

## Quantification and Distribution Characteristics of Polycyclic Aromatic Hydrocarbons in Soil Profiles of Western Delta, Nigeria.

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**Abstract:** Polycyclic Aromatic hydrocarbons (PAHs) are large groups of organic compounds with two or more fused aromatic rings containing carbon and hydrogen only. They are by-products of combustion and are present in industrial chemical wastes, biogenesis and volcanic eruptions. The U.S. Environmental Protection Agency considered them as priority pollutants. The concern of this study is to investigate the depth-wise distribution of top (0-15cm) and sub (16-30cm) soil of 16 PAHs in 16 urban and 8 control samples in Western-Delta Nigeria. After extraction and purification, quantification of PAHs was done using GC-FID. Reagents used are of chromatographic grade. The total concentration of 16 PAHs varied between 1.14 and 652.81  $\mu\text{g}\cdot\text{g}^{-1}$  dry weight. Cluster analysis showed the existence of 6 cluster groups with sample points B<sub>62</sub>, C<sub>19</sub>, A<sub>21</sub>, A<sub>51</sub> and A<sub>41</sub> as entropy members. Pearson Correlation matrix indicates positive and high correlation between sample points at  $\alpha = 0.01$  and  $r = \geq 0.70$  for most sample pairs. Depth-wise distribution of PAHs showed the existence of relatively low percentage concentration of PAHs in top soil (0.18 B[g]p – 40.43 Phe) over sub soil (0.10 Acy – 45.15 Phe). Percentage distribution of ring PAHs showed higher concentration of HPAHs over LPAHs in sample site A and B than the control site (C). Source identification revealed a dominance of pyrolytic over petrogenic PAHs. Descriptive statistics showed that the obtained concentration of PAHs in most sample points has log-normal distribution and are consistent with results reported from other soil matrix. The obtained PAHs values in this study could help to set a baseline concentration benchmark and evaluation of exposure risk to organisms in the rapidly urbanizing area.

**Keywords:** Pyrolytic and Petrogenic PAHs, Soil Profile Contamination, Western Delta, Nigeria.

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### I. Introduction:

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds with two or more fused aromatic rings in linear, angular or cluster arrangement and containing carbon and hydrogen only (Zeng, 2000, CCME, 2008). The octanol water partition coefficient (Koc), Henry's law constant, vapour pressure and aqueous solubility are chemical specific properties that are of direct relevance in predicting environmental fate, its multimedia behaviour, bioavailability and resistance to biotic and abiotic degradation (CCME, 2008). PAHs are formed mainly as a result of pyrolytic processes especially the incomplete combustion of organic materials during industrial and anthropogenic activities such as: processing of coal and crude oil; combustion of natural gas and refuse; vehicular emission; tobacco smoke and natural processes such as carbonization (Yunker *et al.*, 2002; Macdonald *et al.*, 2005).

PAHs have been tagged priority pollutants due to their carcinogenicity, induce tumor, immunodeficiency, reproduction and respiratory problems hence are classified as "endocrine disruption substances" (ATSD, 1995). Several researches have established a varied amount of PAHs produced by both stationary and diffused sources (Kamaljit *et al.*, 2010; Krauss and Wilcke, 2003; Morillo *et al.*, 2008). The greater amount of PAHs observed in most urban soils and the close proximity of these soils to human population may increase the probability of human exposure or dermal contact (Abrahams, 2002). Therefore, investigating PAHs concentration and distribution in urban soil is relevant for discerning the sources, fate and transport in soil matrix. Consequently, this research is aimed at evaluating the distribution of PAHs in soil profile of the study area.

### II. Materials And Method

**Study Area Description.** The study area is located on the Benin River just below the confluence of River Ethiopie and Jamison. It has a human population of about 142,652 with geographical coordinates of 5° 54' – 5° 9' N and 5° 40' – 5° 66' E. 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. The Niger Delta region is situated in the gulf of Guinea between 5° - 8°E and 3° - 6°N (Opofunso, 2007).

**Table 1: Study Area Showing Sample Sites, Sample Point, and Geographical Coordinates.**

S/N	SAMPLING SITE	SAMPLE POINT	COORDINATE
1	A	1, 11, 41, 51	05°51.470'N-05°51.933'N 005°41.589'E-005°41.674'E
		21, 31, 61, 71	
2	B	2, 12, 42, 52	05°51.914'N-05°51.959'N 005°41.622'E-005°41.707'E
		22, 32, 62, 72	
3	C	9, 19, 49, 59	05°53.553'N-05°53.926'N 005°37.151'E-005°38.461'E
		29, 39, 69, 79	

**Sample Collection and Preparation.** Top (0-15cm) and sub (16-30cm) soil samples were collected in November, December and January in three sampling sites 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, photooxidation and evaporation of analytes.

**Extraction and Analysis:** The PAHs were extracted from 10 g of dry soil by a continuous extractor with 60 ml of methylene 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<sub>2</sub>O<sub>3</sub> 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<sup>-1</sup> and 120 –300 °C at 3 °C min<sup>-1</sup>. 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<sup>-1</sup>. 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 analytes 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<sup>-1</sup> 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.

