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

Emoyan Onoriode Onos*, Agbaire Patience Odafe, Akporido Samuel Omorovie

Environmental and Food Chemistry Research Group, Department of Chemistry, Delta State University, P.M.B. 1 Abraka, Nigeria

Email address:
onostica_pub@yahoo.com (Emoyan O. O.)

To cite this article:
Emoyan Onoriode Onos, Agbaire Patience Odafe, Akporido Samuel Omorovie. Variability in Polycyclic Aromatic Hydrocarbons (PAHs) Isomer Pair Ratio: Source Identification Concern. International Journal of Environmental Monitoring and Analysis. Vol. 3, No. 3, 2015, pp. 111-117. doi: 10.11648/j.ijema.20150303.11

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[ghi]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 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 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 used 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]. Phenanthrene and anthracene 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 pyrolytic 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 pyrolytic 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[a]h[a]) is functional in delineating petrogenic and pyrolytic sources of PAHs, (Socol, et.al., 2000). The ratio of LPAHs/HPAHs greater than 1 is suggestive of petroleum origin while ratio less than 1 is of pyrolytic 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 9°54' – 5° 9' N and 6°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. Niger Delta region is situated in the gulf of Guinea between Longitude 5° - 8°E and Latitude 3°N and 6°N [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 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 Al2O3 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 methane chloride (40 ml), the resulting solution was dried and redissolved in 1ml of isoctane.

Quantification of PAHs was determined using Varian 300 gas chromatograph interfaced with flame ionization detector (GC-FID). The initial oven temperature was 60 °C for 10 min and was then increased to 120 °C at 5 °C min-1 and 120 – 300 °C at 3 °C min-1. The injector and detector temperatures were 200 °C and 300 °C respectively. Concentration determination was carried out by the internal standard method using Supelco and Merck standards; detection limit for PAHs is 0.001 µg 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 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[a]h[a]) is functional in delineating petrogenic and pyrolytic sources of PAHs, (Socol, et.al., 2000). The ratio of LPAHs/HPAHs greater than 1 is suggestive of petroleum origin while ratio less than 1 is of pyrolytic 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 9°54' – 5° 9' N and 6°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. Niger Delta region is situated in the gulf of Guinea between Longitude 5° - 8°E and Latitude 3°N and 6°N [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 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 Al2O3 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 methane chloride (40 ml), the resulting solution was dried and redissolved in 1ml of isoctane.

Quantification of PAHs was determined using Varian 300 gas chromatograph interfaced with flame ionization detector (GC-FID). The initial oven temperature was 60 °C for 10 min and was then increased to 120 °C at 5 °C min-1 and 120 – 300 °C at 3 °C min-1. The injector and detector temperatures were 200 °C and 300 °C respectively. Concentration determination was carried out by the internal standard method using Supelco and Merck standards; detection limit for PAHs is 0.001 µg 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 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[a]h[a]). Working standards were prepared by dilution with isoctane. 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 pyrolytic) 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  | Dry    | Mechanic Workshop/Urban   | 05°51.470’N-05°51.933’N 005°41.589’E-005°41.674’E |
|     |                  | 21,31,61,71  | Wet    |                            |                                 |
| 2   | B Okonumere      | 2, 12, 42, 52| Dry    | Mechanic Workshop/Urban   | 05°51.914’N-05°51.959’N 005°41.622’E-005°41.707’E |
|     |                  | 22, 32, 62, 72| Wet |                            |                                 |
| 3   | C Amukpe         | 3, 13, 43, 53| Dry    | Charcoal Factory/Urban    | 05°51.019’N-05°51.088’N 005°43.551’E-005°43.649’E |
|     |                  | 23, 33, 63, 73| Wet |                            |                                 |
| 4   | D Okirighwe      | 4, 14, 44, 54| Dry    | Charcoal Factory/Urban    | 05°52.318’N-05°52.347’N 005°42.991’E-005°43.142’E |
|     |                  | 24, 34, 64, 74| Wet |                            |                                 |
| 5   | E Sapele         | 5, 15, 45, 55| Dry    | Road Side/Urban           | 05°42.169’N-05°51.512’N 005°42.538’E-005°43.164’E |
|     |                  | 25, 35, 65, 75| Wet |                            |                                 |
| 6   | F Okirighwe      | 6, 16, 46, 56| Dry    | Road Side/Urban           | 05°52.194’N-05°53.490’N 005°40.580’E-005°42.468’E |
|     |                  | 26, 36, 66, 76| Wet |                            |                                 |
| 7   | G Sapele         | 7, 17, 47, 57| Dry    | Refuse Dump Road Side     | 05°52.550’N-05°51.684’N 005°41.296’E-005°41.507’E |
|     |                  | 27, 37, 67, 77| Wet |                            |                                 |
| 8   | H Sapele         | 8, 18, 48, 58| Dry    | Refuse Dump Road Side     | 05°52.728’N-05°52.874’N 005°41.037’E-005°41.226’E |
|     |                  | 28, 38, 8, 78| Wet    |                            |                                 |
| 9   | I Amukpe         | 9, 19, 49, 59| Dry    | Control/Forest            | 05°53.553’N-05°53.926’N 005°37.151’E-005°38.461’E |
|     |                  | 29, 39, 69, 79| Wet |                            |                                 |
| 10  | J Ogborekoko     | 10, 2, 50, 60| Dry    | Control/Forest            | 05°50.246’N-05°50.824’N 005°43.124’E-005°43.625’E |
|     |                  | 30, 40, 70, 80| Wet |                            |                                 |

