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Original Research Article

Concentration characteristics of polycyclic aromatic hydrocarbons (PAHs) in dept – wise soils, Sapele, Nigeria

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Polycyclic Aromatic Hydrocarbons (PAHs) are byproducts of incomplete combustion of organic materials during industrial and anthropogenic activities and their toxicity has been established. The objective of this investigation was to determine the depth-wise distribution and profile characteristics of 16 priority PAHs which is lacking in the study area. After extraction and purification quantification of PAHs was done using GC-FID with strict adherence to standard quality control/assurance measures. Results of descriptive statistics showed that the obtained concentrations of PAHs in most sample points are log-normal. Also, results revealed the concentration (%) of PAHs in top-sample D, E and F varied from 0.18 (Flu) – 20.25% (B[ghi]p), 0.78 (Ace) – 18% (I[123-cd]p) and 2.06 (B[k]f)/(B[b]f) – 18.02% (Phe) respectively. While in sub-profile sample D, E and F ranges from 0.37(Flu) – 41% (B[ghi]p), 0.73 (Flu) – 20.02% (B[ghi]p) and 0.61(Flu) - 23.04% (B[ghi]p) respectively. Percentage distribution of PAHs profile showed the prevalence of LPAHs in top-samples over HPAHs and HPAHs over LPAHs in sub-samples. Agglomerative dendogram of top and sub-samples showed that most PAHs homogeneity were built along molecular structure were LPAHs dominated the first and second cluster groups, while third and fourth cluster groups having HPAHs. The obtained PAHs values in this study could help to set a baseline concentration benchmark and evaluation of exposure risk to terrestrial and aquatic ecosystem in the rapidly urbanizing area since recorded mean concentrations are above permissible limits for soil use.

Key words: PAHs profile, distribution pattern, homogeneity and toxicity.

INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) are classes of organic compounds containing two or more fused aromatic rings coupled in linear, angular or cluster arrangements and containing carbon and hydrogen atoms only (CCME, 2008; WHO, 2002; Lubecki and Kowalewska 2010). Most point and non point sources (natural industrial and anthropogenic sources) of PAHs to the environment and to the atmosphere with emission from human activities predominating (WHO, 1998). The primary natural sources of air-borne PAHs are from forest fire and volcanic eruptions. While industrial power generation, waste incineration, production of asphalt, coal tar and coke, thermal and/or catalytic cracking of petroleum and aluminum are important stationary industrial sources accounting for about 50% of total annual PAHs (WHO, 1998). However, since closed systems and recycling are involved, the emission of PAHs during industrial production and processing are not generally thought to be important in comparison with the release of PAHs from incomplete combustion processes (WHO, 1998)

Octanol-water partition co-efficient (Kow), organic carbon-water partition co-efficient(Koc), Henry's Law constant, vapour pressure and aqueous solubility are chemical specific properties that are relevance in predicating the environmental fate, its multimedia partitioning behavior, bioavailability, resistance to biochemical degradation and toxicity of these un-Substituted PAHs, (WHO, 2000). PAHs are non-polar

hydrophobic compounds i.e. their solubility in water decreases as the molecular weight increases and exhibit high affinity for suspended particles, hence soil and sediments are major sinks for particles–sorbed contaminants such as PAHs (Wloka et al. 2014).

PAHs have been known for their carcinogenic properties, respiration and reproduction problems hence are called 'endocrine disruption' substances (EDSs) ATSDR, (1995). The distribution of low and high molecular weight PAHs (LPAHs and HPAHs) is functional in delineating petrogenic and pyrolitc sources and toxicity of PAHs. Soclo et al., (2000) stated that the higher the LPAHs/HPAHs ratio, the prevalence of petrogenic and the lower the ratio the prevalence of pyrolitic sources of PAHs respectively. Similarly, WHO/IPCS (1998), as adapted in CCME (2008), listed LPAHs (Nap, Ace, Acy, Flu, Ant and Phe) as other PAHs and HPAHs (Flt, Pyr, B[a]a, Chr, B[b]f, B[k]f, B[a]p, B[ghi]p, I[123-cd]p and D[ah]a) as carcinogenic and mutagenic PAHs among the 16 US-EPA PAHs.

Sapele city has an average human population of about 142, 652 and is home to several commercial and industrial production and processing facilities that releases PAHs to the environment without adherence to national environmental guidelines. Therefore, knowledge regarding the concentration and distribution characteristics of PAHs in soil profile is relevant for effective pollution partitioning. Thus, this study is aimed at investigating the concentration and distribution behaviour of PAHs profile along soil depth which hitherto is lacking in the study area. This may also serve as baseline data for future environmental pollution assessment, policy formulation and implementation.

Study area description

The study area designated as sample station D, E and F with geographical coordinates range of 05°51.019'N-05°51.088'N and 005°43.551'E-005°43.649'E, 05°52.318'N-05°52.347'N and 005°42.991'E-005°43.142'E and 05°50.246'N-05°50.824'N and 005°43.124'E-005°43.625'E respectively. Sample stations D, E and F are in Sapele which is located on the Benin River just below the confluence of River Ethiope and Jamison. It has a human population of about 142,652 with geographical coordinates range of 5° 54' – 5° 9' N and 5°40' - 5° 66'E. (Emoyan et al. 2015b) The weather and climatic conditions of the area are of the Niger Delta region, i.e. high temperature, rain forest zone and high humidity. The southwest monsoon wind (April – September) and the north east trade wind (October – March) are the two prevailing air masses of the area. Opofunso, (2007) stated that Niger Delta region is situated in the gulf of Guinea between 5° - 8°E and 3°- 6°N.

MATERIALS AND METHODS

Materials and methods are as reported in OIEWG, 1999; Cavalcante et al. 2009 and Emoyan et al. 2015a and b).

Sample collection and preparation

Top (0-15cm) and sub (16-30cm) soil samples were collected in November, December and January in three sampling stations as shown in Table 1. Stones and residual roots were removed from each soil core and stored in black polyethylene bags, lyophilised before extraction and analysis to avoid microbial degradation, photo-oxidation and evaporation of analytes.

