Comparative Correlation Investigation of Polynuclear Aromatic Hydrocarbons (PAHs) in Soils of Different Land Use: Sources Evaluation Perspective

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Abstract—Polycyclic Aromatic Hydrocarbons (PAHs) are formed mainly because of incomplete combustion of organic materials during industrial, domestic activities or natural occurrence. Their toxicity and contamination of terrestrial and aquatic ecosystem have been established. However, with limited validity index, previous research has focused on PAHs isomer pair ratios of variable physicochemical properties in source identification. The objective of this investigation was to determine the empirical validity of Pearson Correlation Coefficient (PCC) and Cluster Analysis (CA) in PAHs source identification along soil samples of different land uses. Therefore, 16 PAHs grouped, as Endocrine Disruption Substances (EDSs) were determined in 10 sample stations in top and sub soils seasonally. PAHs was determined the use of Varian 300 gas chromatograph interfaced with flame ionization detector. Instruments and reagents used are of standard and chromatographic grades respectively. PCC and CA results showed that the classification of PAHs along pyrolitic and petrogenic organics used in source signature is about the predominance PAHs in environmental matrix. Therefore, the distribution of PAHs in the studied stations revealed the presence of trace quantities of the vast majority of the sixteen PAHs, which may ultimately inhabit the actual source signature authentication. Therefore, factors to be considered when evaluating possible sources of PAHs could be; type and extent of bacterial metabolism, transformation products/substrates, and environmental factors such as salinity, pH, oxygen concentration, nutrients, light intensity, temperature, co-substrates, and environmental medium are hereby recommended as factors to be considered when evaluating possible sources of PAHs.

Keywords—Comparative correlation, kinetically, polynuclear aromatic hydrocarbons, thermodynamically- favored PAHs, sources evaluation.

I. INTRODUCTION

POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs) are classes of ubiquitous organic compounds possessing two or more condensed benzene rings arranged in cluster, angular or linear form and containing carbon and hydrogen atoms only [1]-[5]. Organic Carbon-Water Partition Co-efficient (Koc), Henry's Law constant, Octanol-Water Partition Co-efficient (Kow), vapour pressure and aqueous solubility are chemical specific characteristics that are of relevance in evaluating environmental fate, multimedia

partitioning behavior, bioavailability, resistance to biochemical degradation and toxicity of these un-substituted PAHs [2], [3]. PAHs are non-polar hydrophobic compounds i.e. their solubility in water increases as the molecular weight decreases and exhibit low affinity for suspended particles, hence sediments and soil are major sinks for contaminants [6].

Unsubstituted PAHs can be categorized as kinetically-favoured. Those preferentially produced through combustion processes (i.e., pyrogenic PAHs), thermodynamically-favoured, which are energetically stable over long periods of time and tending to dominate in more mature environmental/geological compartments such as crude oil or coal deposits (i.e., petrogenic PAHs) and PAHs derived directly from plant products which are synthesized at least in part through biologically-mediated processes [2], [3]. The compositional pattern of PAHs can be used to distinguish between combustion-based (pyrogenic) versus thermodynamically-favoured (petrogenic) inputs. The PAH composition in contaminated environmental samples is also useful in delineating between different anthropogenic sources.

PAHs are known for their carcinogenicity, reproduction and respiratory toxicity, hence classified as EDSs [7], [8]. Several researches have established varied amount of PAHs produced by stationary and diffused [9]-[11]. The high concentration of PAHs observed in most urban soils with characteristics close proximity to human population may increase the probability of terrestrial exposure or dermal contact [12]. The evaluation of PAHs in soil from circumscribed sites is complex due to the potential and kinetic variability of industrial, domestic, and natural contributions, fate, and transport [3]. Impacted soil could receive PAHs from air (wet and/or dry deposition), rainwater, and industrial and urban sewage systems. In addition, the potential fumes from vehicles (petrol and/or diesel engine) and motorbikes could also contribute greatly to the pollution load of an area. Preferential biodegradation of lower congeners, preferential bioaccumulation of higher congeners and differential water solubility can alter the original PAHs properties [13].

