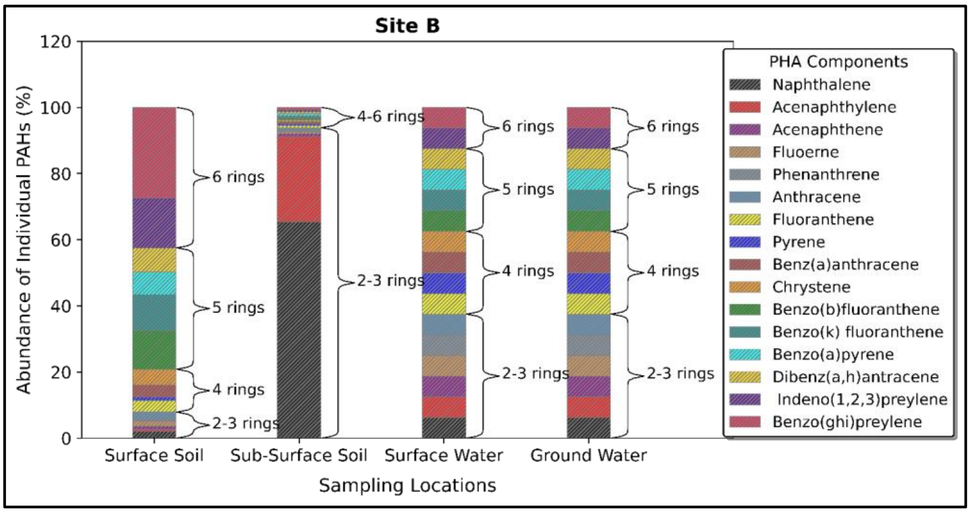

Figure 9: Distribution of PAHs rings for site B

3.2 Discussion

3.2.1 PAHs Levels of contamination at the Sites

The results from the concentrations of the 16 priority PAHs for the three sites showed elevated PAHs concentration on 2 out of the 3 sites. For the PAHs concentrations in the surface soil for the three sites, showed that the PAHs concentration in site A was greater than the other two sites. The PAHs concentrations in site A, site B and site C were 98.09, 64.77 and 16.26mg/kg, respectively. It was observed that the PAHs concentration in the surface soil at site A was 1.5 and 6 times more that the PAHs concentration recorded at sites B and C respectively. This result showed that the surface soil at site A had the most contamination with PAHs. The PAHs concentration recorded in the surface soil at the three sites used for this study were relatively higher than PAHs recorded in the surface soil in similar studies done in the Niger Delta and other parts of the world. Samuel *et a*l. (2010) in their study of PAHs in soils from oil exploration areas of the Niger Delta reported that the mean PAHs concentration recorded in the surface soil was 0.08mg/kg. Eucharia *et al.* (2016) in similar study done in the Niger Delta reported that the mean PAHs concentration found in the surface soil of two communities affected by oil spill in Delta state were 1.261 and 4.631mg/kg. Emeka (2014) in his study reported that the mean PAHs concentration recorded in the surface soil of NNPC oil depot at Aba was 7.40mg/kg. From the results of similar studies done on contaminated surface soil with crude oil and related products, showed that the PAHs concentration recorded in the surface soil in this study was clearly above all the PAHs concentration recorded in other contaminated surface soil in the Niger Delta. This result showed that Emohua surface soil is more polluted with crude oil contaminant than other regions in the Niger Delta. Similar studies of surface soil contaminated from oil exploration or related activities from other countries showed that the PAHs concentration recorded in the surface soil in Emohua was still greater than the mean PAHs concentration recorded in other parts of the world. Jackie *et al.* (1999) in their study of surface soil contaminated with fuel/oil in Antarctica reported that the mean PAHs recorded in the soil was 8.11mg/kg. Wang *et al.* (2018) reported that the mean PAHs in contaminated surface soil was 5.22mg/kg. The only study that reported similar elevated mean PAHs concentration as found in the surface soil in the current study was a study done in Texas (Peter and Heidi, 2007). Heidi and Peter (2007) in their study of crude oil contaminated soil reported that the mean PAHs concentration recorded in the surface soil was 86.4mg/kg, which was close to the mean PAHs concentration recorded in site A of the current study. Judging by similar studies one on surface soil contaminated with crude oil and related product both in Nigeria and other parts of the world showed that the PAHs concentration recorded in the surface soil at the three sites at Emuhoa are among the highest in the World. The elevated concentration of PAHs in the surface soil at oil spill sites at Emuhoa should be a serious source of concern and measure should be taken to ensure that the PAHs concentration is reduced to acceptable limit.

