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Variability in Polycyclic Aromatic Hydrocarbons (PAHs) Isomer Pair Ratio: Source Identification Concern

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Abstract: Polycyclic Aromatic Hydrocarbons (PAHs) toxicity and contamination of both terrestrial and aquatic ecosystem have been established PAHs are formed mainly as a result of incomplete combustion of organic materials during industrial and anthropogenic activities. Previous research has focused on various and many PAHs isomer pair ratio of variable physicochemical properties in source identification. The objective of this investigation was to determine the empirical validity of these 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) in source identification along sample station. In this way, 16 priority PAHs were determined in 10 sample stations in top and sub soil seasonally. After extraction, purification and quantification of PAHs was done using GC-FID. Reagents used are of chromatographic grade. Results showed that ratios are skewed either towards pyrolitic and/or petrogenic, and evaluation for petrogenic and pyrolitic source is different with isomer pair in each sample station even in areas were anthropogenic or industrial activity suggest otherwise. A suitable model/mechanism that shall take account of transformation products, type and extent of bacterial metabolism 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.

Keywords: PAHs Isomer Pair, Petrogenic, Pyrolitic, Variability, Sources Identification

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large groups of organic compounds with two or more fused benzene rings in linear, angular or cluster arrangement and containing carbon and hydrogen atoms only [1,2]. PAHs are formed mainly as a result of pyrolitic 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 of carbonization etc [3,4].

PAHs octanol water partition coefficient (Koc), Henry's law constant, vapor pressure and aqueous solubility are chemical specific behaviour that are of direct relevance in predicting environmental fate, its multimedia behaviour, bioavailability and resistance to biotic and chemical transformation [2]. Several researches have established a varied amount of PAHs produced by both stationary and diffused sources [5-7]. 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 [8].

PAHs are tagged priority pollutants due to their carcinogenicity, induce tumor, immunodeficiency, reproduction and respiratory problems hence are classified as "endocrine disruption substances" [9]. The evaluation of PAHs in soil from circumscribed sites is complex due to the potential and kinetic variability of anthropogenic and natural contribution, their fate and transport. Impacted could receive PAHs from air (water and/or dry deposition), rain water and industrial and urban sewage systems. In addition, the potential fumes from vehicles (petrol and/or diesel engines) could also contribute greatly to the pollution load of the area.

Though factors such as differential water solubility, preferential bioaccumulation of higher congener's and preferential biodegradation of lower congeners can change the original PAHs pattern [10], there are several approaches that

can be use to assign sources of PAHs mixtures found in sediments/soil [11].

Anthracene/178 ratio greater than 0.1 is indicative of petroleum origin, while ratio less than 0.1 indicate the presence of combustion PAHs [12]. For mass 202, a (Flt/Flt+Pyr) ratios below 0.5 is indicative of most petroleum samples and above 0.5 is kerosene, grass, coal and wood combustion samples [13]. Benzo[a]anthracen/228 ratio over 0.5 has been ascribed to combustion while a ratio below 0.5 has been attributed to low temperature diagenesis [13]. Combustion products of gasoline, kerosene, diesel and crude oil have ratio of I[123-cd]p/I[123-cd]p+B[ghi]p below 0.5 and ratio greater than 0.5 implies grass, wood and coal combustion [13].

Fluoranthene and pyrene, both with a mass of 202 have a greatest range in stability and hence are good indicators of thermodynamic versus kinetic effects [10]. Phenenthren and anthracen both have mass of 178 with different structural isomers. The Phe/Ant ratio above 10 is suggestive of petrogenic origin while ratio below 10 is typical of pyrolitic source, [14]. Chrysene and B[a]a both with mass of 228 have different structural isomers. The PAHs ratio lower than 1 is derived from pyrolitic sources while ratio higher than 1 are of petrogenic source [11,12]. 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 pyrolitic sources of PAHs, (Soclo, *et.al.*, 2000). The ratio of LPAHs/HPAHs greater than 1 is suggestive of petroleum origin while ratio less than 1 is of pyrolitic processes [12,15].

The empirical accuracy in identifying PAHs signature in the presence of possible diverse sources could be eliminated by use of molecular ratio of PAHs with different physicochemical properties. This may precludes accurate hypothesizing possible processes/sources that generate and/or contribute to PAHs pollution load. Therefore, this investigation is aimed to empirically evaluate PAHs sources using isomer pair ratios.

2. Materials and Methods

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. Niger Delta region is situated in the gulf of Guinea between Longitude $5^0 - 8^0$E and Latitude 3^0N and 6^0N [16].