Identifying and distinguishing sources of PAHs pollution is relevant in controlling their emission in different environmental media since they are ubiquitous, toxic and with diverse sources (point and/or non-point). This may accurately hypothesize possible processes that generate and/or sources that contribute to PAHs pollution load of the study area. Several approaches have been applied to assign sources of PAHs found in sediments or soil (partitioning PAHs along

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petrogenic and pyrolitic using PAHs isomer pair ratios and LPAHs and HPAHs models). However, their empirical validity index is unreliable [3], [8], [13]-[15]. Pearson correlation coefficient (PCC) is a statistical value that assesses the degree that two quantitative variable are linearly related in a sample [16]. While cluster analysis (CA) is an exploratory data analysis tool for organizing clusters which maximize the similarity of cases with each cluster while maximizing the dissimilarity between groups that are initially [16]. Several researches have used PCC and CA for source apportionment of PAHs and other contaminants in environmental studies [17]-[19]. Therefore, this investigation is aimed to further evaluating the empirical validity index and suitability in the application of PCC and CA in PAHs source identification. This may provide a guideline data for future environmental pollution monitoring, policy formulation and implementation regarding sources of environmental PAHs and other related contaminants.

II. MATERIALS AND METHODS

A. 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 [5], [8], [18], [19]. The weather and climatic conditions of the area are of the Niger Delta region, i.e. high temperature, rain forest zone and high [5], [8], [18], [19]. The southwest monsoon wind (April – September) and northeast trade wind (October – March) are the two prevailing air masses of the area. Niger Delta region is situated in the gulf of Guinea between Longitude 5^0 - 8^0E and Latitude 3^0N and 6^0N [20].

B. Sample Collection and Preparation

Sample collection and preparation are as reported in Top (0-15cm) and sub (16-30cm) soil samples were collected in November, December, January and February (dry season) and June, July, August and September (wet season) in ten sampling sites as shown in Table I [5], [8], [18], [19], [21], [22]. Stones and residual roots were removed from each soil core and stored in black polyethylene bags stored below 4^0C before extraction and analysis to avoid evaporation of analytes, photo-oxidation and microbial degradation.

C. Extraction and Analysis

PAHs were extracted from 10 g of dried soil by a continuous extractor with 60 ml of methylen chloride for 8 hrs. Mixture of four deuterated PAHs (d10-acenaphthene, d10-phenanthrene, d12-chrysene and d12-perylene) was added to the sample as internal standard before extraction [22], [5], [8], [18], [19]. .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). After the addition of the sample, the column glass column was filled with 8 g of Al_2O_3.

TABLE I
STUDY AREA SHOWING SAMPLE STATIONS, ACTIVITY, AND GEOGRAPHICAL COORDINATES, ADAPTED IN PART [5], [8], [18], [19]

S/N	Sampling Station	Activity	Coordinate
1	A Sapele	Mechanic Workshop/Urban	05°51.470'N-05°51.933'N 005°41.589'E-005°41.674'E
2	B Okonumere	Mechanic Workshop/Urban	05°51.914'N-05°51.959'N 005°41.622'E-005°41.707'E
3	C Amukpe	Charcoal Factory/Urban	05°51.019'N-05°51.088'N 005°43.551'E-005°43.649'E
4	D Okirighwre	Charcoal Factory/Urban	05°52.318'N-05°52.347'N 005°42.991'E-005°43.142'E
5	E Sapele	Road Side/Urban	05°42.169'N-05°51.512'N 005°42.538'E-005°43.164'E
6	F Okirighwre	Road Side/Urban	05°52.194'N-05°53.490'N 005°40.580'E-005°42.468'E
7	G Sapele	Refuse Dump Road Side	05°52.550'N-05°51.684'N 005°41.296'E-005°41.507'E
8	H Sapele	Refuse Dump Road Side	05°52.728'N-05°52.874'N 005°41.037'E-005°41.226'E
9	I Amukpe	Control/Forest	05°53.553'N-05°53.926'N 005°37.151'E-005°38.461'E
10	J Ogborekoko	Control/Forest	05°50.246'N-05°50.824'N 005°43.124'E-005°43.625'E

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 re-dissolved in 1ml of isooctane [5], [8], [18], [19]. [22],

Quantification of PAHs was determined using Varian 300 gas chromatograph interfaced with flame ionization detector (GC-FID). The initial oven temperature was 60^0C for 10 min and was then increased to 120^0C at 5^0C min^{-1} and 120 –300^0C at 3^0C min^{-1}. The injector and detector temperatures were 200^0C and 300^0C respectively. Concentration determination was carried out by the internal standard using Supelco and Merck standards; detection limit for PAHs is $0.001\mu g.g^{-1}$. Concentration of PAHs was carried out through extrapolation from the standards.

