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Seasonal Concentration Variation of Polycyclic Aromatic Hydrocarbons (PAHs) of Soils at Sapele Municipality, Nigeria

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Abstract
Polycyclic Aromatic Hydrocarbons (PAHs) are large class of persistence toxic substances (PTS) which are emitted as by-products of virtually every type of combustion technology or biomass burning. The purpose of this investigation represents the season-wise distribution characteristics of 16 priority PAHs in 24 samples. After extraction and purification, quantification, of PAHs was done using GC-FID. Reagents used are of chromatographic grade. Results showed that the total concentration of 16 PAHs varied between 3.08 and 584.44µg.g^{-1} dry weight and high variability of PAHs concentration between sample stations and season as shown in the statistical distributionof arithmetic mean, standard deviation and Geometricmean. Rectangular bar chart showed that dry season recorded higher concentration of PAHs over wet season. Cluster analysis (hierarchical dendogram) of dry and wet season revealed strong similarities in the homogeneity of studied PAHs and season -wise could be related to their physicochemical characteristics and common source. Equilibrium Partitioning (EqP) of 13 PAHs suggest potential for adverse toxicity effects from PAHs to terrestrial invertebrates. This investigation has shown that there is potential for adverse contamination of terrestrial population living in the vicinity of the sources of these carcinogens hence the need for clean-up and possible relocation of industrial and/or anthropogenic activities that emit these PTS.

1. Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) are large class of persistence toxic substances (PTS) which are emitted as by products of virtually every type of combustion technology or biomass burning.[1-3] PAHs are composed of only carbon and hydrogen atoms arranged in the form of fused benzene rings in linear, cluster or angular arrangements.[4,5] The lower molecular weight compounds where aromatic rings< 3 are more water soluble, volatile and less lipholitic than their higher molecular weight counterparts with aromatic rings > 4.[6,7] They are resistance to degradation over a long period in different environmental compartments.[8,9] However, the rates of degradation vary and generally decrease with increasing number(s) of aromatic rings, oxygen concentration, temperature and light intensity.[9] Also, the characteristics of the soil environment particularly the soil organic matter (SOM) content, and the competence of the soil microbial community to degrade these compounds is of importance in

determining their fate and transport importance in determining their fate and transport. The Kow, Koc, Henry's Law constant and aqueous solubility are chemical specific properties that are relevant in determining its multimedia behaviour.[7,9,10]

The prevalent mechanism of PAHs toxicity to invertebrates is narcosis (additive), which results in the degradation of cell membrane.[11] This degradation can result in mild toxic effects or mortality depending upon the quantity and duration of exposure.[12] Photo-activated toxicity, carcinogenicity and teratogenicity have also been reported to occur due to exposure to certain PAHs, (eg, B[a]p). In general, unless conditions result in elevated Uv levels, narcosis is the most common mode of action with PAHs in sediment or soil.[13] Each of the above characteristics results in factors contributing to the nature of the PAHs exposure and kind of PAH toxic effects. Equilibrium Partitioning (EqP) and the application of narcosis (additive)theory has been used in determining whether or not sufficient PAHs are present to cause adverse effect.[12,14,15]

PAHs have been an issue of public concern due to their demonstrated carcinogenic, mutagenic and toxicity properties.[16-18] Though soil and sediments act as a major sink for these PTS in the environment, these compounds are soluble in soil and river waters depending on their individual and/or combined physicochemical properties.

Knowledge regarding the distribution of PAHs in soil profiles and long range transport has been reported.[8,16,17,19,20] However, there are limited information on the seasonal variation and PAHs distribution in the study area. This investigation is aim to seasonally quantify 16 PAHs tagged priority pollutants, evaluate their homogeneity and risk to soil invertebrates using cluster and EqP models respectively.