### III. Results And Discussion

Statistics summary of the concentration of sixteen PAHs in forty- eight samples representing top and sub sampling in twenty- four sample points are presented in Table 2, 3 and 4. In sampling station A, ΣPAHs ranged from 57.32 (A61t) – 652.81 µg.g<sup>-1</sup> (A41t) with mean PAHs values ranging from 0.5 (Nap) – 78.38 µg.g<sup>-1</sup> (B[ghi]p). Similarly, at sampling station B, ΣPAHs ranged between 11.77 (B72t) and 106.89 µg.g<sup>-1</sup> (B2s) with mean PAHs concentration ranging from 0.93 (Nap) – 11.63 µg.g<sup>-1</sup> (B[ghi]P). At sampling site C, the ΣPAHs concentration ranged between 1.14 µg.g<sup>-1</sup> (C39t) and 51.49 µg.g<sup>-1</sup> (C19s), with mean PAHs values ranging from 0.23 (B[gl]p) and 24.24 µg.g<sup>-1</sup> (Phe).

**Table 2: Statistics Summary of Measured PAHs at Sample Station A (µg / g<sup>-1</sup>)**

PAHs	Range	Mean	Standard Dev.	Median	Geomean	Standard Skewness	Standard Kurtosis
Nap	0.04 – 1.68	0.56	0.72	0.13	0.22	1.22	0.17
Acy	0.12 – 4.31	1.58	1.72	0.78	0.79	0.95	-0.94
Ace	0.41 – 1.24	0.83	0.58	0.83	0.72	na	na
Flu	1.31 – 8.46	3.77	2.36	3.12	3.23	1.33	0.77
Phe	2.42 – 89.78	12.24	27.28	3.15	4.75	3.15	9.94
Ant	4.25 – 186.17	40.61	54.15	7.62	17.40	1.98	4.43
Flt	6.34 – 109.25	19.27	33.76	8.03	10.64	3.00	8.98
Pyr	3.24 – 37.04	13.41	8.26	12.49	11.35	1.78	4.94
Chr	3.15 – 90.36	19.44	30.54	6.02	8.82	1.99	2.87
B[a]a	5.12 – 18.32	8.52	3.93	7.43	7.95	2.31	6.03
B[a]p	2.15 – 67.34	13.90	17.20	9.15	8.88	2.86	9.02
B[b]f	4.15 – 28.35	10.71	7.21	8.37	8.98	1.54	1.91
B[k]f	4.15 – 28.35	10.53	6.13	10.10	9.26	1.98	5.28
B[ghi]p	15.85 – 241.10	78.38	71.01	61.32	53.65	1.32	1.01
I[123cd]p	2.43 – 31.56	17.69	9.85	19.02	14.25	-0.15	-1.43
D[ah]a	2.43 – 44.41	16.67	12.14	14.02	13.00	1.34	2.18

**Table 3: Statistics Summary of Measured PAHs at Sample Station B ( $\mu\text{g} / \text{g}^{-1}$ )**

PAHs	Range	Mean	Standard Dev.	Median	Geomean	Standard Skewness	Standard Kurtosis
Nap	0.11 – 2.14	0.93	0.54	0.92	0.74	0.54	1.37
Acy	0.89 – 3.46	1.48	0.77	1.14	1.35	1.85	3.09
Ace	0.46-3.46	2.00	1.02	2.11	1.71	0.09	-1.17
Flu	1.35 – 7.11	4.14	2.31	4.35	3.48	-0.02	-2.04
Phe	1.11 – 5.14	2.77	1.28	3.12	2.47	0.23	-0.47
Ant	2.12 – 11.76	5.52	2.98	4.45	4.89	1.17	0.32
Flt	0.46 – 4.13	2.17	1.21	2.13	1.81	0.33	-0.47
Pyr	0.49 – 7.13	3.17	1.90	2.89	2.59	0.79	0.44
Chr	0.95 – 4.21	2.74	1.17	2.79	2.48	-0.15	-1.79
B[a]a	0.46 – 3.15	1.88	0.94	1.85	1.63	0.11	-0.81
B[a]p	0.93 – 3.82	2.36	0.88	2.31	2.20	0.16	-0.27
B[b]f	1.15 – 11.75	4.79	3.43	3.5	3.70	0.86	-0.11
B[k]f	1.15 – 9.46	5.18	2.88	4.68	4.34	0.19	-1.54
B[ghi]p	2.11 – 34.81	11.63	10.40	7.70	8.44	1.67	1.91
I[123cd]p	0.93 – 19.46	7.60	5.92	5.36	5.82	1.49	1.31
D[ah]a	2.43 – 22.79	8.51	6.31	5.71	6.90	1.59	1.74