D. Quality Control

Reagents are of chromatographic grade. A standard solution of the anlytes contains the following 16 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 evaluations were carried out by means of four deuterated PAHs (1000 µg.ml^{-1} each in methylene chloride. Containers and equipments were thoroughly cleaned to avoid cross contamination during sample collection and preparation. Four sub-samples were used to form a composite.

III. RESULTS AND DISCUSSION

PCC and CA was applied to identify the possible sources that generate LPAHs-petrogenic (Nap, Acy, Ace, Flu, Phe and Ant) and HPAHs-pyrolitic (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) PAHs in the study area. Accepted data from [5], [8], [18], [19] in Table II were used to generate PCC Tables III and IV and CA values in Tables V and VI.

A. Pearson Correlation Coefficient

Results of PCC pairs from total PAHs in each sample station and mean PAHs in each sample station showed that there is high and positive correlation between sample station C-D, C-E, C-F, C-G, E-F and E-G. In addition, there is high and positive correlation between PAHs pairs Phr-Chr, Phr-B[a]a, Phr-B[a]p, Chr-B[a]a, Chr-B[a]p and B[k]f – B[b]f.

B. Cluster Analysis

Cluster analysis was used to characterize the relationship and homogeneity between sample stations and between PAHs. Results of CA pairs from total PAHs in each sample station and mean PAHs in each sample station showed that there is high and positive correlation between sample stations and among PAHs pairs. Table V showed the homogeneity between sample stations in the following order: B-J, B-I, A-C, B-H, A-G, A-F, A-D, A-E and A-B. The agglomerative hierarchical clusters in Table V showed that sample station B, J, I and H formed a cluster while sample station A, C, G, F D and E

formed an independent and longer cluster. Finally, the study area was joined at step 9 with A and B, this kind of cluster formation revealed that the sources/properties of PAHs in sample station B, J, I and H are related, while sample station A, C, G, F, D and E received PAHs with related properties. Similarly, Table VI showed the agglomerative hierarchical clusters and homogeneity between PAHs through cluster formation in the following order; B[b]f, B[k]f and Flu formed a cluster, while Acy, Ace, Nap and B[a]a clustered separately. Also, Pyr, B[a]p, Chr and Flt formed another cluster with I[123-cd]p, D[ah]a and Phe forming the last cluster. Table VI further reveal that Ant and B[ghi]p are *entropy members* or *outliers* and are independent of the existing clusters. Results from the cluster analysis further confirm the significant relationship between PAHs on one hand and between sample stations by PCC.

TABLE II
TOTAL MEAN CONCENTRATION OF PAHS IN THE STUDY AREA, ADAPTED IN PART FROM [5], [8], [18], [19]