2. Materials and Method

2.1. Study Area Description

The study area 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 of 5^0 54' – 5^0 9' N and $5^0$40' - 5^0 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 5^0 - 8^0E and 3^0- 6^0N.[21]

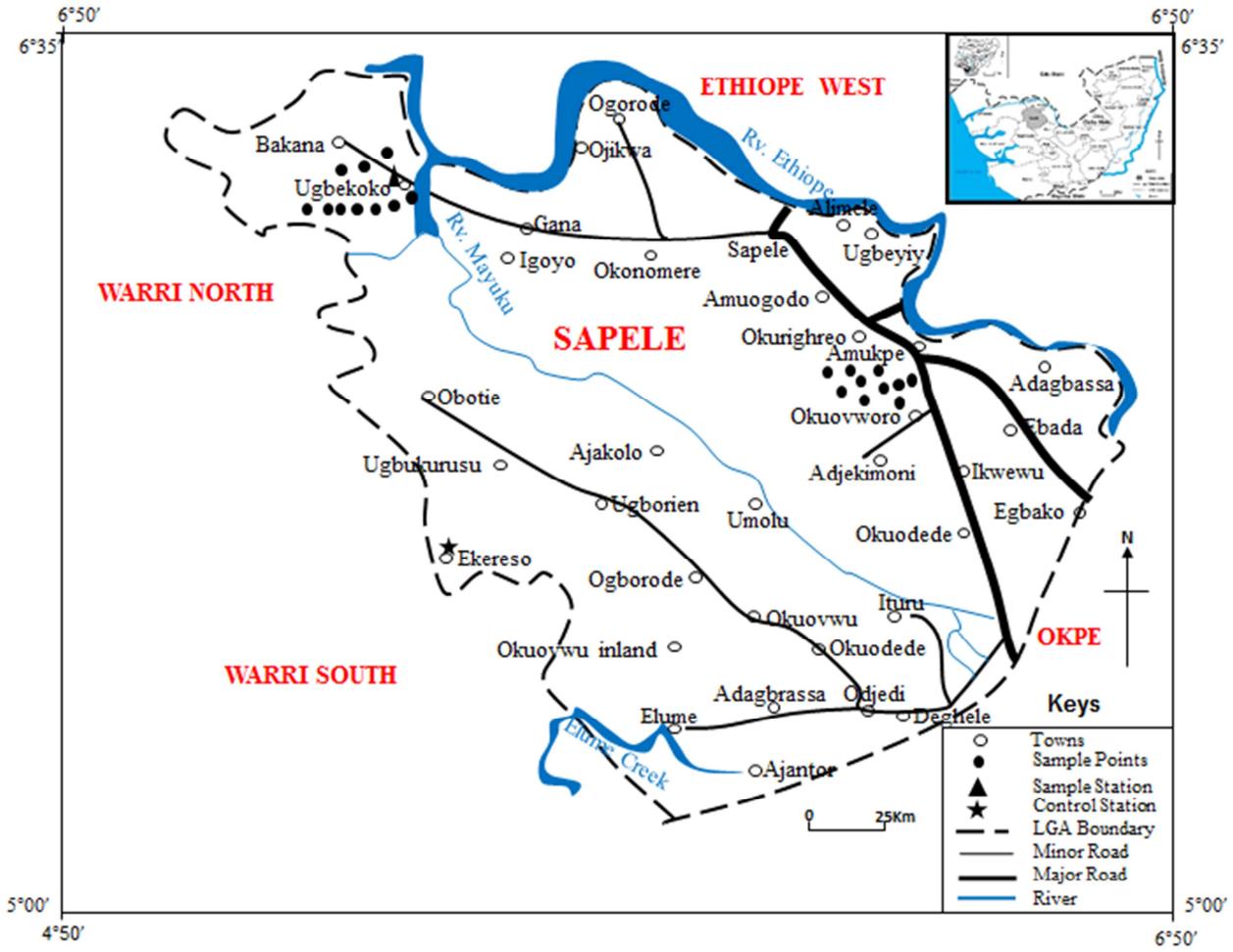

Fig. 1. *Map of the Study Area showing sample Sites and Station.*

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 21,31,61,71	05°51.470'N-05°51.933'N 005°41.589'E-005°41.674'E
2	B	2, 12, 42, 52 22, 32, 62, 72	05°51.914'N-05°51.959'N 005°41.622'E-005°41.707'E
3	C	9, 19, 49, 59 29, 39, 69, 79	05°53.553'N-05°53.926'N 005°37.151'E-005°38.461'E

2.2. Sample Collection and Preparation

Sample collection and preparation were carried out using standard technique.[22] Top (0-15cm) and sub (16-30cm) soil samples were collected in November, December, January and February in three sampling sites as shown in Table 1 and Figure 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.