Extraction and analysis

Extraction and analysis were carried out according to PAHs were extracted from 10 g of dry soil by a continuous extractor with 60 ml of methylen chloride for 8 hrs. Before extraction, the mixture of four deuterated PAHs (d10-acenaphthene, d10-phenanthrene, d12-chrysene and d12-perylene) was added to the sample as internal standard. Methylene chloride was removed by a rotary evaporator at temperature below 35 °C; the extract was purified by solid phase extraction after recovery with three portions of n-hexane (1 ml each). A glass column was filled with 8 g of Al_2O_3 after the addition of the sample onto the column. The removal of hydrocarbon and other non-polar impurities was done by use of 40 ml of n-hexane. PAHs were then eluted by means of methylene chloride (40 ml), the resulting solution was dried and redissolved in 1ml of isooctane. Quantification of PAHs was determined using Varian 300 gas chromatograph interfaced with flame ionization detector (GC-FID). The initial oven temperature was 60 °C for 10 min and was then increased to 120 °C at 5 °C min^{-1} and 120 –300 °C at 3 °C min^{-1}. The injector and detector temperatures were 200 °C and 300 °C respectively. Concentration determination was carried out by the internal standard method using Supelco and Merck standards; detection limit for PAHs is 0.001µg.g^{-1}. Concentration of PAHs was qualified and quantified through extrapolation from the standards.

Quality control

Reagents and chemicals are of chromatographic grade. A standard solution of the anlytes contains the following sixteen PAHs: Nap, Acy, Ace, Flu, Phe, Ant, Flt, Pyr, Chr, B[a]a, B[b]f, B[k]f, B[a]p, I[123-cd]p. B[ghi]p and D[ah]a. Working standards were prepared by dilution with isooctane. Quantitative determinations were performed by means of four deuterated PAHs (1000 µg.ml^{-1} each in methylene chloride. Equipment and containers were thoroughly cleaned to prevent cross contamination during sample collection and preparation. Four sub-samples were used to form a composite to avoid excessive dilution of individual samples.

RESULTS AND DISCUSSION

PAHs distribution and toxicological significant

The evaluation of individual PAH distribution is valid in

Table 1. Depth-Wise Comparative Descriptive Statistical Summary of PAHs at Sample Station D, E and F (μg/g^{-1}). Where: R = Range, $\overline{X}$ = Mean, σ = Standard deviation, M=Median and GM = Geometric Mean

Sample Station	**D**					**E**					**F**				
PAHs	**R**	$\overline{X}$	**Σ**	**M**	**GM**	**R**	$\overline{X}$	**Σ**	**M**	**GM**	**R**	$\overline{X}$	**Σ**	**M**	**GM**
Nap	0.214 – 12.476	3.151	3.876	2.348	1.871	0.214 – 44.321	7.310	14.246	1.714	2.125	1.536 – 9.926	4.845	4.467	3.074	3.605
Acy	0.948 – 3.949	1.975	1.180	1.451	1.746	0.894 – 2.485	1.866	0.685	2.043	1.744	0.676 – 3.496	2.430	1.045	2.636	2.164
Ace	1.214 – 3.452	2.333	1.583	2.333	2.047	0.821 – 2.198	1.722	0.613	1.935	1.612	1.114 – 5.211	2.092	1.753	1.454	1.715
Flu	0.415 – 1.215	0.696	0.377	0.578	0.628	0.114 – 3.451	1.684	1.294	1.884	1.017	2.568 – 6.547	3.875	1.518	3.145	3.665
Phe	0.241 – 107.710	21.762	35.271	4.746	6.628	2.151 – 102.178	33.798	36.069	9.385	16.688	2.457 – 21.394	10.898	9.206	9.871	7.558
Ant	0.251 – 10.211	6.571	5.494	9.251	2.873	1.458 – 8.189	3.991	3.661	2.327	3.029	1.356 – 7.726	3.412	2.911	2.284	2.716
Flt	0.64 – 53.353	14.251	13.323	9.866	9.616	5.134 – 22.871	14.018	5.713	12.764	12.865	0.235 – 5.456	2.978	2.156	3.111	1.871
Pyr	2.128 – 28.174	13.967	10.964	13.317	9.399	2.119 – 28.145	13.882	9.202	12.628	10.517	3.433 – 4.325	3.841	0.451	3.764	3.823
Chr	3.345 – 33.922	17.423	12.921	21.468	12.420	0.125 – 25.381	12.852	9.162	13.538	6.335	1.254 – 1.254	1.254	na	1.254	1.254
B[a]a	2.212 – 8.485	5.318	2.105	5.290	4.921	1.942 – 15.384	7.111	4.910	7.451	5.585	0.542 – 2.561	1.552	1.428	1.552	1.178
B[a]p	0.452 – 39.802	15.013	16.831	7.172	6.075	1.831 – 20.425	10.783	6.517	8.848	8.617	2.113 – 4.347	3.230	1.580	3.230	3.031
B[b]f	0.311 – 8.423	2.907	2.250	2.895	2.054	1.125 – 25.38	8.673	7.317	6.129	6.280	1.126 – 5.213	2.955	1.869	2.534	2.458
B[k]f	0.521 – 11.385	4.106	3.169	3.414	3.070	1.125 – 19.356	9.404	5.507	7.806	7.563	1.126 – 15.121	7.172	7.013	2.552	4.373
B[ghi]p	20.450 – 267.313	78.098	98.135	27.925	45.623	10.851 – 115.115	46.445	36.092	42.561	34.870	1.384 – 4.488	2.936	2.195	2.936	2.492
I[123cd}p	2.521 – 81.384	31.719	22.784	26.818	22.801	1.345 – 85.634	32.860	26.002	25.268	21.609	3.318 – 6.354	4.872	1.091	4.984	4.765
D[ah]a	2.521 – 55.361	29.134	17.342	25.117	22.026	2.438 – 52.112	25.635	17.010	18.117	19.067	4.136 – 25.189	12.721	7.652	13.316	10.651