**Table 4: Statistics Summary of Measured PAHs at Sample Station C ( $\mu\text{g} / \text{g}^{-1}$ )**

PAHs	Range	Mean	Standard Dev.	Median	Geomean	Standard Skewness	Standard Kurtosis
Nap	0.35 – 8.92	4.45	4.30	4.08	2.32	0.39	-1.01
Acy	0.49 – 2.42	1.18	0.82	0.73	0.97	0.96	2.98
Ace	0.11 – 3.11	1.03	1.23	0.45	0.57	1.74	0.25
Flu	0.15 – 4.55	2.54	1.54	2.35	1.75	-0.31	na
Phe	2.46 – 44.99	24.24	21.29	25.27	14.08	-0.22	na
Ant	0.72 – 3.42	2.02	1.36	1.91	1.68	0.35	0.84
Flt	0.23 – 1.46	0.73	0.53	0.61	0.59	1.08	na
Pyr	1.76 – 3.44	2.60	1.19	2.60	2.46	na	na
Chr	1.26 – 1.26	1.26	na	1.26	1.26	na	na
B[a]a	0.45 – 0.57	0.51	0.08	0.51	0.51	na	na
B[a]p	0.12 – 0.35	0.23	0.16	0.23	0.20	na	0.13
B[b]f	0.13 – 2.59	1.06	1.12	0.76	0.59	1.10	3.02
B[k]f	0.13 – 10.12	3.51	4.52	1.90	1.41	1.71	na
B[ghi]p	0.39 – 3.49	1.94	2.19	1.94	1.16	na	2.32
I[123cd]p	0.31 – 3.45	1.37	1.15	1.29	0.99	1.35	3.36
D[ah]a	1.45 – 17.53	12.09	7.23	14.68	8.60	-1.77	na

Descriptive statistics for all forty-eight samples are listed in Table 2, 3 and 4. Included in the statistics for each analyte is the range, mean, standard deviation, median, geomean, standard skewness and Kurtosis. All statistics reported in Table 2, 3 and 4 was performed on the primary data assuming that the distribution of each variable (PAH) is normal. These values appear to be consistent with concentration of other literature reported for anthropogenic background in small to medium sized residential, commercial and light industrial areas (Bradley *et al.*, 1994; MA DEP, 2002; Gaga 2004; Mauro *et al.*, 2006).

Standard deviation of most measured PAHs are in the order of concentration indicating high fluctuation from one sample to another. If the distributions of data are normal, arithmetic mean and standard deviation are used to describe the data. But PAHs concentrations in soil are controlled by many and variable properties that is why soil species distribution are usually log-normal (Kannclutt *et al.*, 1994; Van Belle, 2002; Gaga, 2004; Shi *et al.*, 2005).

Closeness of the geometric mean and median with each other and the reverse for arithmetic mean and standard deviation is an indication of log-normal distribution (Ogbeibu, 2005; Gaga, 2004). As shown in Table 2, 3 and 4, geometric mean and median are very close to each other and for most of the PAHs and they are lower than the arithmetic mean and this observation is due to very high concentration of PAHs detected in few of the samples. For instance, in Table 2 median and geomean values for Phe are 3.15 and 4.75 respectively, which are very close to each other. However, arithmetic mean and standard deviation of Phe are 12.24 and 27.28 respectively, which is significantly higher than geomean and median and it correspond to concentration values where only small numbers (N) of data point exist. The high concentration differences strongly suggest that the data are log-normal. This observation was explored further using standard skewness and kurtosis were most of

the standard skewness values are higher than 0 showing right tailed distribution, with standard kurtosis showing similar trend.

Cluster analysis was used to identify the similarity and dissimilarities between sample points. Figure 2 showed the homogeneity between sample points with the squared euclidean distance ranging between 1.98 and 58965.58. As shown in the hierarchical dendrogram in Figure 1 cluster solutions were observed with high similarities of cluster pairs between stage 1 and 12. The first cluster group (C<sub>9</sub>, C<sub>59</sub>, C<sub>39</sub>, B<sub>72</sub> and C<sub>29</sub>) joined cluster group 2 (C<sub>49</sub>, C<sub>79</sub>, C<sub>69</sub>,) at stage 9. Also cluster group 3 (B<sub>12</sub> and B<sub>42</sub>) joined cluster group 4 (B<sub>2</sub>, B<sub>32</sub> and B<sub>52</sub>) at stage 11. Finally, cluster group 5 (A<sub>31</sub>, A<sub>71</sub>, A<sub>61</sub> and B<sub>2</sub>) was joined at stage 21 with cluster group 6 (A<sub>1</sub> and A<sub>11</sub>). The dendrogram further revealed that B<sub>62</sub>, C<sub>19</sub>, A<sub>21</sub>, A<sub>51</sub> and A<sub>41</sub> are *entropy* members and are independent of existing clusters while various clusters were linked at stage 9, 13, 18 and 21.