2.3. Extraction and Analysis

Extraction and analysis were carried out according to standard methods.[20,23]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 ^{0}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. [20]

Quantification of PAHs was determined using Varian 300 gas chromatograph interfaced with flame ionization detector (GC-FID).The initial oven temperature was 60 ^{0}C for 10 min and was then increased to 120 ^{0}C at 5 ^{0}C min^{-1} and 120 –300 ^{0}C at 3 ^{0}C min^{-1}.The injector and detector temperatures were 200 ^{0}C and 300 ^{0}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.[20]

2.4. 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.

3. Results and Discussion

3.1. Seasonal Concentration Variation and Toxicological Significance

Twenty four samples that were collected and quantified for 16 priority PAHs compounds in wet and dry season regimes in sample station A, B and C are statistically presented in Table 2, 3 and 4.Total PAHs concentrations (∑PAHs) were in range of 3.08-584.44μg.g^{-1} at sample station C_{59} and A_4, respectively. Strong variability between arithmetic mean and standard deviation and arithmetic mean and Geometric mean is an indication oflog-normal distribution of data set.[24-26] The relatively high difference in arithmetic mean and standard deviation of most PAHs in dry and wet season in Table 2, 3 and 4 suggest a high distribution of PAHs concentration in few samples, i.e. an indication of log-normal distribution of PAHs detected.

Seasonal concentration distributions of (∑PAHs) are presented in Figure 2.At sample station A, seasonal ∑ concentration distribution is in order A11<A1<A_{51}<41 (dry season) and A3<A61 <A71< A21 (wet season) while at sample station B, B52<B12 <B_{42}<B_2 (dry season) and B72<72 <B32 < B62<22 (wet season).Also, C59 < C9 <C49 < 19 (dry season) and C39< C29 < C79 < 69 (wet season), representing sample station C ∑PAHs seasonal concentration distribution.Similarly, as shown in Figure 3 and 4, mean concentration of individual 16 PAHs at sample station A range from bdl (Ace) – 126.49 (B[ghi]p and 0.03 (Nap) – 20.74 (Flt) in dry and wet season respectively.At sample station B, mean PAHs distribution ranged between 0.71 (Nap) and 15.65 (B[ghi]p in dry season while wet season concentration ranged from 1.12 (Nap)-7.45 (B[ghi]P.Similarly, mean PAHs distribution at sample station C ranged from bdl (Ace, Chr, B[ghi]p - 8.78 (Phe) in dry season and 0.04 (Nap and B[a]p-3.97 (D[ah]a in wet season regime.

Table 2. *Season-Wise Comparative Descriptive Statistical Summary of PAHs At Sample Station A (µg/g^{-1}). Where: R = Range, $\bar{X}$ = Mean, σ = standard deviation and GM = Geometric Mean.*

Sample Station	**A**							
Season	**DRY**				**WET**			
PAHs	**R**	$\bar{X}$	**Σ**	**GM**	**R**	$\bar{X}$	**σ**	**GM**
Nap	1.28	0.32	0.56	1.28	0.06	0.03	0.03	0.06
Acy	1.60	1.34	0.66	1.16	0.17	0.04	0.07	0.17
Ace	-	-	-	-	0.62	0.21	0.25	0.36
Flu	3.03	1.86	1.15	2.44	4.23	2.85	1.67	3.78
Phe	48.10	13.05	20.26	5.52	4.64	2.25	1.7	2.73
Ant	122.11	40.18	49.51	14.76	67.90	20.74	28.77	7.66
Flt	59.42	17.50	24.32	11.58	8.75	4.18	3.1	5.18
Pyr	25.96	9.64	10.45	5.54	3.41	13.82	1.49	13.74
Chr	75.88	21.67	31.38	13.02	4.73	2.63	1.71	3.4
B[a]a	13.89	5.20	5.25	5.37	4.43	4.38	1.78	4.09
B[a]p	33.67	13.88	13.26	13.23	9.75	8.7	3.79	8.00
B[b]f	22.63	10.88	8.75	8.10	3.77	7.86	1.77	7.65
B[k]f	17.14	9.79	6.36	7.91	4.93	8.64	1.8	8.44
b[ghi]p	160.18	126.49	61.31	113.61	15.91	20.47	6.53	19.24
I[123-cd]p	6.61	12.95	2.39	12.71	12.32	9.16	4.78	6.64
D[ah]a	13.04	13.69	5.14	12.86	12.32	7.27	4.71	5.21