Where n= 8

determining the susceptibility of PAH to biotic and/or abiotic degradation. To this end, PAHs and their percentage distribution in the study area were evaluated for total mean (Table 1), percentage distribution of top and sub profile (Figure 1-7). Analysis of results in sample station D showed that the mean concentration of PAHs ranged between 0.696 μg.g^{-1} (Flu) and 78.098 μg.g^{-1} (B[ghi]p), while the total PAHs concentration ranged between 15.399 μg.g^{-1} (Dt) and 325.818 μg.g^{-1} (Ds). The mean concentration of PAHs at sample station E ranged between 1.684 μg.g^{-1}(Flu) and 46.445 μg.g^{-1} (B[ghi]p), while the total PAHs concentration ranged from 8.091 μg.g-1 (Et) – 258.529 μg.g^{-1} (Et). Similarly, at sample station F, the mean concentration of PAHs ranged from 1.254 μg.g^{-1} (Chr) – 12.721 μg.g^{-1}(D[ah]a). The total PAHs concentration ranged between 1.356 μg.g^{-1}(Fs) and 59.77μg.g^{-1} (Fs). As shown in Table 1, the relatively high observed closeness of the geometric mean to median and the reverse for arithmetic mean to standard deviation of PAHs concentration is an indication of log-normal distribution. The log-normal distribution of PAHs concentration in the study area is a product of a high concentration of PAHs in few sample points (Ogbeibu, 2005; Emoyan 2014 and Emoyan et al., 2015b).

At sample station D, the percentage distribution of the total mean, mean of top and sub profile samples in Figure 1 ranges from 0.28 (Flu) – 31.44 (B[ghi]p), 0.18 (Flu) – 20.25 (B[ghi]p) and 0.37(Flu) – 41 (B[ghi]p) respectively. In the same vein, Figure 2 showed the percentage distribution of total mean, mean of top and sub profile samples at sample station E, the ranges are from 0.73 (Flu) – 20.02 (B[ghi]p), 0.78 (Ace) – 18 (I[123-cd]p) and 0.61(Flu) - 23.04(B[ghi]p) respectively. Also at sample station F, Figure 3, the percentage distribution of total mean, mean of top and sub profile samples ranged from 1.77 (Chr) – 17.9 (D[ah]a), 2.06 (B[k]f)/(B[b]f) – 18.02 (Phe) and 0.82 (B[a]a) – 22.27 (D[ah]a) respectively.

Polycyclic aromatic hydrocarbons are susceptible to degradation in the environment through biotic and/ or abiotic processes (Earl et al., 2003). In soil or sediments, microbial metabolism is the major process for degradation of PAHs (WHO/IPCS, 1998), although microbial degradation is limited to the

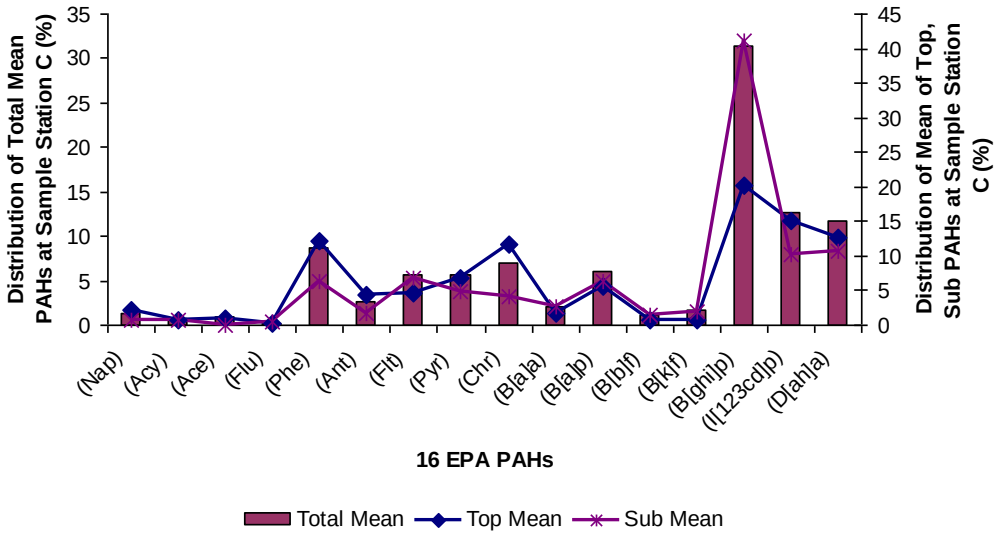

Figure 1: Distribution of total mean, mean of top and sub samples in sample station D

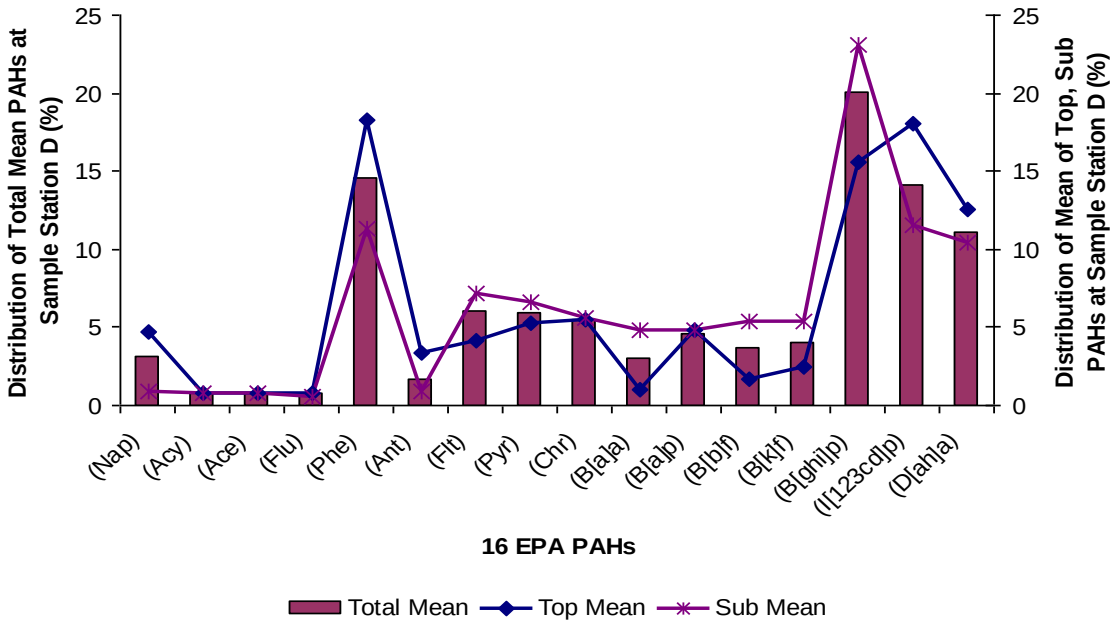

Figure 2: Distribution of total mean, mean of top and sub samples in sample station

bioavailable fractions in soil-pore water or of the surfaces of the soil particles (Miller and Alexander, 1991). Because PAHs have widespread distribution and significant potential for causing adverse human physiological toxicity, the Ministers of the Environment and of Health from the Federal Government of Canada developed and collated sets of criteria for environmental compliance. Since toxicity of PAHs depends on a number of variables which includes; the species, route of exposure and molecular structure of the PAHs, the observed individual and/or combined LPAHs and HPAHs in the study area is of toxicological significance since observed values are relatively higher than tabulated standards (Table 2).