The mean PAHs concentration recorded in the surface soil at sites A and B were significantly greater that the permissible limit of 40mg/kg set by Department of Petroleum Resources (DPR) for oil spill sites. Only site C had mean PAHs concentration that was significantly lower than DPR limit. The PAHs contamination level in the surface soil at the three sites were also classified according to Malizewkwa Kordybach classification level. Maliszewska (1996) proposed that soil with PAHs concentration less than 0.2mg/kg are not contaminated, soil with PAHs concentration level of 0.2-0.6mg/kg are light contaminated, soil with PAHs concentration level of 0.6-1mg/kg are moderately contaminated and soil with PAHs concentration greater than 1mg/kg are heavily contaminated. Judging the Malizewkwa Kordybach classification, the mean PAHs concentration recorded in the surface soil at the three sites were far greater than the heavily polluted limit by a factor of 98, 64, and 16 respectively. Going by Malizewkwa Kordybach classification level, it is obvious that the surface soil at the three sites were heavily contaminated with PAHs.

The result of the mean PAHs concentration in the sub-surface soil showed that site A had higher mean PAHs concentration than the other two sites. The PAHs concentration recorded at site A was 3.45mg/kg while the mean PAHs concentration recorded at sites B and C were 1.55 and 0.144mg/kg, respectively. The mean PAHs concentration at site A was almost 3 and 24 times as much as the mean PAHs concentration recorded at sites B and C, respectively. Comparing the mean PAHs concentration recorded in this study to previous but similar study was difficult, as most of the previous studies on PAHs concentration in Niger Delta region solely focused on the PAHs in the surface soil. Just few studies focused on the PAH concentration in sub-surface soil, but even at that most of the studies focused on shallower depth (0.2-0.5m) than what was investigated in the current study (4.0-8.0m). Emeka (2014) in his study reported that, the PAHs concentration in the sub-surface soil at depth of 0.2-0.3m was 6.3mg/kg. Jackie *et al.* (1999) in their study reported that the mean PAHs concentration in the sub-surface soil at a depth of 0.2-0.3m was 2.54mg/kg. Wang *et al.* (2018) in their study reported that the mean PAHs concentration in the sub-surface soil at depth of 0.3-0.5m was 2.203mg/kg. Comparing the mean PAHs concentration in the current study with previous studies, it was observed that the mean PAHs was relatively within the same range. Though in the current study, the PAHs concentration in the sub-surface soil was investigated at a deeper depth. From the current study and previous studies, it was observed that there is a relationship between the PAHs concentration and the depth of investigation. The result from current study showed that there was a 96.5%, 98.12% and 99.11% reduction in the mean PAHs concentration in the surface soil at site A, B and C respectively. This shows that as the depth of the soil increases the mean PAHs concentration tend to reduce. Kanaly and Harayama (2000) attributed the decrease in PAHs concentration in soil as the depth increases might be due to leaching of the PAHs. The mean PAHs recorded at the three sites were significantly lower than DPR permissible limit of 40mg/kg. This indicates that the PAHs at the sub-surface soil is within acceptable limit. Malizewkwa classification criteria showed that the sub-surface soil at sites A and B were heavily contaminated with PAHs but site C had no contamination.

The mean PAHs concentration for surface water recorded at sites A, B, and C were all 0.144mg/l. The mean PAHs concentration was relatively low compared to similar study done in the Niger Delta region. Nganja *et al.* (2011) in their study reported that the mean PAHs concentration recorded in the surface water contaminated with fuel-oil was 57.83mg/l which was higher than what was obtained in the current study.

The mean PAHs concentration obtained for the surface water were significantly lower than DPR maximum permissible limit of 70mg/l. for the distribution of the individual PAHs components, the result showed that all the individual PAHs components had equal amount of concentration. The surface water for all sites were not polluted judging by the PAHs concentration and also by the DPR limit. The low concentration of PAHs in surface water might be attributed to the self-cleaning characteristic of rivers and stream.

The mean PAHs concentration for groundwater showed that just site A had elevated concentration of PAHs. Sites B and C had very low PAHs concentration. The mean PAHs concentration at sites A, B and C were 27.57, 0.144 and 0.144mg/l respectively. The mean PAHs concentration at the 3 sites were significantly lower than DPR permissible limit of 70mg/l. The result showed that the groundwater at the three sites was not polluted with PAHs.