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[alp]    |                | 13.897| 2.361| 15.013| 10.783| 4.392| 2.891| 23.970| 6.429| 0.230| 3.230|
| 12  | B[k]jF    |                | 10.709| 4.790| 2.907| 8.673| 10.401| 9.480| 6.067| 14.027| 1.060| 2.955|
| 13  | B[g]hF    |                | 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
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 pyrolytic 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 pyrolytic source. Similarly, 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, C and D with ratio suggestive of pyrolytic source. 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 and E with pyrolytic process ratio.

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 pyrolytic 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 pyrolytic 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, 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 samples received PAHs via petroleum processes except D and H with ratios of pyrolytic 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 pyrolic 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 pyrolic 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 pyrolic 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 pyrolic 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 pyrolic ratios.

Generally, Flu/Pyr ratio above 1 indicates pyrolic origin, while values below 1 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 pyrolic 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 pyrolic 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 pyrolic 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 pyrolic 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 pyrolic sources. Similarly, the ratio of 0.81 and 0.64 at sample station B and G are very close to pyrolic ratio of greater than 1. 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 pyrolic 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 pyrolic 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 pyrolic 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 pyrolic for all sample stations. The Phe/Ant ratios of the mean of sub sample showed that the sources of PAHs is pyrolic 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 pyrolic PAHs. Similarly, Phe/Ant ratios of the mean of wet season samples showed that all samples stations received PAHs via pyrolic 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 pyrolic 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 pyrolic 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 pyrolic 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.

| PAH     | Ring | Mean half-life (h) | Range of half-lives (h) |
|---------|------|-------------------|------------------------|
| Nap     | 2    | 1700              | 1000 – 3000            |
| Aey     | 3    | na                | na                     |
| Ace     | 3    | 5500              | 3000 – 1000            |
| Flu     | 3    | 5500              | 3000 – 1000            |
| Phe     | 3    | 5500              | 3000 – 1000            |
| Ant     | 3    | 5500              | 3000 – 1000            |
| Ft     | 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                | na                     |
| B[b]f   | 5    | 17000             | 1000 – 3000            |
| B[k]f   | 5    | 17000             | 1000 – 3000            |
| B[ghi]p | 6    | na                | na                     |
| I(123-cd)p | 6  | 17000             | 1000 – 3000            |
| D[a]h[a] | 6  | 17000             | 1000 – 3000            |

na = not available

The LPAHs/HPAHs ratios of the total mean reveal that the origin of PAHs is pyrolic 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 pyrolic 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 pyrolic for all sample stations except I and J with petroleum ratio of wet season samples.

Petrogenic and pyrolic contamination are characterized with the predominance of LPAHs and HPAHs respectively [10-13, 21]. Also, [10], suggested that the constitution of 90% HPAAHs 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 pyrolic 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 pyrolytic (HPAHs) PAHs into the same environment with the same physicochemical properties, LPAHs are expected to reduce in quantity than HPAHs. This is due to their susceptibility to teaching, volatilization, biotic and/or abiotic degradation, shorter half-lives (16 to 123 days) than HPAHs as shown in Table 4, [25,26].