Profile pattern and homogeneity

Stratifying PAHs into different class depending on the number of aromatic rings present in their structure explore the identification of PAHs in terms of pyrolitic or petrogenic

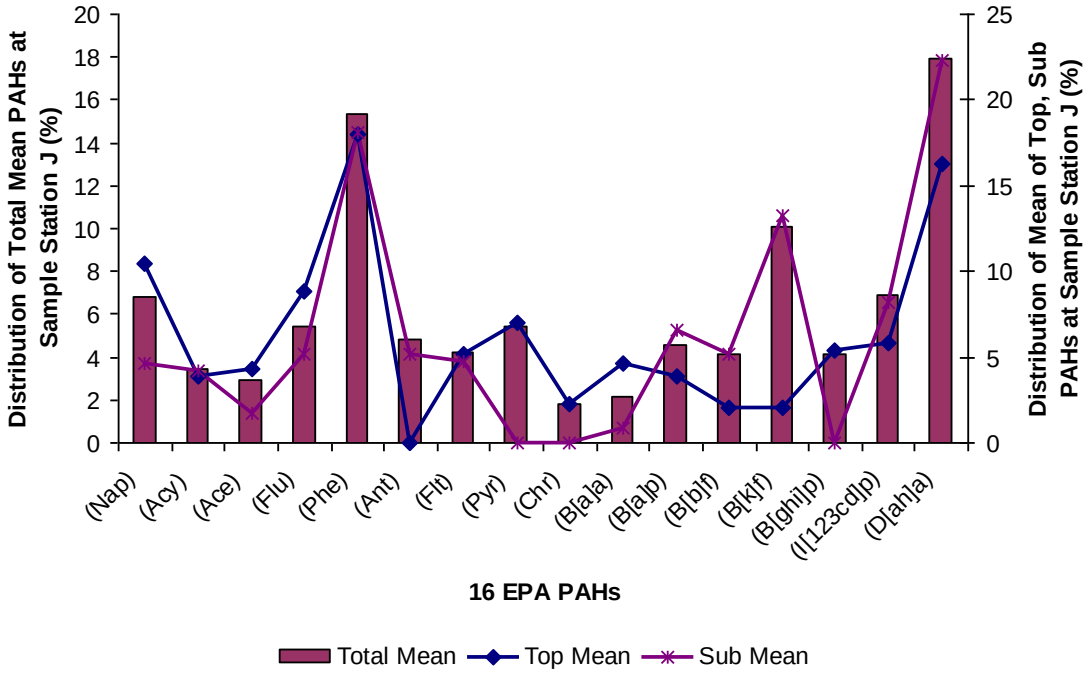

Figure 3: Distribution of total mean, mean of top and sub samples in sample station F

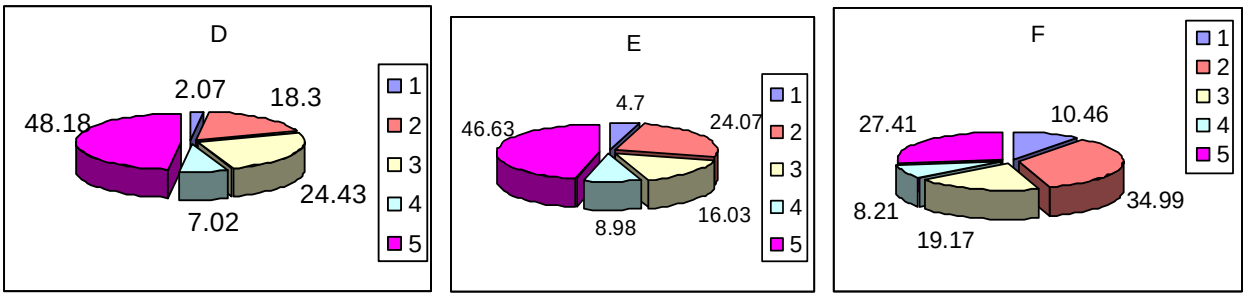

Figure 4: Mean concentration distribution of Ring PAHs in Top samples station of D, E and F

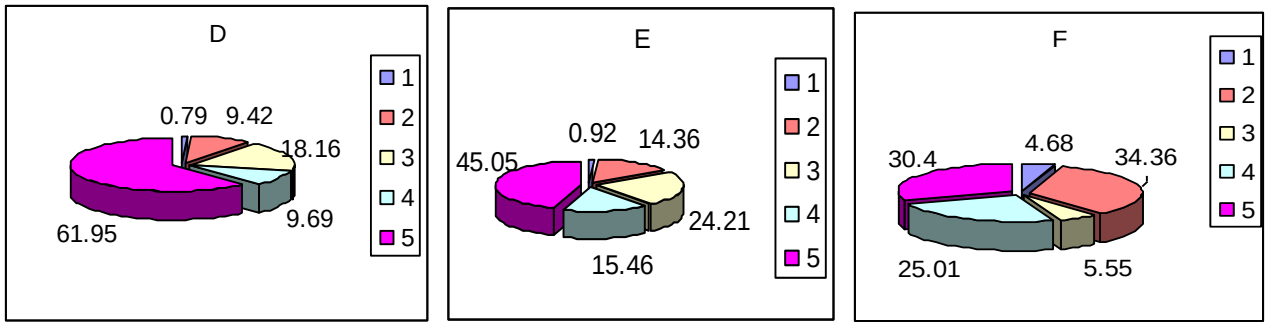

Figure 5: Mean concentration distribution of Ring PAHs in Sub samples station of D, E and F
Where: 2 ring, 3 Ring, 4 Ring, 5 Ring and 6 Ring

sources. Within the 16 US-EPA PAHs, 2 and 3 ring PAHs belong to LPAHs which are predominantly petroleum PAHs, while 4, 5 and 6 ring PAHs belong to HPAHs which are predominantly pyrolitic PAHs (Soclo et al., 2000; Liu et al., 2009).