In a related scheme, the internal structure of the mean data in the summary statistics were determine using Pearson Correlation Coefficient to find association between the variables using Pair-Wise deletion from SPSS 20.0 software assuming that the data have normal distribution. The evaluated PAHs were considered as object and the sample points as variable resulting in Pearson Correlation matrix in Table 5. The many significant correlated pairs in the correlation matrix were further assessed at value were  $r \geq 0.70$ , results showed that several sample points have positive and high correlation The clustered and correlated pairs in the hierarchical dendrogram and correlation matrix showed that the sources and physiochemical properties of the examined PAHs have common association. Results also confirm significant relationship between sample points. The tendency of sample points or experimental variables to cluster or correlate is a function of many factors which includes: either sources of contaminant(s) or their degradation pattern and/or mobility indexes are similar in the environment (Spiff and Horsfall, 2004; Hair and Black, 2004).

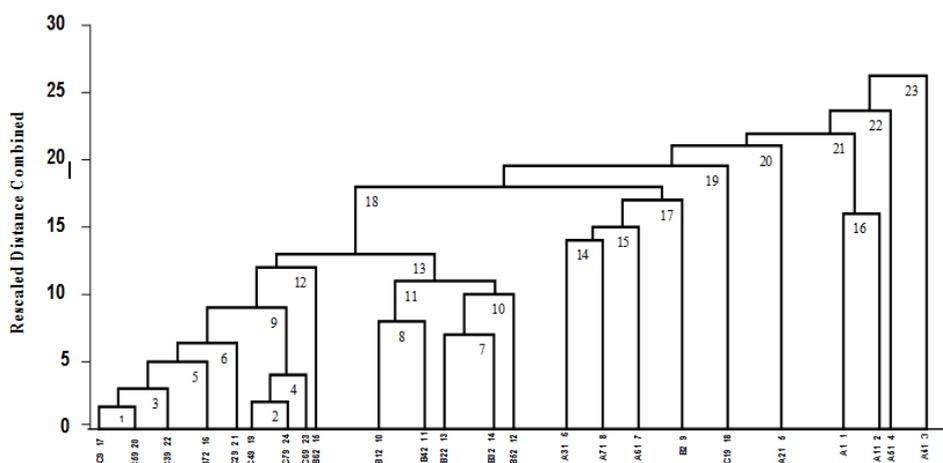
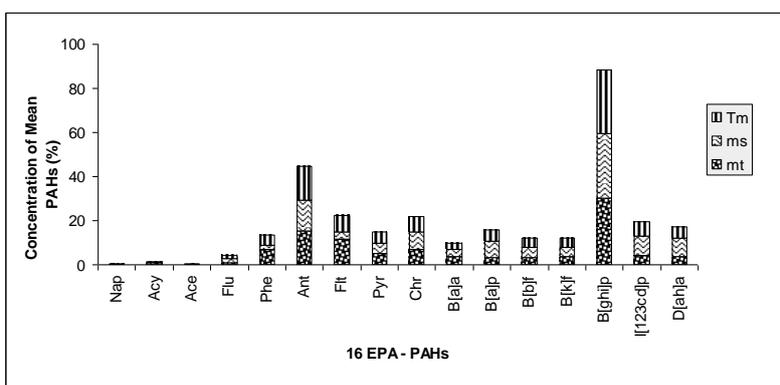


Figure 11: Dendrogram showing complete linkages of Hierarchical Clustering between 24 sample points

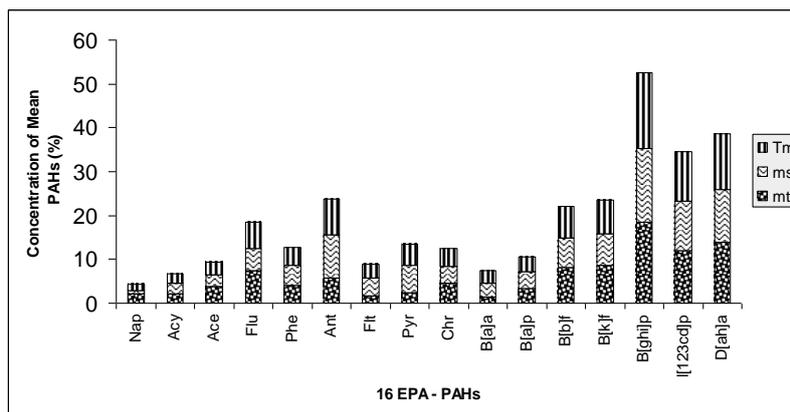
Table 8: Pearson Correlation Matrix of the Sample Site using Pearwise Deletion from SPSS Software 20.0 (n = 24, df = 22,  $\alpha = 0.01$ )