Table 3. *Season-Wise Comparative Descriptive Statistical Summary of PAHs at Sample Station B (µg/g^{-1}). Where: R = Range, $\bar{X}$ = Mean, σ = standard deviation and GM = Geometric Mean.*

Sample Station	**B**							
Season	**DRY**				**WET**			
PAHs	**R**	$\bar{X}$	**Σ**	**GM**	**R**	$\bar{X}$	**σ**	**GM**
Nap	1.52	0.71	0.55	0.85	1.07	1.12	0.42	0.33
Acy	1.63	1.32	0.69	1.14	0.62	1.13	0.23	0.87
Ace	3.21	1.74	1.37	1.04	2.15	2.15	0.85	1.10
Flu	3.27	4.32	1.25	4.16	1.69	1.69	0.60	1.08
Phe	3.07	2.31	1.18	2.06	1.08	2.14	0.41	1.44
Ant	4.02	5.26	1.64	4.91	3.50	5.24	1.38	2.73
Flt	1.32	1.50	0.49	1.40	1.16	1.16	0.45	0.85
Pyr	4.54	2.63	1.61	1.73	1.56	3.06	0.58	2.04
Chr	3.83	2.16	1.68	2.48	1.01	1.91	0.40	1.20
B[a]a	0.94	1.03	0.35	0.97	1.57	1.57	0.57	1.10
B[a]p	3.20	1.52	1.27	1 .11	0.89	1.96	0.33	1.40
B[b]f	4.57	4.05	1.72	3.74	6.53	7.10	2.66	1.56
B[k]f	4.52	4.51	1.75	4.23	5.38	5.96	2.03	1.88
B[ghi]p	26.56	15.65	10.84	12.89	6.38	7.45	2.64	3.69
I[123-cd]p	16.41	8.39	6.46	6.51	4.70	5.16	2.04	2.06
D[ah]a	18.07	9.06	7.09	6.90	5.51	6.72	2.38	2.87

Table 4. *Season-Wise Comparative Descriptive Statistical Summary of PAHs at Sample Station C (µg/g^{-1}). Where: R = Range, $\bar{X}$ = Mean, σ = standard deviation and GM = Geometric Mean.*

Sample Station	**C**							
Season	**DRY**				**WET**			
PAHs	**R**	$\bar{X}$	**Σ**	**GM**	**R**	$\bar{X}$	**σ**	**GM**
Nap	6.50	1.63	2.81	6.50	0.17	0.04	0.07	0.17
Acy	1.54	0.85	0.67	0.76	0.99	0.33	0.40	0.58
Ace	-	-	-	-	1.39	0.65	0.55	-
Flu	2.27	1.04	1.05	2.08	2.08	0.86	0.87	0.58
Phe	35.13	8.78	15.21	35.13	1.23	0.31	0.53	1.23
Ant	0.96	0.33	0.39	0.59	1.71	0.43	0.74	1.71
Flt	0.23	0.06	0.1	0.23	0.85	0.31	0.35	0.57
Pyr	0.88	0.22	0.38	0.88	1.72	0.43	0.74	1.72
Chr	-	-	-	-	0.63	0.16	0.27	0
B[a]a	0.23	0.06	0.10	0.23	0.28	0.07	0.12	0.28
B[a]p	0.06	0.01	0.02	0.06	0.17	0.04	0.07	0.17
B[b]f	0.06	0.02	0.03	0.06	1.29	0.51	0.50	0.61
B[k]f	0.06	0.02	0.03	0.06	5.06	1.74	1.97	1.58
B[ghi]p	-	-	-	-	1.75	0.48	0.73	0.58
I[123-cd]p	0.76	0.55	0.32	0.73	1.73	0.48	0.73	0.55
D[ah]a	7.56	2.07	3.18	2.34	8.77	3.97	4.02	7.90

The percentage rectangular chart of total seasonal PAHs concentration in sample point A, B and C in Figure 2 showed that there is high difference in seasonal concentration of PAHs hence the rectangular bar shape.This can be deduced from the bar chart in terms of the total seasonal concentration ratio i.e., AD and AW (8:3), BD and BW (6:3) and CD and CW (4:3).Observation of concentration distribution in Figure 2, 3 and 4 suggest high percentage of PAHs in dry season over wet season in all sample stations.Similarly, mean concentration of individual PAHs was comparatively higher in dry season over wet season as shown in Figure 3 and 4.Analytical observation of PAHs concentration distribution pattern in Figure 3 and 4 characterize the presence of HPAHs over LPAHs which indicate the abundance of human carcinogenic PAHs in the study area.