PAHs	Ring	t½	Molecular Formula	Molecular Weight	A	B	C	D	E	F	G	H	I	J
			Properties		**SAMPLE STATION**									
Nap	2	6	$C_{10}H_8$	128.18	0.559	0.932	3.151	7.310	3.118	2.496	2.775	2.226	4.449	4.845
Acy	3	6	$C_{12}H_8$	152.20	1.578	1.484	1.975	1.866	1.665	2.428	0.671	1.696	1.179	2.430
Ace	3	6	$C_{12}H_{10}$	154.20	0.826	2.001	2.333	1.722	4.243	3.292	3.250	6.981	1.032	2.092
Flu	3	6	$C_{13}H_{10}$	166.23	3.767	4.14	0.696	1.684	6.594	5.417	12.906	11.635	2.540	3.875
Phe	3	6	$C_{14}H_{10}$	178.24	12.239	2.766	21.762	33.798	11.648	7.894	14.762	7.539	24.239	10.898
Ant	3	6	$C_{14}H_{10}$	178.24	40.612	5.516	6.571	3.991	na	0.326	9.217	10.618	2.02	3.412
Flt	4	7	$C_{16}H_{10}$	202.26	19.270	2.169	14.251	14.018	3.608	3.787	6.920	3.375	0.727	2.978
Pyr	4	7	$C_{16}H_{10}$	202.26	13.408	3.165	13.967	13.882	7.273	3.971	18.883	10.148	2.600	3.841
Chr	4	7	$C_{18}H_{12}$	228.30	19.437	2.742	17.423	12.852	10.418	6.224	24.479	11.896	1.257	1.254
B[a]a	4	7	$C_{18}H_{12}$	228.30	8.517	1.884	5.318	7.111	3.185	2.964	7.704	6.226	0.509	1.552
B[a]p	5	7	$C_{20}H_{12}$	252.32	13.897	2.361	15.013	10.783	4.392	2.891	23.970	6.429	0.230	3.230
B[k]f	5	7	$C_{20}H_{12}$	252.32	10.709	4.790	2.907	8.673	10.401	9.480	6.067	14.027	1.060	2.955
B[k]f	5	7	$C_{20}H_{12}$	252.32	10.526	5.178	4.106	9.404	10.231	8.512	5.340	16.181	3.511	7.172
B[ghi]p	6	7	$C_{22}H_{12}$	276.34	78.376	11.629	78.098	46.445	129.926	95.058	92.846	8.138	1.938	2.936
I[123cd}p	6	7	$C_{22}H_{12}$	276.34	17.687	7.600	31.719	32.860	23.236	32.873	20.037	7.016	1.369	4.872
D[ah]a	6	7	$C_{22}H_{14}$	278.35	16.669	8.512	29.134	25.635	20.991	41.568	21.354	8.186	12.087	12.721

Were n= 8.

TABLE III
RELATIONSHIP OF THE TOTAL MEAN BETWEEN SAMPLE STATIONS OBTAINED BY PEARSON CORRELATION COEFFICIENT. N=10, DF=8, A=0.05

	A	B	C	D	E	F	G	H	I	J
A	1									
B	0.757	1								
C	0.843	0.789	1							
D	0.647	0.706	0.907	1						
E	0.958	0.809	0.925	0.751	1					
F	0.790	0.884	0.940	0.814	0.952	1				
G	0.873	0.737	0.942	0.755	0.953	0.899	1			
H	0.133	0.342	-0.047	-0.030	0.070	0.029	0.074	1		
I	-0.067	0.062	0.145	0.445	-0.015	0.066	-0.010	-0.014	1	
J	-0.075	0.307	0.161	0428	-0.010	0.187	-0.028	0.099	0.834	1

TABLE IV
RELATIONSHIP BETWEEN PAHs OBTAINED BY PEARSON CORRELATION COEFFICIENT N=16, DF=14, A=0.05

	Nap	Acy	Ace	Flu	Phe	Ant	Flt	Pyr	Chr	B[a]a	B[a]p	B[b]f	B[k]f	B[ghi]p	I[123-cd]p	D[ah]a
Nap	1															
Acy	0.208	1														
Ace	-0.171	0.039	1													
Flu	-0.325	-0.455	0.724	1												
Phe	0.786	-0.104	-0.405	-0.457	1											
Ant	-0.535	-0.209	-0.188	0.055	-0.154	1										
Flt	-0.011	0.030	-0.375	-0.333	0.425	0.676	1									
Pyr	0.033	-0.410	0.082	0.307	0.370	0.411	0.699	1								
Chr	-0.195	-0.430	0.120	0.370	0.196	0.527	0.687	0.961	1							
B[a]a	-0.113	-0.273	0.132	0.313	0.221	0.626	0.774	0.915	0.908	1						
B[a]p	-0.080	-0.462	-0.027	0.329	0.252	0.393	0.631	0.957	0.945	0.826	1					
B[b]f	-0.273	0.097	0.630	0.485	-0.282	0.432	0.195	0.260	0.343	0.545	0.087	1				
B[k]f	-0.128	0.229	0.683	0.434	-0.257	0.351	0.087	0.125	0.151	0.412	-0.008	0.921	1			
B[ghi]p	-0.190	-0.050	0.088	0.149	-0.003	0.286	0.349	0.428	0.580	0.379	0.444	0.337	0.040	1		
I[123-cd]p	0.191	0.277	-0.025	-0.192	0.352	-0.030	0.545	0.473	0.491	0.446	0.416	0.257	0.013	0.741	1	
D[ah]a	0.169	0.388	-0.072	-0.191	0.235	-0.208	0.283	0.192	0.249	0.156	0.212	0.088	-0.136	0.670	0.884	1