The percentage distribution of aromatic rings (2, 3, 4, 5,

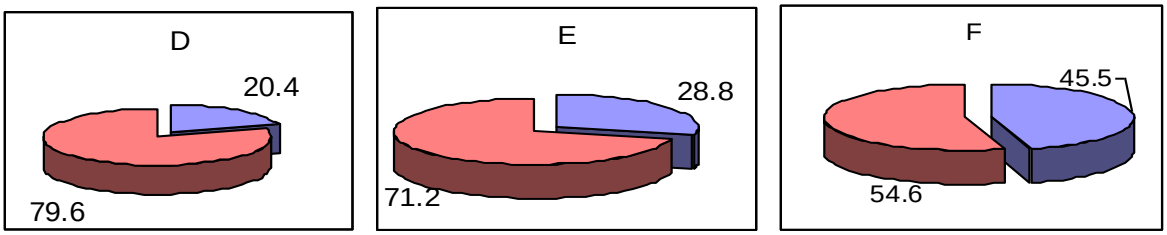

Figure 6: Mean concentration distribution of LPAHs and HPAHs in Top sample station D, E and F (%)

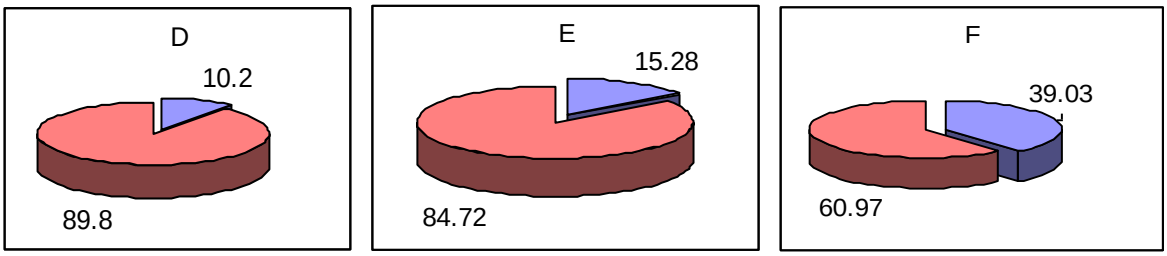

Figure 7: Mean concentration distribution of LPAHs and HPAHs in Sub sample station D, E and F (%)
Where: LPAHs, HPAHs

Table 2: Netherland, Danish and New Jessey's Permissible Limits for Soil Use (μg.g^{-1} d.w) (CCME 2008)

	NMPC$_{soil}$	Danish DSQC$_{soil}$	New Jersey	
PAHs			**RDCsoil**	**NRDsoil**
Nap	0.14		230	4.200
Acy				
Ace			3,400	10,000
Flu			2300	10,000
Phe	0.51		10,000	10,000
Ant	0.12			
Flt	2.6		2,300	10,000
Pyr			1,700	10,000
Chr	10.7		9	40
B[a]a	0.25		0.9	4
B[a]p	0.26	0.1* , 0.1**	0.66	0.66
B[k]f	2.4		0.9	4
B[ghi]p	7.5			
B[b]f			0.9	4
D[ah]a		0.1*	0.66	0.66
I[123-cd]p				
∑PAHs		1.0*, 1.5**		

and 6) in top and sub PAHs profile samples (Figure 4 and 5) showed that 2 and 3 ring PAHs in top profile samples ranged, from 2.07(D) - 10.46(F) and 18.30(D) – 34.99(F) respectively. Also, 4 and 5 PAHs ranged from 16.03(E) – 24.43 (D) and 7.02(D) 8.98(E) respectively. While 6 ring percentage ranged from 27.41(F) – 48.18(D). Similarly, 2 and 3 ring PAHs in sub profile samples ranged from 0.79(D) - 4.68(F) and 9.42(D) -34.36(F) respectively. In the same vein, 4 and 5 rings PAHs ranged from 5.55(F) – 24.21% (E) and 9.69(D) – 25.01(F) respectively while 6 ring ranged from 30.40(F) – 61.95(D). Observation of percentage distribution of rings showed that six > five > four > three > two.

The percentage distribution of LPAHs and HPAHs in top samples ranged from 20.37(D) – 45.45 (F) and 54.55 – 79.63(D) respectively. Also, percentage distribution of LPAHs and HPAHs in sub samples ranged from 10.21(D) - 39.03(F) and 60.97(F) – 89.79(D) respectively. This is because two and 3 rings PAHs are more sensitive to photo-oxidation than 4, 5 and 6 rings PAHs. Also, due to high degree of lipophilicity and partial solubility in water, 4, 5 and 6 ring PAHs exhibit much greater tendency to be

Table 3: Summarized half-Lives for PAHs in soil, Adapted in Part (Mackay et al., 1991).

PAH	Ring	Mean half-life (h)	Range of half-lives (h)
Nap	2	1700	1000 – 3000
Acy	3	Na	
Ace	3	5500	3000 – 1000
Flu	3	5500	3000 – 1000
Phe	3	5500	3000 – 1000
Ant	3	5500	3000 – 1000
Flt	4	17000	1000 – 3000
Pyr	4	17000	1000 – 3000
Chr	4	17000	1000 – 3000
B[a]a	4	17000	1000 – 3000
B[a]p	5	Na	
B[b]f	5	17000	1000 – 3000
B[k]f	5	17000	1000 – 3000
B[ghi]p	6	Na	
I[123-cd]p	6	17000	1000 – 3000
D[ah]a	6	17000	1000 – 3000

na = not available

asorbed to soil or sediment - which makes them unavailable for biotic degradation – rather than partition into water or air like their 2 and 3 ring counterparts.