The inhabitants of the study area may be exposed to the observed concentration of these carcinogenic PAHs through primary/secondary sources (cigarette and motor vehicle smoke, inhalation andingestion of contaminated air and food resources).However, population living in the vicinity of combustible hazardous waste sites may be at greater risk of potential exposure than the general population through the possible primary contacts.[27]

Mean and ∑PAHs concentration obtained in this study are in agreement with those reported in other studies.[28-31]

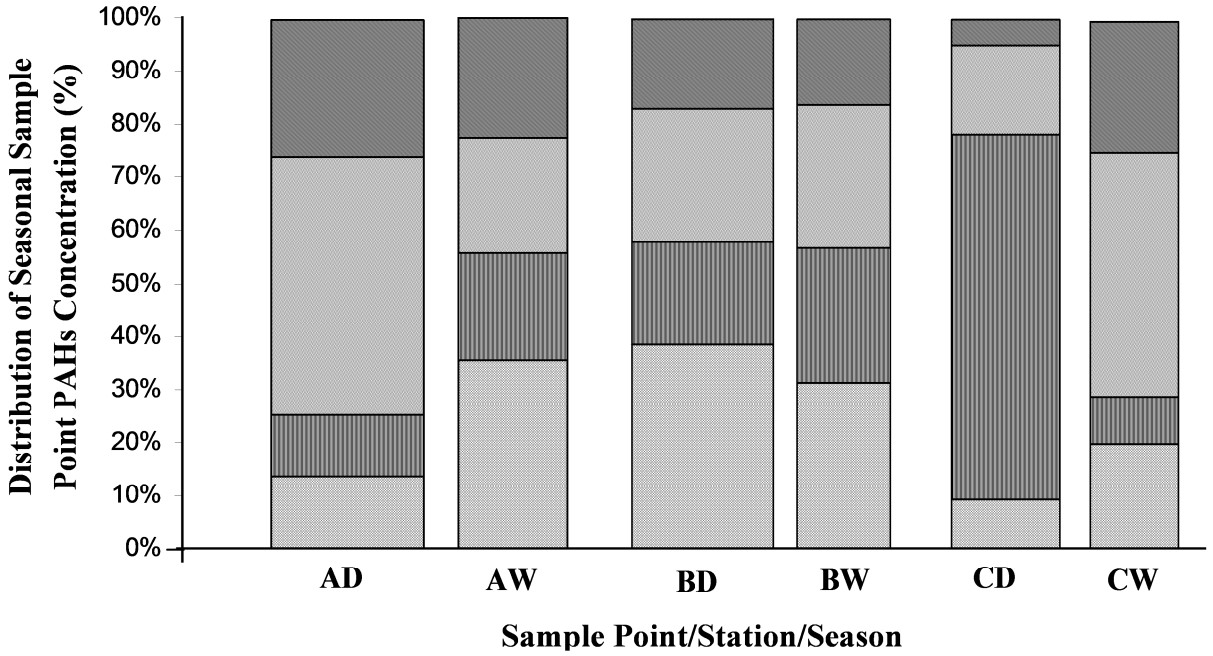

Figure 2. *Percentage Rectangular Chartshowing sample Point seasonal PAHs Concentration in Sample Station A, B and C. where D = Dry Season, W = Wet Season.*