2.2. Sample Collection and Preparation

Sample collection and preparation are of standard methods [17]. 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 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 [18] and as reported in [19]. 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.

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 [19].

*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 [19].

3. Results and Discussion

In order to identify the possible sources of PAHs (petroleum or pyrolitic) in the study area, PAHs isomer pair (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) were used as in other studies [10-13,20-24].

These ratios were computed for in this study for total mean, mean of top, mean of sub, mean of dry and mean of wet samples as shown in Table 2 and 3, in this way source apportionments was deduced.

Table 1. *Study Area Showing Sample Stations, Sample Points, Season, Activity, and Geographical Coordinates.*

S/N	sampling station	sample point	season	activity	coordinate
1	A Sapele	1, 11,41,51 / 21,31,61,71	Dry / Wet	Mechanic Workshop/Urban	05°51.470'N-05°51.933'N 005°41.589'E-005°41.674'E
2	B Okonumere	2, 12, 42, 52 / 22, 32, 62, 72	Dry / Wet	Mechanic Workshop/Urban	05°51.914'N-05°51.959'N 005°41.622'E-005°41.707'E
3	C Amukpe	3, 13, 43, 53 / 23, 33, 63, 73	Dry / Wet	Charcoal Factory/Urban	05°51.019'N-05°51.088'N 005°43.551'E-005°43.649'E
4	D Okirighwre	4, 14, 44, 54 / 24, 34, 64, 74	Dry / Wet	Charcoal Factory/Urban	05°52.318'N-05°52.347'N 005°42.991'E-005°43.142'E
5	E Sapele	5, 15, 45, 55 / 25, 35, 65, 75	Dry / Wet	Road Side/Urban	05°42.169'N-05°51.512'N 005°42.538'E-005°43.164'E
6	F Okirighwre	6, 16, 46, 56 / 26, 36, 66, 76	Dry / Wet	Road Side/Urban	05°52.194'N-05°53.490'N 005°40.580'E-005°42.468'E
7	G Sapele	7, 17, 47, 57 / 27, 37, 67,77	Dry / Wet	Refuse Dump Road Side	05°52.550'N-05°51.684'N 005°41.296'E-005°41.507'E
8	H Sapele	8, 18, 48, 58 / 28, 38, 8, 78	Dry / Wet	Refuse Dump Road Side	05°52.728'N-05°52.874'N 005°41.037'E-005°41.226'E
9	I Amukpe	9, 19, 49, 59 / 29, 39, 69, 79	Dry / Wet	Control/Forest	05°53.553'N-05°53.926'N 005°37.151'E-005°38.461'E
10	J Ogborekoko	10, 2, 50, 60 / 30, 40, 70, 80	Dry / Wet	Control/Forest	05°50.246'N-05°50.824'N 005°43.124'E-005°43.625'E

Table 2. *Total Mean Concentration of PAHs in the Study Area.*

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

Were n=8

Table 3. Petrogenic and Pyrolytic Signature Using PAHs Isomer Pair Ratio in the Study Area.