	A1	A11	A41	A51	A21	A31	A61	A71	B2	B12	B42	B52	B22	B32	B62	B72	C9	C19	C49	C59	C29	C39	C69	C79
A1	1.00																							
A11	0.97	1.00																						
A41	0.91	0.92	1.00																					
A51	0.69	0.62	0.61	1.00																				
A21	0.17	0.13	0.12	0.79	1.00																			
A31	0.82	0.81	0.85	0.49	0.13	1.00																		
A61	0.39	0.35	0.26	0.30	0.31	0.41	1.00																	
A71	0.85	0.84	0.76	0.49	0.15	0.81	0.75	1.00																
B2	0.83	0.79	0.67	0.52	0.07	0.53	0.61	0.80	1.00															
B12	0.73	0.61	0.62	0.76	0.48	0.49	0.60	0.67	0.75	1.00														
B42	0.73	0.62	0.60	0.62	0.35	0.59	0.78	0.80	0.75	0.89	1.00													
B52	0.62	0.60	0.50	0.77	0.58	0.39	0.37	0.49	0.56	0.70	0.61	1.00												
B22	0.65	0.59	0.51	0.69	0.46	0.38	0.67	0.69	0.82	0.85	0.74	0.54	1.00											
B32	0.75	0.75	0.63	0.50	0.16	0.49	0.67	0.79	0.95	0.72	0.69	0.50	0.85	1.00										
B62	0.23	0.14	0.19	0.25	0.25	0.26	0.45	0.39	0.10	0.41	0.61	0.46	0.14	-0.01	1.00									
B72	-0.06	-0.11	-0.08	0.23	0.49	0.14	0.24	0.08	-0.21	0.08	0.24	0.07	0.03	-0.20	0.47	1.00								
C9	-0.15	-0.16	-0.31	-0.09	-0.07	-0.31	-0.06	-0.29	0.09	0.06	-0.03	0.07	-0.08	0.10	-0.30	-0.22	1.00							
C19	-0.14	-0.13	0.02	-0.15	-0.19	-0.09	-0.33	-0.20	-0.09	-0.24	-0.30	-0.16	-0.19	-0.15	-0.05	0.14	-0.15	1.00						
C49	-0.01	-0.01	-0.09	0.03	0.04	-0.16	0.49	0.16	0.41	0.26	0.29	0.05	0.55	0.49	-0.07	0.02	0.14	-0.11	1.00					
C59	-0.11	-0.11	-0.24	-0.14	-0.13	-0.18	-0.02	-0.20	0.09	0.03	-0.03	0.14	-0.19	0.08	-0.23	-0.31	0.88	-0.12	-0.10	1.00				
C29	-0.09	-0.16	-0.19	-0.15	-0.06	-0.06	0.05	-0.09	-0.13	0.06	0.20	0.12	-0.24	-0.23	0.42	0.41	0.24	-0.12	-0.15	0.27	1.00			
C39	-0.20	-0.22	-0.02	-0.27	-0.28	-0.01	-0.23	-0.17	-0.27	-0.34	-0.20	-0.13	-0.43	-0.40	0.34	0.16	-0.36	0.68	-0.22	-0.27	0.15	1.00		
C69	-0.04	-0.07	-0.17	0.01	0.06	-0.19	0.55	0.15	0.39	0.33	0.35	0.13	0.55	0.44	0.06	0.04	0.21	-0.19	0.96	0.00	-0.01	-0.25	1.00	
C79	0.22	0.23	0.16	0.10	-0.09	0.01	0.42	0.29	0.56	0.36	0.37	0.14	0.60	0.59	-0.06	-0.11	0.09	-0.12	0.94	-0.13	-0.15	-0.22	0.89	1.00

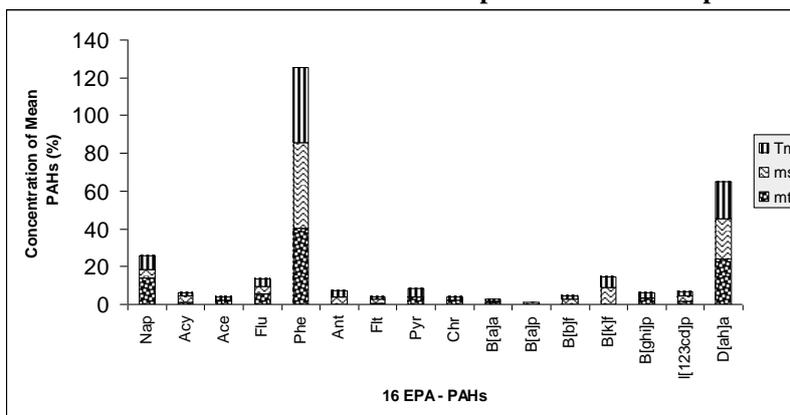
**Dept-Wise Distribution of PAHs:** As shown in Figure 2 - 4, the percentage distribution of the mean concentration of PAHs in top and sub soil in sampling site A ranged from 0.30 (Nap) – 30.07 % (B[ghi]P) and 0.10 (Acy) and 29.255 % (B[ghi]p) respectively. Similarly, at sampling site B, the mean concentration of PAHs in top and sub soil samples ranged from 1.39 (B[g]a) -18.415 % (B[ghi]p) and 0.82 (Nap) -16.86 % (B[ghi]p) respectively. At sampling site C, the mean concentration of PAHs in top and sub soil samples ranged from 0.18 (Bap) – 40.43 % (Phe) and 0.21(Ace) – 45.15 % (Phe) respectively. Analysis of results showed a variable concentration of PAHs across sample sites. Adamezewska *et al.*, (2000), observed that the concentration of PAHs in roadside samples are high and the surface layers are more contaminated due to variable contributing factors such as petro/diesel engine combustion.