Observation of results in Figure.4-7 showed a general trend in the distribution of PAHs from LPAHs – HPAHs. While Nap, Acy, Ace, Phe, Flu, and Ant dominated the lower limits in terms of concentration of PAHs, B[ghi]p, D[ah]a, B[k]f, B[b]f, I[123-cd]p, B[a]a, Chr, B[a]p dominated the upper limits. This phenomenon in which the percentage of HPAHs are higher than LPAHs could be evaluated on the basis that lower than four (Nap, Acy, Ace, Flu, Phe and Ant) ring PAHs can be degraded abiotically in soil through photo oxidation, and may also be lost from soil surface through volatilization (ATSDR, 1995; WHO/IPCS, 1998; Wild and Jones, 1992). On the other hand, volatilization was found not to be an important route to loss Flt, Pyr, Chr, B[a]a, B[b]f, D[ah]a, B[a]p and I[123-cd]p (Park et al., 1990), hence the higher concentration of HPAHs in all samples. Bioticaly, the rate and extent of degradation of PAHs occurs with much higher rates (for all PAHs) under aerobic compared to anaerobic conditions (US-EPA, 1999).

Figure.4-7 showed low percentages of 2 and 3 rings (LPAHs) in top and sub profile samples than 4, 5 and 6 rings (HPAHs) carcinogenic/genotoxic and other PAHs. This trend could be attributed to the physicochemical properties of PAHs. PAHs become increasingly less soluble in water with an increase in number of aromatic rings and hence increased molecular weight. Naphthalene, a two-ring PAH is the most soluble with volatilization from soil reported as 30% in 48hrs (WHO/IPCS, 1998). However, volatilization is also likely to be significant for those PAHs with similar physicochemical properties to Nap (i.e. with two or three rings). While for the higher PAHs (i.e. with four or more rings), volatilization from soil surfaces is described as negligible (WHO/IPCS, 1998). This is a direct consequence of low Henry's law constant for these compounds and higher Kow (relative to Nap), resulting to greater sorption to soil organic carbon (SOC). LPAHs hence other PAHs tends to oxidize and volatilize at a faster rate while HPAHs (carcinogenic/genotoxic) will degrade partially at slow rate to yield various oxygenated metabolites (Earl et al*.,* 2003). Low PAHs may volatilize as indicated by the volatilization half-lives of Nap 0.4-3.2 hrs and Ant 17 hrs (CCME, 2008), while HPAHs such as Pyr has a volatilization half-live of 120 and 283 hrs (Lyman et al., 1990). Similarly, the biodegradation rate of LPAHs is in the following order of half-lives with Phe, Flu, and Ant having 1656, 1536 and 672 hrs respectively. While HPAHs have longer half-lives with B[k]f, D[ah]a and B[a]a having 3432, 4296, 2952 hrs respectively. This could be attributed to the variables nature of half-lives as shown in Table 3. The variation in the values reported for each PAH is indicative of a number of factors that affect the degradation (biotic or abiotic and aerobic or anaerobic) of PAHs in soil - transformation products, type and extent of bacterial/fungi metabolism, competence of the microbial community, and environmental factors such as: pH, temperature, salinity, oxygen concentration, nutrients, light intensity, soil type as well as the presence of co-substrates and environmental matrix, concentration and bioavailability of PAHs (affected by SOC) and ageing - (Earl et al., 2003, Emoyan et al., 2015b). Also, because of their high degree of lipophilicity and sparingly soluble in water, HPAHs exhibit much greater tendency to be sorbed to soil or sediment, rather than partition into water or air like their LPAHs counterparts, hence a higher concentration of HPAHs over LPAHs. This trend of distribution pattern PAHs have been reported (Lubecki and Kowalewska, 2000; Perra et al., 2009; Emoyan, 2014).

Since degradation of PAHs cannot be viewed as linear

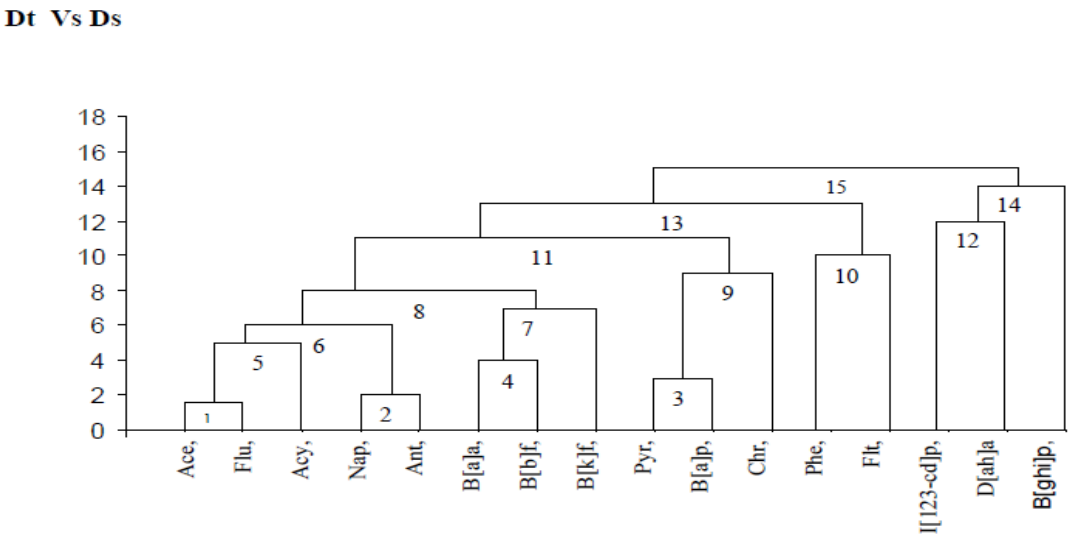

Figure 8: Dendogram showing complete linkages of hierarchical clustering between PAHs in top and sub sample at station D