PAHs	Sample station											Source identification	
	Mean	A	B	C	D	E	F	G	H	I	J	X	Y
Ant /178	Tm	Y	X	X	X	na	X	X	X	X	X		
	mt	Y	X	X	X	na	na	X	X	na	na		
	ms	Y	X	X	X	na	X	X	X	X	X	<0.1	>0.1
	md	Y	X	X	X	na	X	X	X	X	X		
	mw	Y	X	X	na	na	X	X	X	X	X		
Flt/Flt+Pyr	Tm	Y	X	Y	Y	X	X	X	X	X	X		
	mt	Y	X	X	X	Y	X	X	X	X	X		
	ms	X	X	Y	Y	X	X	X	X	Y	Y	<0.5	>0.5
	md	Y	X	X	X	X	Y	X	X	X	Y		
	mw	X	X	X	Y	X	X	X	Y	X	X		
B[a]a/228	Tm	X	X	X	X	X	X	X	X	X	X		
	mt	X	X	X	X	X	X	X	X	X	X		
	ms	X	X	X	X	X	X	X	X	X	X	<0.35	>0.35
	md	X	X	X	X	X	X	X	X	X	X		
	mw	X	X	X	X	X	X	X	X	X	X		
I[123-cd]p/ I[123-cd]p + B[ghi]p	Tm	X	X	X	X	X	X	X	X	X	Y		
	mt	X	X	X	Y	X	X	X	Y	X	Y		
	ms	X	X	X	X	X	X	X	X	Y	Y	<0.2/0.5	>0.5
	md	X	X	X	X	X	X	X	X	Y	Y		
	mw	X	X	X	X	X	X	Y	Y	X	Y		
Flu/Pyr	Tm	X	Y	X	X	X	Y	X	Y	X	Y		
	mt	X	Y	X	X	na	na	X	X	Y	X		
	ms	X	X	X	X	X	Y	X	Y	na	na	<1	>1
	md	X	Y	X	X	Y	Y	X	Y	Y	Y		
	mw	X	X	X	X	X	X	X	Y	X	X		
Phe/Ant	Tm	Y	Y	Y	Y	na	X	Y	Y	X	Y		
	mt	Y	Y	Y	Y	na	na	Y	Y	na	na		
	ms	Y	Y	Y	X	na	X	Y	Y	X	Y	>10	<10
	md	Y	Y	Y	X	na	X	Y	Y	X	Y		
	mw	Y	Y	X	na	na	X	Y	Y	Y	Y		
Chr/B[a]a	Tm	X	X	X	X	X	X	X	X	X	Y		
	mt	X	X	X	X	X	X	X	X	X	Y		
	ms	X	X	X	X	X	X	X	X	na	na	>1	<1
	md	X	X	X	X	X	X	X	X	na	na		
	mw	Y	X	X	Y	X	X	X	X	X	Y		
LPAHs/HPAHs	Tm	Y	Y	Y	Y	Y	Y	Y	Y	X	Y		
	mt	Y	Y	Y	Y	Y	Y	Y	Y	X	Y		
	ms	Y	Y	Y	Y	Y	Y	Y	Y	X	Y	>1	<1
	md	Y	Y	Y	Y	Y	Y	Y	Y	X	X		
	mw	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y		

Where; Total mean (Tm), Mean of Top (mt), Mean of Sub (ms), Mean of Dry (md), Mean of Wet (mw), Petrogenic (X), Pyrolitic (Y) and not available (na).

The Ant/178 ratio of the total mean of PAHs reveal that the origin of PAHs is petroleum for all sample stations except A with a ratio suggestive of pyrolitic source. In the same vein, the Ant/178 ratio for the mean of top and sub soil showed that the origin of PAHs is petroleum for all sample stations except A with ratio indicating pyrolitic source. Similarly, the Ant/178 ratios for the mean of dry and wet season's samples showed that the origin of PAHs is petroleum for all sample stations except A with a ratio suggesting pyrolytic process.

The Flt/Flt+Pyr ratio of the total mean showed a petroleum contribution of PAHs in all sample stations except A, C and D with ratio suggesting pyrolitic source. Also, the Flt /Flt+Pyr ratio of the mean of top soil samples showed that the sources of PAHs in all sample stations is of petroleum processes except sample station A and E with pyrolitic process ratio. Similarly, the Flt/Flt+Pyr ratio of the mean of sub soil samples showed that the sources of PAHs at sample station A, E, F, G and H are of petroleum origin while sample station C, D, I and J received PAHs from pyrolitic processes. In a related development, the Flt/Flt + Pyr ratio of the mean of dry season reveal that the sources of PAHs is pyrolitic for sample station A, F and J while sample station B, C, D, E, G, H and I have ratios that suggest petroleum origin. The wet season mean Flt/Flt+Pyr ratio showed that all sample stations received PAHs via petroleum processes except D and H with ratios of pyrolitic origin. Analytical observation of Flt/Flt + Pyr ratio in all mean samples showed a high contributions from vehicular and crude oil combustion particulate (0..41-0.49) diesel exhaust (0.2-0.58) [13]. The commercial and industrial activities (timber logging, asbestos production, gas flaring activities and vehicular transport) could promote the combustion of petrol and diesel in the study area.

The B[a]a/228 ratio of the total mean, mean of top and sub samples and mean of dry and season sampling showed that all sample stations received PAHs from petroleum combustion process. This trend whereby all sample station would receive PAHs from one source could be attributed to possible

degradation of B[a]a through biotic and/or abiotic processes leaving the denominator intact. This phenomenon was also noticed in Ant/178 ratio in the study area as shown in Table 3.