**Figure 2: Distribution of Mean PAHs in Total Top and Sub Soil Sample at Site A (%)**



**Figure 3: Distribution of Mean PAHs in Total Top and Sub Soil Sample at Site B (%)**



**Figure 4: Distribution of Mean PAHs in Total Top and Sub Soil Sample at Site C (%)**

Similarly, the combustion of grass vegetation, indiscriminate burning of industrial, commercial and domestic wastes and the accumulation of humus in 0-15cm soil layer, PAHs is expected to have high concentration due to high organic carbon content ascribed to “aging” (Lundstedt, 2003; Willeke *et al.*, 2005; Van Zuydam, 2007). However, this study recorded relatively low concentration of PAHs in most top layer probably

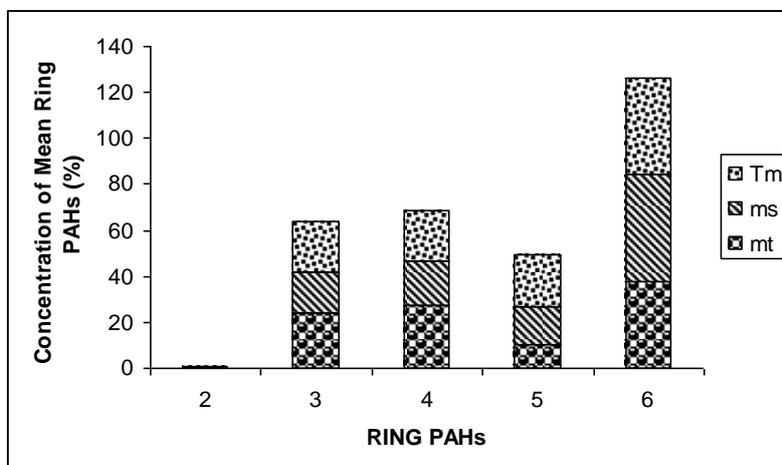
due to high and variable anthropogenic activities in this layer. The observed trend in low concentration of PAHs in most top soil samples could be related to the fact that PAHs can be degraded through the process of photo-oxidation. Under ozone and light, the half-lives of several PAHs vary between a few minutes to few hours (Mackey *et al.*, 1991). The rate of degradation increases with increased dissolve oxygen concentration, temperature, and light intensity, these factors are high in 0-15 cm layer than 16-30 cm layer. Surface runoff could also be responsible for the relatively low concentration of PAHs observed in top soil samples. The mean concentrations of PAHs obtained in this study are in agreement with those reported in other literature (Ikolo, 2006 and Van Zuydam, 2007). The concentration of monitored PAHs also showed that sample site A and B recorded higher percentages than C (control).

**Polycyclic Aromatic Hydrocarbon Profiles in the Soil Profile:**

The removal of PAHs from soil matrix is normally associated with biotic and/or abiotic degradation processes, the rate of degradation vary and generally decreases with increasing number of aromatic rings (CCME, 2008). Stratifying PAHs into different class depending on the number of aromatic rigs present in their structure explore the identification of PAHs in terms of pyrolitic or petrogenic sources. Within the 16 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).

The percentage distribution of aromatic ring – 2 (Nap), 3 (Acy, Ace, Flu, Phe and Ant), 4 (Flt, Pyr, Chr and B[a]a), 5 (B[b]f, B[k]f, B[a]p and I[123-cd]p) and 6 (B[ghi]p and D[ah]a) – PAHs of total mean (Tm), mean of top (mt) and sub (ms) PAHs are presented in Figure 5, 6 and 7. The percentage distribution of aromatic rings of total mean showed that 2 ring PAHs ranged between 0.21 (A) and 7.32 % (C), while three ring percentage ranged from 22.01(A) – 51.05% (C). Similarly, four and five ring percentage ranged from 8.38(C) – 22.62 (A) and 7.90 (C) – 18.44 % (B) respectively. In the same vein, the percentage of six rings PAHs ranged between 25.34 (C) and 42.05 % (A)