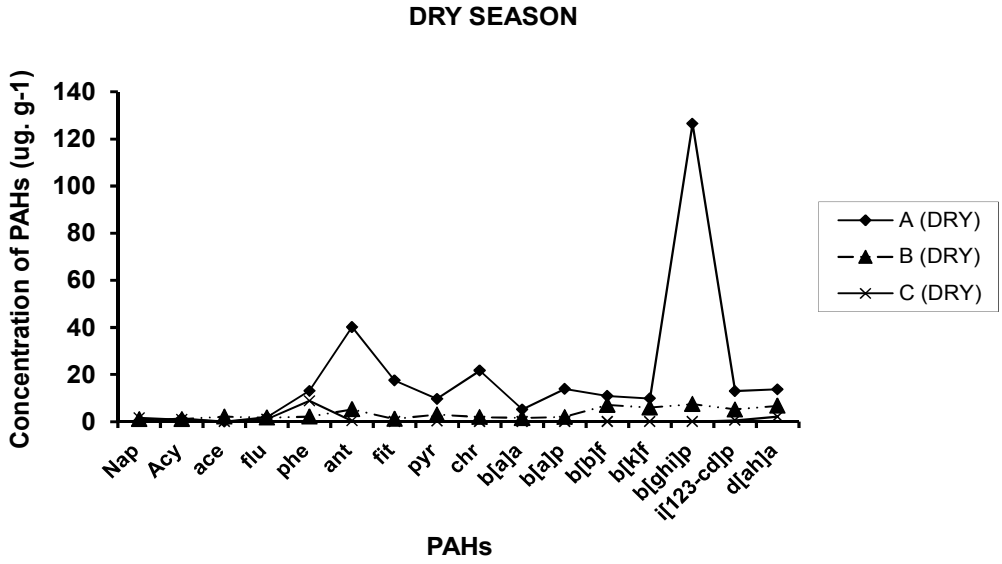

Figure 3. *Dry Season Distribution of Mean PAHs in the Study Area ($\mu g/g^{-1}$).*

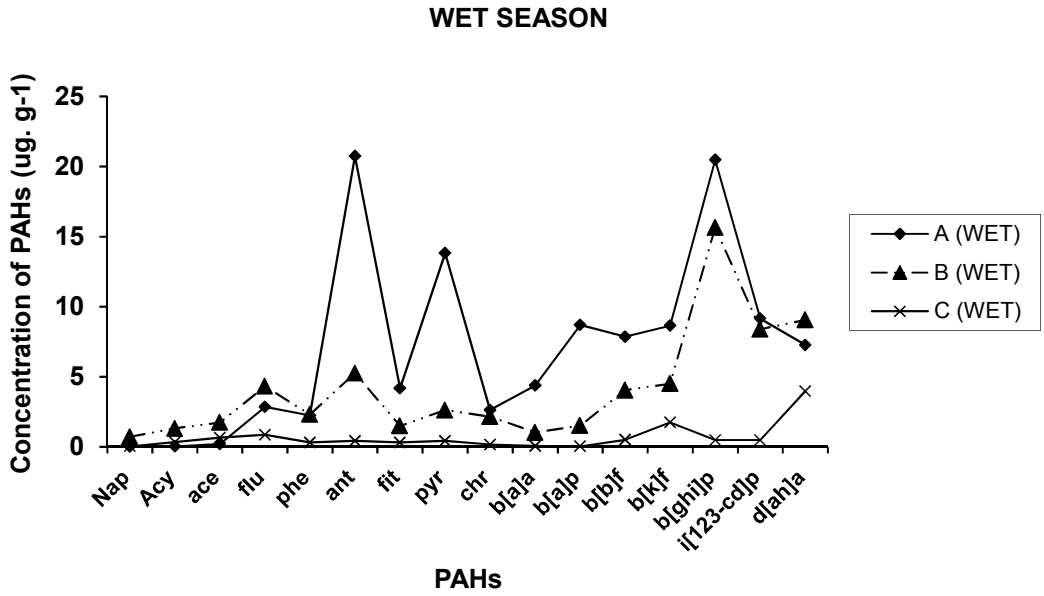

Figure 4. *Wet season Distribution of Mean PAHs in the Study Area (μg/g^{-1})*

3.2. Seasonal and PAHs Homogeneity

Cluster computation was used to identify homogeneity of PAHs in dry and wet season regimes as shown in Figure 5 and 6 respectively.The dry season hierarchical dendogram in Figure 5 showed the existence of four cluster groups of fifteen pairs with Euclidean distance (coefficient) ranging between 1.4 and 13492.4. The first cluster group(B[b]f, B[k]f and Pyr) is join with cluster group two (I[123-cd]p and D[ah]a at stage 9.In similar vein, the third cluster group (Flt, B[a]p and Chr) isjoin to cluster group one and two at stage 11. While the fourth cluster group (Nap, Acy, Ace, Flu and B[a]a) is join to cluster groups one, two and three at stage 13. The hierarchical dendogram also showed thatPhe, Ant and B[ghi]p occurred as *entropy* members. Anthracene and B[ghi]p occurring as entropy members in cluster analysishave been reported.[20]