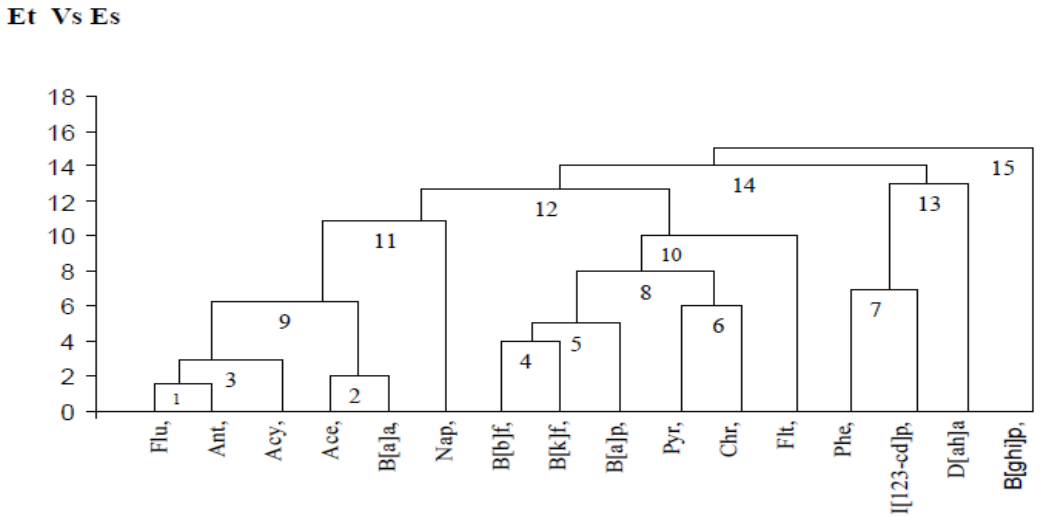

Figure 9: Dendogram showing complete linkages of hierarchical clustering between PAHs in top and sub sample at station E

decay – qualities that grow or decrease at constant rate-process (Earl et al., 2003; Jones et al., 1996), the distribution of LPAHs and HPAHs in this study could be ascribed to the complex nature of factors responsible for the degradation of PAHs in soil matrix and the effect PAHs bioavailability has on biodegradation. Therefore, the phenomenon in which two and three ring PAHs tend to relatively undergo biotic and abiotic degradation over four, five and six ring PAHs that prefers bioaccumulation will tend to quantitatively eliminate the existence of petrogenic and/or pyrolitic sources of PAHs using PAHs isomer pair ratio (Emoyan et al., 2015b).

Homogeneity of PAHs has been used to relate physiochemical properties and sources of PAHs in various environmental compartments (Liu et al., 2009 and Emoyan, et al., 2015a). Cluster agglomerative dendograme was used to identify homogenous pairs of individual PAHs in top and sub soil profile in the study area. Sample station D (Figure 8) differentiated PAHs into five cluster groups. The first cluster group (Ace, Flu, Acy, Nap and Ant) is joined with cluster group two (B[a]a, B[b]f, and B[a]f] at Stage 8, while group cluster group three (Pyr, B[a]p and Chr) is joined to cluster group two at Stage 11. Similarly, cluster group four (Phe and Flt) and five (I[123-cd]p, D[ah]a and B[ghi]p) are joined to group three and four at Stage 13 and 15 respectively. The homogeneity of PAHs in top and sub profile samples at sample station E is shown in Figure 9. The first cluster group (Flu, Ant, Acy, Ace, B[a]a and Nap) is

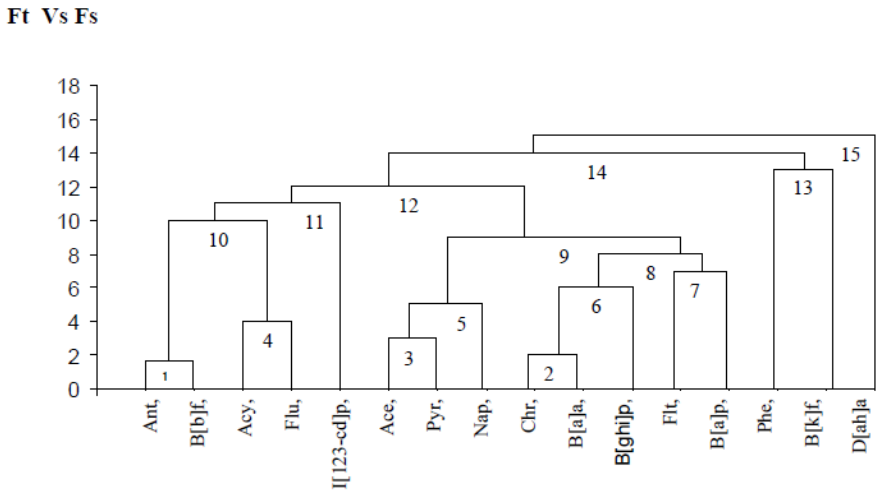

Figure 10: Dendogram showing complete linkages of hierarchical clustering between PAHs in top and sub sample at station E

connected with cluster group two (B[a]f, B[k]f, B[a]p, Pyr, Chr and Flt) at Stage 12. Cluster group three (Phe, I[123 – cd]p and D[ah]a) is connected to cluster group one and two at Stage 14. While an *outlier* B[ghi]p is connected to other cluster groups at stage 15. Also, the relationship of individual PAHs in top and sub sample at sample station F. (Figure 10) showed that cluster group one (Ant, B[b]f, Acy, Flu and I[123 – cd]p) is connected to cluster group two (Ace, Pyr, and Nap) and three (Chr, B[a]a, B[ghi]p, Flt, and B[a]p) at Stage 12, while cluster group four (Phe, B[a]f) connected cluster groups one, two and three at stage 14. The *entropy* member (D[ah]a) is connected to other cluster groups at stage 15. Results of agglomerative dendogram of top and sub profile samples (Figures 8, 9 and 10) showed that most PAHs homogeneity are built along molecular structure i.e. 2-3 rings (LPAHs) and 4-6 rings (HPAHs) with the first cluster groups dominated with LPAHs. This kind of clusters group formation has been reported, (Spiff et al., 2004; Emoyan, 2014; Emoyan et al., 2015a; Bertolotto et al., 2009).

CONLUSION AND RECOMMENDATIONS

Descriptive statistics showed that the obtained concentration and distribution of PAHs in most sample points are log-normal and are consistent with results reported from other soil matrix. Percentage distribution of PAHs profile showed the prevalence of LPAHs in top profile samples over HPAHs and HPAHs over LPAHs in sub profile samples. Agglomerative dendogram of top and sub profile samples showed that most PAHs homogeneity are built along molecular structure with LPAHs dominating the first and second cluster groups while third and fourth groups having HPAHs. The obtained PAHs values in this study could help to set a baseline concentration benchmark and evaluation of exposure risk to terrestrial and aquatic organisms in this rapidly urbanizing area.

REFERENCES

ATSDR (1995). Toxicological Profile for Polycyclic Aromatic Hydrocarbons. U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry. Pp. 487.