3.2.2 Comparative Analysis of PAHs Levels of Contamination

The mean concentration in the surface soil had the highest concentration of PAHs out of the four environmental media due to the fact that the soil tends to trap metal and petroleum hydrocarbon better than any other medium (Adeniyi and Owoade, 2009 and Jiang et al., 2009). Jiang et al. (2009) suggested that the soil acts as a good indicator to check how much pollution is in the environment. It was also observed that low value of PAHs concentration was recorded at site C compared to other sites due to the fact that sites A and B were in close proximity to places that had experienced crude oil spillage from ruptured pipelines. The result indicates that PAHs are typically at elevated level in areas where oil exploration or production was done.

The result obtained from the Kruskal Wallis test gave strong evidence that the activities taking place on sites A and B or within close proximity has resulted in elevated level of PAHs pollution particularly in surface soil in both sites. The result showed that the surface soil at sites A and B is heavily polluted and people should be restricted from those sites.

3.2.3 Rings PAHs Group and Molecular Weights

For the source identification and distribution of the PAHs, the result showed that both petrogenic and pyrogenic sources were identified in all environmental media studied. Moore *et al.* (2015) reported that soil that are polluted by petrogenic (oil spillage contamination) sources tends to have higher percentage of LMW PAHs in their PAHs composition while soil polluted by pyrogenic (coal and fossil fuel combustion) sources tend to have higher percentage of HMW PAHs in their PAHs composition. The result from this study showed the surface soil had higher percentage of HMW PAHs indicating that the possible contaminants of the surface soil at site A originated from pyrogenic sources. The result obtained in this study was similar to the finding from other studies. Moore *et al*. (2015) in their study reported that about 71% of the composition of the molecular weight of the PAHs were HMW PAHs. They attributed the reason of low molecular weight PAHs in soil partly due to the fact that LMW PAHs tends to evaporate in the soil and are highly violate. This might be the possible reason of low molecular weight PAHs in this study due to the fact that the oil spillage on Site A had occurred more than eight years ago and the unstable PAHs which are the LMW PAHS have evaporated due to exposure to sunlight over the years. For sub-surface soil, the graph showed that lower molecular weight PAHs were predominately more than higher molecular weight PAHs. About 52% of the total PAHs found in the sub-surface soil were lower molecular weight PAHs. The reason for the higher percentage of lower molecular weight PAHs can be attributed to the fact that the unstable lower molecular weight PAHs are not directly exposed to sunlight and the evaporation rate of the LWM PAHs to the atmosphere is not as much as to what was observed in surface soil. For both the surface and ground water, more HMW PAHs were recorded for both environmental media at Site A. The percentage of LWM PAHs found in surface and ground water were 37.5 and 31.52%.

It was observed that 2-3 rings group were more present in the sub-surface soil than in the surface soil. The reason for the low percentage of 2-3 rings PAHs group in the surface soil can be attributed to the fact that LMW (2-3 rings) are very unstable and tend to evaporate when in contact with direct sunlight. For the surface water, 2-3 rings groups where the group that was predominant, accounting for 37.5% of the total PAHs concentration. For the ground water it was observed from the plot that 6 rings group were the predominant group, accounting for 42.35% of the total PAHs concentration.

The contrast in the result obtained was due to the fact that the oil spillage on that site occurred about eight years ago, and most of the light molecular weight of the PAH which are unstable would have evaporated from the surface soil remaining significant amount of heavy molecular weight PAH. Abdulazeez (2019) stated that HMW PAHs are more persistence in the environment due to the fact that they have more stable molecular structure and due to their hydrophobicity. Wang et al. (2010), in their study stated that LMW PAH are more hydrophilic and biodegradable than HMW PAH. Result from the isomer ratio of the sub-surface soil showed that when LMW PAH that are not directly exposed to the sunlight and are in relatively moist environment, tend to stay in the environment longer.

IV. CONCLUSIONS

The following conclusions were drawn from the study:

1. There was elevated concentration of PAHs at site A than the two other sites, making site A the most polluted among the three sites.
2. The surface soil was the most contaminated among the environmental media studied (sub surface soil, surface water and ground water) at all the three sites.
3. The mean total PAHs obtained at the three oil spill sites were relatively higher than most of the PAHs concentration obtained at similar sites. The mean total PAHs concentration in the surface soil exceeded the Department of Petroleum Resources (DPR) permissible value at sites A and B. The mean total PAHs did not exceed DPR limit for other environmental media at the three sites.
4. The HMWP were predominant PAHs in all the three sites and for all the environmental media, this is possibly because the spill sites studied were old and the LMWP may have decomposed under the influence of weather elements.
5. The sites call for immediate attention as some PAHs are known carcinogens.

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