The I[123-cd]p/I[123-cd]p+ B[ghi)p ratios of the total mean reveal a petroleum source of PAHs in all sample stations except J with pyrolitic source ratio. Also, the I[123-cd]p/I[123-cd]p+ B[ghi)p ratio of the mean of top soil samples showed that sample station D, H and J received PAHs from pyrolitic source while other samples stations are of petroleum origin. Similarly, the I[123-cd]p/I[123-cd]p+ B[ghi)p ratio of the mean of sub soil samples suggest petroleum origin for all sample stations except I and J indicating ratio of pyrolitic sources. In a related development, the I[123-cd]p/I[123-cd]p+ B[ghi)p ratios of the mean of dry season sample showed that all sample station received PAHs from petroleum origin except I and J with pyrolitic process ratios. Similarly, the I[123-cd]p/I[123-cd]p+ B[ghi)p ratio of the mean of wet season samples showed that all sample station recorded PAHs from petroleum process except G, H, I and J with pyrolitic ratios.

Generally, Flu/Pyr ratio above 1 indicates pyrolitic origin, while values below I are typical of petroleum sources. The ratios of the total mean of PAHs showed that the sources of PAHs in sample station A, C, D, E, G and I are petrogenic while sample station B, F, H and J are of pyrolitic origin. The ratio of 0.68 at sample station G is indicative of vehicular emission; similarly, the ratio of 0.91 and 0.98 at sample station E and I are very close to pyrolitic ratio of greater than 1.

Also, Flu/Pyr ratio of mean of top PAHs samples reveal that sample station B, F and I are indicative of pyrolitic origin, while sample station A, C, D, G, H and J are suggestive of petroleum sources. Similarly, the ratios of 0.83 and 0.66 at sample station G and H are very close to pyrolitic ratio of greater than 1. In the same vein, Flu/Pyr ratio of the mean of sub soil reveal that sample station A, B, C, D, E and G are of petroleum class while sample station F and H received PAHs from pyrolitic sources. Similarly, the ratio of 0.81 and 0.64 at sample station B and G are very close to pyrolitic ratio of > I. Expectedly, the Flu/Pyr ratio of the mean of the dry season samples showed that the source of PAHs at sample station B, E, F, H, I and J is pyrolitic with sample station A, C, D and G having ratios that suggest PAHs of petrogenic origin. Also, the Flu/Pyr ratios of the mean of wet season samples reveal that the sources of PAHs is petrogenic for all sample stations except H with ratio suggesting pyrolitic source. Similarly, the ratio of 0.61, 0.79, 0.78, 0.97 and 0.87 at sample station B, E, F, G and J respectively are relatively close to ratio of pyrolitic boundary of > 1.

The Phe/Ant ratios of the total mean shows that the PAHs are of petroleum sources. Sample station D have ratio (8.47) close to petroleum boundary of > 10. For the mean of top PAHs samples Phe/Ant ratio showed that the source of PAHs is pyrolitic for all sample stations. The Phe/Ant ratios of the mean of sub sample showed that the sources of PAHs is pyrolitic for all sample stations except D, F and I with ratios indicating petrogenic sources. The Phe/Ant ratios of the mean of dry season showed that the sources of PAHs in sample

station D, F and I are of petroleum origin while sample station A, B, C, G, H and J have ratios that suggest pyrolitic PAHs. Similarly, Phe/Ant ratios of the mean of wet season samples showed that all samples stations received PAHs via pyrolitic process except C and F with ratios of petrogenic origin.

The Chr/B[a]a ratio of the total PAHs showed that the source of PAHs in all the sample stations is of petroleum origin except J with ratio of pyrolitic PAHs. Chrysene/B[a]a ratio of the mean of top and sub samples showed that the origin of PAHs is petroleum in all samples except J with pyrolitic PAHs ratio for the top samples. Also, Chr/B[a]a ratios of the mean of dry season samples showed the sources of PAHs are of petroleum origin for all sample stations. While in the wet season mean PAHs showed that Chr/B[a]a ratio suggest pyrolitic source of PAHs for sample station A, B, C and J and sample station C, E, F, G H and I are of petroleum origin.

Table 4. *Summarized half-Lives for PAHs in soil, Adapted in Part [27].*

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

The LPAHs/HPAHs ratios of the total mean reveal that the origin of PAHs is pyrolitic in all sample station except I with petroleum ratio. Similarly, LPAHs/HPAHs ratios of the mean of top and sub samples showed that the sources of PAHs are pyrolitic for all sample station except I with petroleum origin ratio. In the same vein, the LPAHs/HPAHs ratio showed that the sources of PAHs are pyrolitic for all sample stations except I and J with petroleum ratio of wet season samples.