TABLE V
AGGLOMERATIVE HIERARCHICAL CLUSTERING PROCESS BETWEEN PAHs

Step	Euclidean Distance between PAHs (coefficient)	Observation Pair	Cluster Membership (Nap) (Acy) (Ace) (Flu) (Phe) (Ant) (Flt) (Pyr) (Chr) (B[a]a) (B[a]p) (B[b]f) (B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	No. of cluster 16
1	32.052	B[b]f-B[k]f	(Nap) (Acy) (Ace) (Flu) (Phe) (Ant) (Flt) (Pyr) (Chr) (B[a]a) (B[a]p) B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	15
2	36.447	Acy-Ace	(Nap) (Acy-Ace) (Flu) (Phe) (Ant) (Flt) (Pyr) (Chr) (B[a]a) (B[a]p) (B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	14
3	58.449	Pyr-B[a]p	(Nap) (Acy-Ace) (Flu) (Phe) (Ant) (Flt) (Pyr-B[a]p) (Chr) (B[a]a) (B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	13
4	64.717	Nap-Acy	(Nap-Acy-Ace) (Flu) (Phe) (Ant) (Flt) (Pyr-B[a]p) (Chr) (B[a]a) (B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	12
5	92.308	Pyr-Chr	(Nap-Acy-Ace) (Flu) (Phe) (Ant) (Flt) (Pyr-B[a]p-Chr) (B[a]a) (B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	11
6	137.512	Nap-B[a]a	(Nap-Acy-Ace-B[a]a) (Flu) (Phe) (Ant) (Flt) (Pyr-B[a]p-Chr) (B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	10
7	195.839	Flu-B[b]f	((Nap-Acy-Ace-B[a]a) (Phe) (Ant) (Flt) (Pyr-B[a]p-Chr) (Flu-B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	9
8	270.482	Nap-Flu	(Phe) (Ant) (Flt) (Pyr-B[a]p-Chr) (Nap-Acy-Ace-B[a]a-Flu-B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p) (D[ah]a)	8
9	315.315	I[123-cd]p-D[ah]a	(Phe) (Ant) (Flt) (Pyr-B[a]p-Chr) (Nap-Acy-Ace-B[a]a-Flu-B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p- D[ah]a)	7
10	323.906	Flt-Pyr	(Phe) (Ant) (Flt-Pyr-B[a]p-Chr) (Nap-Acy-Ace-B[a]a-Flu-B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p- D[ah]a	6
11	667.840	Nap-Flt	(Phe) (Ant) (Flt-Pyr-B[a]p-Chr-Nap-Acy-Ace-B[a]a-Flu-B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p- D[ah]a	5
12	1229.788	Nap-Ant	(Phe) (Ant-Flt-Pyr-B[a]p-Chr-Nap-Acy-Ace-B[a]a-Flu-B[b]f-B[k]f) (B[ghi]p) (I[123-cd]p- D[ah]a	4
13	1433.449	Phe-I[123-cd]p	(Ant-Flt-Pyr-B[a]p-Chr-Nap-Acy-Ace-B[a]a-Flu-B[b]f-B[k]f) (B[ghi]p) (Phe-I[123-cd]p- D[ah]a)	3
14	2340.486	Nap-Phe	(Ant-Flt-Pyr-B[a]p-Chr-Nap-Acy-Ace-B[a]a-Flu-B[b]f-B[k]f-Phe-I[123-cd]p- D[ah]a) (B[ghi]p)	2
15	24531.773	Nap-B[ghi]p	(Ant-Flt-Pyr-B[a]p-Chr-Nap-Acy-Ace-B[a]a-Flu-B[b]f-B[k]f-Phe-I[123-cd]p- D[ah]a-B[ghi]p)	1