Also, the percentage distributions of ring PAHs in top samples showed that the percentage of two and three rings ranged from 0.3(A) – 14.28 % (C) and 23.25 (B) – 48.78 % (C) respectively. Four and five rings percentages ranged from 7.63 (B) – 27.24 % (A) and 0.58 (C) – 20.23 % (B) respectively. The percentage of six rings ranged between 28.73 (C) and 44.37 % (B). In sub samples, the percentage of ring PAHs showed that two and three rings ranged from 0.14 (A) – 2.21 % (C) and 17.83 (A) – 56.60 % (C) respectively. Similarly, four and five rings percentage ranged from 2.97 (C) – 19.17 % (A) and 12.10 (C) – 17.60 % (H) respectively. The percentage distribution of six rings ranged between 24.12 (C) and 46.63 % (A). Percentage distribution in Figure 5 showed that ring PAHs are in the order 6 > 4 > 3 > 5 > 2. Also, PAHs ring percentage distribution in Figure 6 and 7 are in the order 2 < 4 < 5 < 3 < 6 and 3 > 6 > 2 > 5 > 4 respectively. Observation of percentage distribution of ring PAHs in Figure 5, 6 and 7 showed relatively low percentages in top than sub samples. The observed trend in low concentration of PAHs in most top soil samples could be related to the fact that PAHs can be degraded through the process of photo-oxidation. Under ozone and light, the half-lives of several PAHs vary between a few minutes to few hours (Mackey *et al.*, 1991). The rate of degradation increases with increased dissolve oxygen concentration, temperature and light intensity, these factors are high in 0 – 15 cm layer than 16 – 30 cm layer. Also, the LPAHs tend to oxidize and volatilize at a faster rate –shorter half-lives – while four, five and six (HPAHs) PAHs will degrade partially at a slow rate –longer half-live – (Earl *et al.*, 2003). Hence the observed higher concentration of HPAHs over LPAHs



**Figure 5: Distribution of Ring PAHs in Total Top and Sub Soil Sample at Site A (%)**

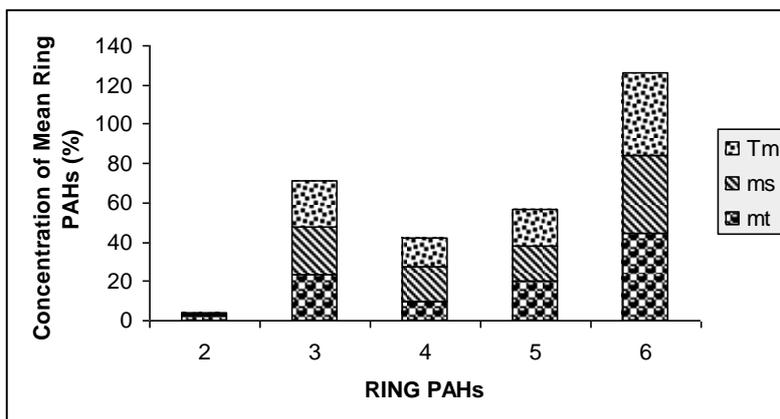


Figure 6: Distribution of Ring PAHs in Total Top and Sub Soil Sample at Site B (%)

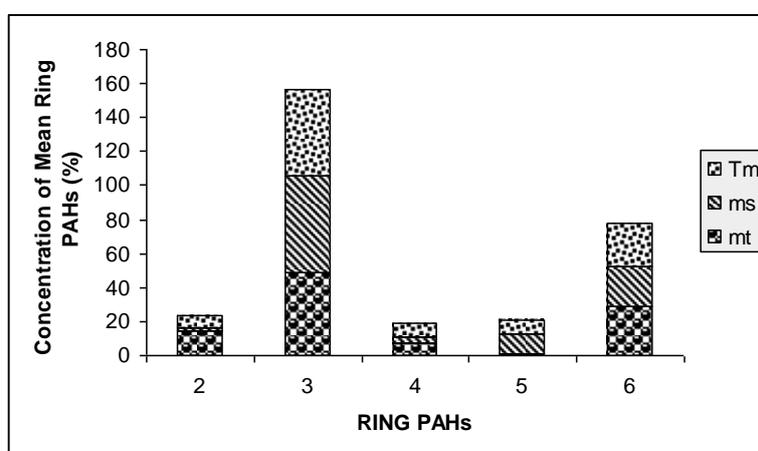


Figure 7: Distribution of Ring PAHs in Total Top and Sub Soil Sample at Site C (%)

Also, two and three rings PAHs are more sensitive to photo-oxidation than four, five and six ring PAHs. Because of their high degree of lipophilicity and are partially soluble in water, four, five and six ring PAHs exhibit much greater tendency to be sorbed to soil or sediment - which makes them unavailable for biotic degradation – rather than partition into water or air like their two and three ring counterparts.

Basically the phenomenon in which two and three ring PAHs tends 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 over pyrolytic PAHs.

**Source Identification:** The evaluation of PAHs in soil from circumscribed sites (soil profiles) is complex due to the potential and kinetic variability of anthropogenic and natural contribution, fate and transport. In order to identify the possible sources of PAHs (petroleum/or pyrolytic), PAHs isomer pairs (Ant/178, Flt/Flt+Pyr, B[a]a/228, I[123-cd]p/I[123-cd]p + B[ghi]p, Flu/Pyr, Phe/Ant, Chr/B[a]a and LPAHs/HPAHs) used in other studies (Benlahcen, 1997; Soclo *et al.*, 2000; Magi *et al.*, 2002; Bertolotto *et al.*, 2003; Gaga, 2004; Lizhong and Jing 2004; Azza, 2006; Emoyan *et al.*, 2008; Perra, *et al.*, 2009) were computed for in this study for total mean, mean of top and mean of sub samples as shown in Table 6. In this way source apportionments were deduced. Results showed that there is high variability of sources of PAHs as seen in the ratios of the various sample sites.