Similarly, the wet season hierarchical dendogram in Figure 6 revealed a five cluster group arrangement with Euclidean distance (coefficient) range of 0.1 and 262.7.Figure 6 showed that first cluster group (Nap,sAcy and Ace) join the second cluster group (Flt and B[a]a and third cluster group (Phe, Chr, and Flu) at stages 10 and 11.Also, cluster group four (B[b]f, I[123-cd]p, B(k)f, B[a]p, D[ah]a and Pyr) and cluster group five (Ant and B[ghi]p are join with other cluster groups at stage 14 and 15.The hierarchical dendogram of dry and wet season in Figure 5 and 6 showed similarities in the homogeneity of PAHs in the studied environmental regimes.This homogeneity of PAHs could be related to their physicochemical properties and common sources of PAHs (LPHAs and HPAHs).

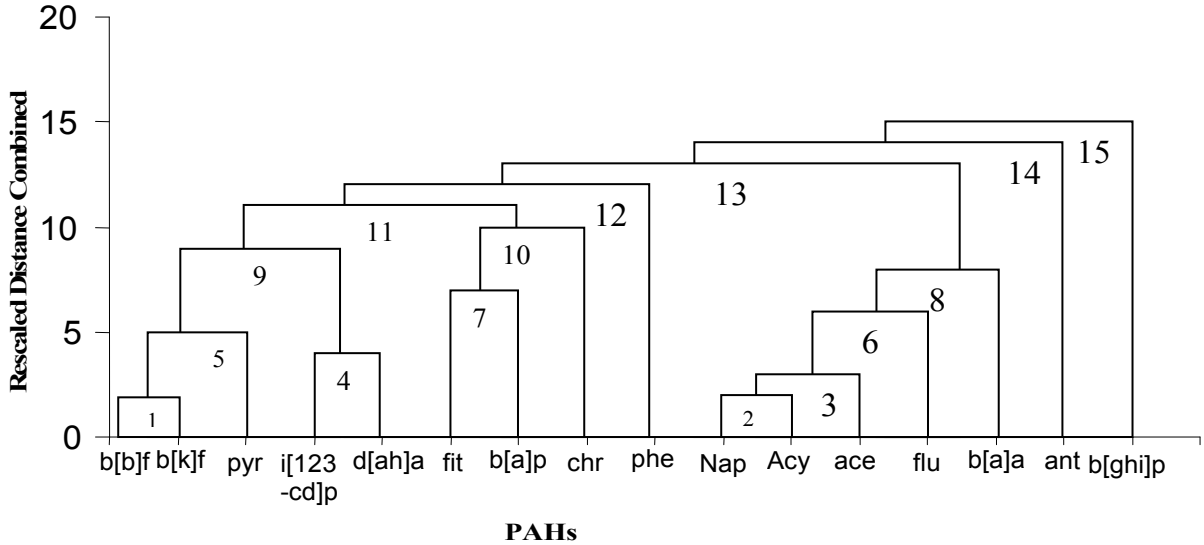

Figure 5. *Dendogram showing complete linkages of Hierarchical clustering between PAHs in Dry Season*