Petrogenic and pyrolitic contamination are characterized with the predominance of LPHAHs and HPAHs respectively [10-13, 21]. Also, [10], 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. Similarly, [10,14], had argued that the use of PAHs isomer pair of the same molecular mass represent a well-established method for interpreting PAHs composition and evaluating sources. Therefore, the use of LPAHs and HPAHs and other PAHs pair with different physicochemical behavior in classifying petroleum and pyrolitic origin of PAHs respectively may not be empirically valid in environmental chemistry when dealing with seasonal and profile samples.

The discrimination between LPAHs and HPAHs based on molecular weight and structural complexity is useful in that the hydrophobicity, volatility tendency for bioaccumulation, ageing, and resistance to biodegradation, chemical oxidation and overall environmental resistance increases with increasing molecular weight. HPAHs (four or more rings) sorb strongly to soils and sediments and are more resistant to microbial degradation. Therefore, the release of the same quantity of mixtures of petroleum (LPAHs) and pyrolitic (HPAHs) PAHs into the same environment with the same physiochemical properties, LPAHs are expected to reduce in quantity than HPAHs. This is due to their susceptibility to leaching, volatilization, biotic and/or abiotic degradation, shorter half-lives (16 to 123 days) than HPAHs as shown in Table 4, [25,26].

The presence of petroleum source of PAHs over pyrolitic sources and viz a viz in this study is a function of the various PAHs isomer pair used. Generally the sources of PAHs in the various sample stations are petrogenic and pyrolitic, though skewed to petroleum origin. 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 pyrolitic PAHs in all sample station can be adduced to the fact that once produced PAHs can be widely distributed regionally and continentally as gases or aerosols during winter without significant biotic and/or abiotic degradation by atmospheric transport or through stream pathways and eventual accumulation in soil and aquatic sediments [28-30].

Table 5. *Problem Evaluation Using Different Computational/Determination Techniques.*

S/N	Problem	Method	S/N	Problem	Method
1	Radio Isotopic Dating	$K = \dfrac{In2}{t\frac{1}{2}}$ $\dfrac{lo}{I} = e^{-dt}$	4	Determination of Iron	Spectroscopic (Uv) Gravimetric Atomic Absorption Spectroscopy
2	Simultaneous Linear Equation	Cramer's Rule Gaussian Elimination Gauss-Jordan Factorization	5	Determination of Ascorbic Acid	Iodiometric Titrimetry Indophenol Spectroscopic Clegg-Anthrone
3	Quadratic Equation	Completing the Square Quadratic Formula	6	Carbohydrate	Phenol-Sulphuric Acid Chow

Diagonistic ratio in source identification is been widely used, however, their reliability index is limited [30]. The ultimate objective of source identification using PAHs isomer pair ratio is to evaluate the fraction contribution of different PAHs source for a given sample. Results in Table 3 showed that the use of PAHs isomer pair with different physicochemical behavior can be seen with lopsided source, either tilting towards petroleum or pyrolitic, (Ant/178, B[a]a/228, Chr/B[a]a, Phe/Ant and LPAHs/HPAHs). Structural isomers, Phe is more thermodynamically stable than Ant hence Phe/Ant ratio is very high during petrogenic pollution [10]. While high temperatures during combustion processes help the formation of Ant and lowering of the Phe/Ant ratio. Therefore, due to their dissimilarities in physicochemical behavior, their ratio cannot provide a picture of PAHs source since ratios are not constant. Hence the use of PAHs isomer pair ratio as seen in Table 3 is suggestive of a "*rule of thumb*" that lacked empirical validity since evaluation for petrogenic and pyrolitic source is different with isomer pair in each sample station. This is at variance in scientific and mathematical computation/evaluation were different methods have been employed to resolve specific problem within the limits of experimental/computational error as shown in Table 5.

4. Conclusion and Recommendations

This study has shown that source signature is a function of many and different ratios of PAHs with varied physicochemical characteristics i.e. susceptibility to volatility, biotic and abiotic transformation of original/parent PAHs.

However, the use of PAHs isomer ratio with different (constant and variable) physicochemical behavior in delineating sources is empirically invalid since results are either skewed to pyrolitic and/or petrogenic sources and evaluation for petrogenic and pyrolitic source is different with isomer pair in each sample station even in areas were anthropogenic or industrial activity suggest otherwise. Since PAHs degradation cannot be regarded as a linear decay process, a suitable model/mechanism that shall take account of transformation products, type and extent of bacterial metabolism 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 should be developed.

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