The ratio of LPAHs (Nap, Acy, Ace, Flu, Phe and Ant) and HPAHs (Flt, Pyr, Chr, B[a]a, B[a]p, B[b]f, B[k]f, B[ghi]p, I[123-cd]p and D[ah]a) is functional in delineating petrogenic and pyrolytic sources of PAHs, (Soclo, *et al.*, 2000). The ratios of LPAHs/HPAHs greater than 1 are suggestive of petroleum origin while ratios less than 1 are of pyrolytic processes (Witt and Trost, 1999; Soclo *et al.*, 2000). The LPAHs/HPAHs ratio of the total mean reveal that the origin of PAHs is pyrolytic in sample sites A and B except C having petroleum ratio. Similarly, LPAHs/HPAHs ratios of the mean of top and sub samples showed that the source of PAHs is pyrolytic in sample site A and B except C with petroleum origin ratio.

Soclo *et al.*, (2000); Bertolotto *et al.*, (2003); Perra *et al.*, (2009); Magi *et al.*, (2002); Gaga, (2004); Emoyan *et al.*, (2008), had earlier stated that petrogenic and pyrolytic contamination are characterized with the predominance of LPAHs and HPAHs respectively. Also, Perra *et al.*, (2009), suggested that the constitution of

90% HPAHs contamination of Orbetello Lagoon might have originated mainly from atmospheric pollution caused by the burning of fossil fuel.

Generally, from the percentage distribution of the ratios of all isomer pairs in Table 6, the source of PAHs in the sample sites are petrogenic and pyrolytic. This indicates a considerable vehicular and combustion fleet of petrol and diesel engine and burning of wood and refuse. Furthermore, the presence of both petroleum and pyrolytic PAHs in all sample station can be adduced to the fact the PAHs can be transported regionally and continentally as gases or aerosols during winter without significant biotic and/or abiotic degradation on atmospheric particles (Monali *et al.*, 2000; Earl *et al.*, 2003)

**Table 6: Ratio of PAHs Isomer Pairs in the Study Area.**

PAHs	Mean	A	B	C	X	Y
Ant /178	Tm	0.230	0.030	0.010		
	tm	0.250	0.020	na	<0.1	>0.1
	sm	0.190	0.040	0.010		
Flt/Flt+Pyr	Tm	0.590	0.410	0.220		
	tm	0.700	0.400	0.120	<0.5	>0.5
	sm	0.400	0.400	1.000		
B[a]a/228	Tm	0.040	0.008	0.002		
	tm	0.050	0.003	0.002	<0.35	>0.35
	sm	0.030	0.010	0.002		
I[123-cd]p/ I[123-cd]p + B[ghi]p	Tm	0.180	0.400	0.410		
	tm	0.120	0.390	0.320	<0.2/0.5	>0.5
	sm	0.230	0.400	1.000		
Flu/Pyr	Tm	0.280	1.300	0.980		
	tm	0.230	2.960	1.290	<1	>1
	sm	0.340	0.810	na		
Phe/Ant	Tm	0.300	0.500	12.000		
	tm	0.470	0.710	na	>10	<10
	sm	0.120	0.460	11.750		
Chr/B[a]a	Tm	2.280	1.460	2.470		
	tm	1.770	3.270	2.220	>1	<1
	sm	2.670	1.210	Na		
LPAHs/HPAHs	Tm	0.290	0.340	1.400		
	tm	0.330	0.340	1.710	>1	<1
	sm	0.220	0.340	1.550		

Where: Total mean (Tm), Top Mean (tm) , Sub Mean (sm), Pyrolytic (x) and Petrogenic (y)

#### IV. Conclusion Recommendations

Contemporary information on the concentration, distribution and multimedia behavior in soil were reviewed. The partitioning of these compounds in soil profile was evaluated in this research. The total values of 16 PAHs varied between 1.14 and 652.81 $\mu\text{g}\cdot\text{g}^{-1}$ . Dept-wise distribution of PAHs showed the existence of relatively low percentage concentration of PAHs in top soil ranging from (0.18 B[g]p – 40.43 Phe) and sub soil (0.10 Acy – 45.15 Phe). Source identification revealed the presence of pyrolytic and petrogenic PAHs. Cluster analysis showed the existence of 6 cluster groups with sample points B<sub>62</sub>, C<sub>19</sub>, A<sub>21</sub>, A<sub>51</sub> and A<sub>41</sub> as *entropy* members. Also, Pearson Correlation matrix indicates positive and high correlation between sample points at  $\alpha = 0.01$  and  $r = \geq 0.70$  for most sample pairs. Descriptive statistics showed that the obtained concentration of PAHs in most sample points has log-normal distribution and are consistent with results reported from other soil matrix. This study has revealed the degree of contamination of PAHs in the study area; therefore, the obtained concentration of PAHs could help to set a baseline benchmark and evaluation of exposure risk to terrestrial organisms in the rapidly urbanizing study area.

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