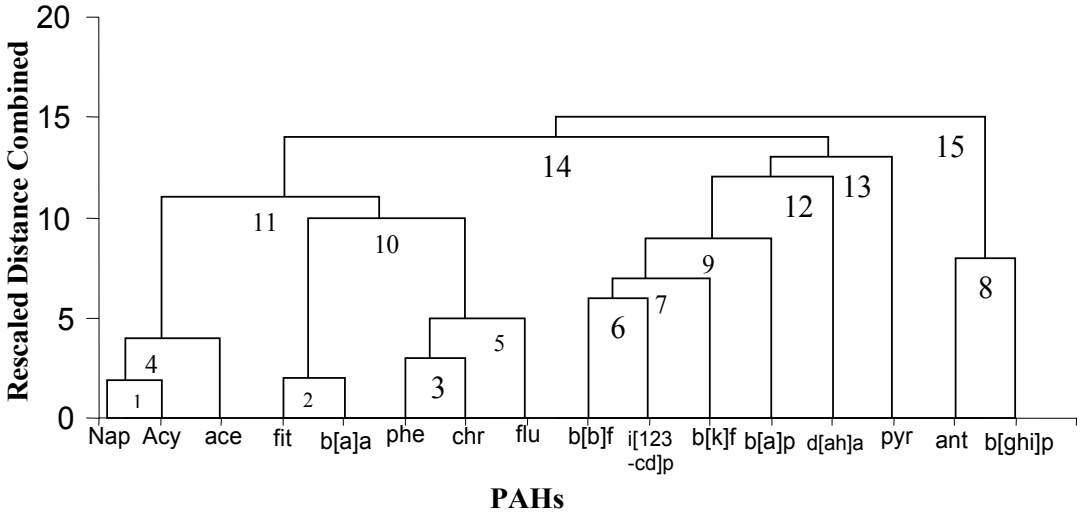

Figure 6. *Dendogram showing complete linkages of Hierarchical clustering between PAHs in Wet Season*

3.3. Assessment of Risk to Soil Invertebrates from PAHs

Table 5.*Toxic Unit for Thirteen PAHs Mixtures for the Protection of Invertebrate Organism in the Study Area*

PAHs	A	B	C
Flu	0.13	0.14	0.13
Phe	0.38	0.08	1.16
Ant	1.27	0.17	0.1
Flt	0.5	0.06	0.03
Pyr)	0.36	0.08	0.11
Chr	0.43	0.06	0.04
B[a]a	0.19	0.04	0.02
B[a]p	0.27	0.04	0.007
B[k]f	0.2	0.09	0.03
B[k]f	0.2	0.1	0.1
B[ghi]p	1.33	0.19	0.05
I[123cd]p	0.29	0.12	0.04
D[ah]a	0.27	0.14	0.31
$\sum ESBTU_{FCVi}13$	5.84	1.31	2.13
$\frac{\sum ESBTU_{FCVi}13}{\cdot 11.5}$	67.16	15.07	24.46

As shown in Table 5 thirteen instead of total (34) PAHs mixtures were used for the risk assessment.The thirteen PAHs used were selected based on the basis of their physicochemical properties with regards to molecular weight and high bioavailability and biotic and/or abiotic degradation. If the Equilibrium Partitioning Benchmark is to be protective of invertebrate organisms, some assumption must be made regarding the contribution of unmeasured 21 PAHs, because of the toxicological contributions of all 34 PAHs as recommended.For a confidence level of 95%, the uncertainty factor for 13 PAHs mixture (11.5) was multiplied by the calculated $\Sigma ESBTU_{FCVi13}$ for an estimated value of $\Sigma ESBTU_{FCVi34}$. Since Table 5 showed that the calculated values of $\Sigma ESBTU_{FCVi13}$ at 95% confidence level in all sample stations are greater than one, it suggest the potential for adverse toxicity effects from PAHs to invertebrates (snail, annelid etc.).Result also showed that the toxic unit is in the order: 66.93 (A) > 24.46 (I) and > 15.07(B)

4. Conclusion and Recommendations

PAHs distribution characteristics and seasonal variation where studied and results showed high variability of PAHs concentration between sample stations and season as shown in arithmetic mean, standard deviation and Geometric mean. Rectangular bar chart showed that dry season recorded higher concentration of PAHs over wet season. Cluster analysis (hierarchical dendogram) of dry and wet season revealed strong similarities in the homogeneity of studied PAHs wish could be related to their physicochemical characteristics and common sources. Equilibrium Partitioning (EqP) of 13 PAHs suggest potential for adverse toxicity effects from PAHs to terrestrial invertebrates. This investigation has shown that there is potential for adverse contamination of terrestrial population living in the vicinity of the sources of these carcinogens hence the need for clean-up and possible relocation of anthropogenic sources.

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