TABLE VI
AGGLOMERATIVE HIERARCHICAL CLUSTERING PROCESS BETWEEN SAMPLE STATIONS

Step	Euclidean Distance between Sample Station (coefficient)	Observation Pair	Cluster Membership (A) (B) (C) (D) (E) (F) (G) (H) (I) (J)	No. of cluster 10
1	194.675	B-J	(A) (B-J) (C) (D) (E) (F) (G) (H) (I)	9
2	440.134	B-I	(A) (B-J-I) (C) (D) (E) (F) (G) (H)	8
3	604.742	A-C	(A-C) (B-J-I) (D) (E) (F) (G) (H)	7
4	700.889	B-H	(A-C) (B-J-I-H) (D) (E) (F) (G)	6
5	768.616	A-G	(A-C-G) (B-J-I-H) (D) (E) (F)	5
6	1590.069	A-F	(A-C-G-F) (B-J-I-H) (D) (E)	4
7	2532.181	A-D	(A-C-G-F-D) (B-J-I-H) (E)	3
8	3690.166	A-E	(A-C-G-F-D-E) (B-J-I-H)	2
9	8730.794	A-B	(A-C-G-F-D-E-B-J-I-H)	1

Comparative analysis of PCC and CA pairs of sample station showed that sample stations with many and variable dissimilar activities formed pairs. In addition, results in Table IV and VI showed that paired groups are partitioned along

variable physicochemical properties (t½, molecular weight/structure) of PAHs. The observed pairs are tied along non-alternate/ carcinogenen, LPAHs/non-alternate, alternate/HPAHs, LPAHs/LPAHs, alternate/alternate, non-alternate/non-alternate, HPAHs/carcinogen, non-carcinogen/HPAHs, non-carcinogen/non-carcinogen and alternate/LPAHs. This is at variance with earlier established mechanisms/models [3], [18], [23] used in apportioning sources of PAHs where kinetically-favoured PAHs are grouped as LPAHs while thermodynamically–favoured PAHs are classed as HPAHs. Similarly [17], [24] had argued that the tendency of chemical substances or variables to cluster is a function of many factors, which include having similar sources of contaminant(s) or that their physicochemical properties are similar or that their degradation pattern and/or mobility indexes are similar in the environment. This study has also shown that transformation products, type and extent of bacterial metabolism and environmental factors such as: pH, temperature, salinity, oxygen concentration, nutrients, light intensity, co-substrates and environmental matrix as earlier argued by [8] are physicochemical factors that may be applied in the evaluation PAHs sources in any environmental medium. Analysis of results showed that PCC and CA simply partitioned the observed PAHs along structural composition i.e. variability in the physiochemical properties of these EDSs (hydrophobicity, resistance to biodegradation, tendency for bioaccumulation, environmental persistence and toxicity). Furthermore, PCC and CA pairs in Tables III-VI provide no empirical explanation as to why the couples exist to rather it provide in term of the class to which members belong i.e. the degree that two quantities are linearly related. Observation within each group is similar to one another with respect to some variables or attributes of interest and dissimilar to those in other groups. Comparative analysis of PCC and CA pairs in Tables III and IV and observed PAHs pairs in Tables V and VI could be related to physiochemical properties of these priority pollutants. Though the compositional pattern of PAHs can be used to distinguish between combustion-based versus petrogenic in delineating different (industrialize, domestic and natural) sources, this research has showed that the classification of PAHs along kinetically and thermodynamically-favoured processes used in source signature [3], [23] is about the predominance PAHs are likely to be. Therefore, the observed PAHs in the studied stations have trace quantities of the vast majority of the studied sixteen un-substituted PAHs, this may ultimately inhabit the actual source signature authentication.

IV. Conclusion and Recommendations

PCC and CA pairs showed that sample stations with dissimilar activities formed pairs. In addition, results showed that PAHs paired groups are partitioned along variable physicochemical properties. This research has showed that the classification of PAHs along kinetically and thermodynamically-favoured used in source signature is about the predominance PAHs are likely to be. The observed PAHs in the studied stations have trace quantities of the vast majority of the sixteen un-substituted PAHs which may ultimately inhabit actual sources signature. Therefore, type and extent of bacterial metabolism, transformation products/ substrates, and environmental factors such as: salinity, pH, oxygen concentration, nutrients, light intensity, temperature, co-substrates and environmental medium are hereby recommended as factors to be considered when evaluating possible sources of PAHs

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