Bertolotto RM, Ghioni F, Frignani M, Alvarado-Aguilar D, Bellucci LG, Cuneo C, Picca MR Gollo E (2003). Polycyclic Aromatic Hydrocarbons in Surficial Coastal Sediments of the Ligurian Sea. Baseline/Marine. Pollution Bulletin. (46): 903-917.

Cavalcante RM, Sousa FW, Nascimento RF, Silveira ER Freire GSS (2009). The Impact of Urbanization on Tropical Mangroves (Foertaleza, Brazil): Evidence from PAH Distribution in Sediments. J. Environ. Manag. (91): 328-335.

CCME (2008). Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health: Benzo [a] Pyrene. In: Canadian Environmental Quality Guidelines. Canadian Council of Ministers of the Environment, Winnipeg, Canada. Pp 235.

Earl N, Cartwright CD, Horrocks SJ, Worboys M, Swift S, Kirton A, Askan AU, Kelleher H Nancarrow DJ (2003). Fate and Transport of Selected Contaminants in the Soil Environment. Draft Technical Report P5-079/TR1. Environmental Agency, Bristol. Pp. 182.

Emoyan OO (2014). Quantification and Distribution Characteristics of Polycyclic Aromatic Hydrocarbons (PAHs) in soil Profiles of Western Delta, Nigeria. IOSR J. Environ. Sci., Toxicol. Food Technol. 8(3) 1. 31-39.

Emoyan OO, Agbaire PO, Akporido SO (2015b). Variability in Polycyclic Aromatic Hydrocarbons (PAHs) Isomer Pair

Ratio: Source Identification Concern. Int. J. Environ. Monitoring and Analysis.

Emoyan OO, Akporido SO Agbaire PO. (2015a). Seasonal Concentration Variation of Polycyclic Aromatic Hydrocarbons (PAHs) of Soils at Sapele Municipality, Nigeria. Am. J. Environ. Eng. Sci.2(2): 9-16.

Emoyan OO, Agbaire PO, Akporido SO (2015b). Variability in Polycyclic Aromatic Hydrocarbons (PAHs) Isomer Pair Ratio: Source Identification Concern. Int. J. Environ. Monitoring and Analysis. 3(3):111-117.

Jones KC, Alcock RE, Johnson DL, Northcott GL, Semple KT Woolger PJ (1996). "Organic Chemicals in Contaminated Land: Analysis, Significance and Research Priorities". Land Contamination and reclamation 4(3): 189-197.

Liu Y, Chen L, Huang QH, Li WY, Tang YJ, Zhao JF (2009). Source Apportionment of Polycyclic Aromatic Hydrocarbons (PAHs) in Surface Sediments of the Huangpu River, Shanghai, China. Science of the Total Environment. 407:2931–2938.Crossref

Lubecki G, Kowalewska G (2010). Distribution and Fate of Polycyclic Aromatic Hydrocarbons in Recent Sediments from the Gulf of Gdansk (SE Baltic). Oceanologia. 54 (4):669-703.Crossref

Lyman WJ, Reehl WF Rosenblatt DH (Eds.) (1990). Handbook of Chemical Property Estimation Methods. Washington DC, American Chemical Society. Pp 913

Mackay D, Shiu WY, Ma KC (1991). Illustrated handbook of physico-chemical properties and environmental fate for organic chemicals: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins and Dibebenzofurans. Boca Raton Publishers, pp. 367.

Miller M, Alexander M (1991). "Kinetics of Bacterial-Degradation of Benzylamine in a Montmorillonite Suspension." Environ. Sci. Technol. 25:240-245.Crossref

Ogbeibu AE (2005). Biostatistics: A Practical Approach to Research and Data Handling. Mindex Benin City. Pp 264.

OIEWG (1999). Sampling Protocols and Analytical Methods for Determining Petroleum Products in Soil and Water. Ministry for the Environment Wellington. Pp. 40.

Opafunson ZO (2007). 3D Formation Evolution of an oil Field in the Niger Delta Area of Nigeria using Schlumbeger Petrol Workflow Tool. J. Eng. Appl. Sci. 2(11): 1651-1660.

Park KS, Simms RC, Dupont RR, Doucette WL, Matthews JE (1990). "Fate of Polynuclear Aromatic-Hydrocarbons Compounds in two Soil Types: Influence of Volatilization, Abiotic Loss and Biological Activity." Environ. Toxicol. Chem. 9: 187-195.Crossref

Perra G, Renzi M, Guerranti C, Focardi SE (2009). Polycyclic Aromatic Hydrocarbons Pollution in Sediments: Distribution and Sources in a Lagoon System (Orbetello Central Italy). Transitional Waters Bulletin. 3: 45-58.

Soclo HH, Garrigues P, Ewald M (2000). Origin of Polycyclic Aromatic Hydrocarbons in Coastal Marine Sediments: Case Studies in Cotonou (Benin) and Aquitaine (France) Areas. Maine Pollution Bulletin. 40: 387-396.

Spiff AI, Horsfall M Jnr (2004). Trace Metal Concentrations in Inter-Tidal Flat Sediments of the Upper New Calabar River in the Niger Delta Area of Nigeria Scientia Africana. 3(1): 19-28.

US-EPA (1999). Guidance of Conducting Health Risk Assessment of Chemical Mixtures. Risk Assessment Forum Technical Panel Report. External Scientific Peer Review. Pp188

WHO/IPCS (1998). Environmental Health Criteria 202: Selected Non-Heterocyclic Polycyclic Aromatic Hydrocarbon. International Program on Chemical Safety, United Nations Environmental Program, World Health Oganization. Geneva. Pp. 883.

Wild SR, Jones KC (1992). Organic Chemicals Entering Agricultural Soils in Sewage Sludges: Screening for their Potentail to Transfer to Crop Plants and Livestock. Science of Total Environment. 119: 85-119.Crossref

Włóka D, Kacprzak M, Grobelak A, Grosser A, Napora A (2014). The Impact of PAHs Contamination on the Physicochemical Properties and Microbiological Activity of Industrial Soils. Polycyclic Aromatic Compounds. Crossref

World Health Oganization. (2002). Health Risk of Persisent Organics Pollutants from Long-Range Transboundary Air Pollution. European Centre for Environment and Health. Bonn. P. 200