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

| S/N | Problem                                      | Method                        | S/N | Problem                                      | Method                        |
|-----|----------------------------------------------|-------------------------------|-----|----------------------------------------------|-------------------------------|
| 1   | Radio Isotopic Dating                        | \[ K = \frac{2}{t} \]       | 4   | Determination of Iron                       | Spectroscopic (UV)            |
|     | \[ \frac{1}{t} = e^{-\alpha} \]            |                               |     | Gravimetric                                  | Atomic Absorption Spectroscopy|
| 2   | Simultaneous Linear Equation                 | Cramer’s Rule Gaussian Elimination|
|     | Gauss-Jordan                                 | Iodometric Titrimetry         | 5   | Determination of Ascorbic Acid              | Indophenol                    |
| 3   | Quadratic Equation                           | Completing the Square         | 6   | Carbohydrate                                 | Spectroscopic                |
|     | Quadratic Formula                           | Quadratic Formula             |     | Clegg-Anthrone                               | Phenol-Sulphuric Acid         |
|     |                                              | Chow                           |     |                                              |                               |

Diagnostic 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 pyrolytic, (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 pyrolytic 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.

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 pyrolytic and/or petrogenic sources and evaluation for petrogenic and pyrolytic 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.

References

[1] Zeng, Y., Hong, P.K.A., and Wavrek, D. A. (2000). Integrated Chemical-Biological Treatment of B[a]p. Environmental Science and Technology: 34: 854-862

[2] CCME, (2008). Canadian soil quality guidelines for the protection of environmental and human health: Benzo [a] Pyrene. In: Canadian environmental quality guidelines. Canadian Council of Ministers of the Environment, Winnipeg, Canada, pp 235.

[3] Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., and Sylvestre, S. (2002). PAHs in the Fraser River Basin: A Critical Appraisal of Polycyclic Aromatic Hydrocarbons Ratios as Indicators of PAH Source and Composition. Organic Geochemistry, 33 : 489-515.
[4] Macdonald, R.W., Harner, T.T., and Feyfe, J. (2005). Recent Climate Change in the Arctic and its Impact on Contaminant Pathways and Interpretation of Temporal Trend Data. *Science of the Total Environment*, 342:5-86.

[5] Kamaljit, B., Gurpal, S.T., Tait, C. and Lena M. (2010) Polycyclic Aromatic Hydrocarbons in Urban Soils of Different land Uses in Miami, Florida. *Soil and Sediment Contamination*, 19:231-243.

[6] Krauss, M and Wilcke, W. (2003) Polychlorinated Naphthalene in Urban soils: Analysis, Concentration and Relation to Other Persistent Organic; Pollutants. *Environmental Pollution*, 122:75-89.

[7] Morillo, E., Romero, A.S., Madrid, L., Villaverde, J. and Maqueda, C. (2008). Characterization Sources of PAHs and Potentially Toxic Metals in Urban Environment of Sevilla, Southern Spain. *Water air Soil Pollution*, 187:41-51.

[8] Abrahams, P.W. (2002) Soils: Their Implications to Human Health. *Science of the Total Environment*, 291:1-32.

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

[10] Perra, G., Renzi, M., Guerriani, C. and Focardi, S.E. (2009). Polycyclic Aromatic Hydrocarbons pollution in sediments: Distribution and sources in a Lagoon System (Orbetello Central Italy). *Transitional Waters Bulletin*, 3: 45-58.

[11] Bertolotto, R.M., Ghioni, F., Frignani M., Alvarado-Aguilar D., Bellucci L.G., Cuneo C., Pica M.R. and Gollo E. (2003). Polycyclic Aromatic Hydrocarbons in Surficial Coastal Sediments of the Ligurian Sea. *Baseline/Minerate* 34: 903-917.

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

[13] Gaga, E.O. (2004). *Investigation of polycyclic aromatic hydrocarbons deposition* in Ankara, Ph.D Thesis, pp. 233.

[14] Budzinski, H., Jones, I., Bellocq J., Pierrad C. and Garrigues, P. (1997). Evaluation of Sediment Contamination by Polycyclic Aromatic Hydrocarbons in the Gironde Estuary. *Marine Chemistry*, 58: 85-97.

[15] Witt, G. and Trost, E. (1999). Polycyclic Aromatic Hydrocarbons in Sediments of the Baltic Sea and of the German Coastal Waters. *Chemosphere*, 38 (7):1603-1614.

[16] Opafunson, Z.O. (2007). 3D Formation Evolution of an oil Field in the Niger Delta Area of Nigeria using Schlumberger Petroil Workflow Tool. *Journal of Engineering and Applied Sciences*, 2 (11): 1651-1660.

[17] OHEWG, (1999). *Sampling Protocols and Analytical Methods for Determining Petroleum Products in Soil and Water*. Ministry for the Environment Wellington, pp. 40.

[18] Cavalcante, R.M., Sousa F.W., Nascimento R.F., Silveira E.R. and Freire G.S.S. (2009). The Impact of Urbanization on Tropical Mangroves (Foertaaleza, Brazil): Evidence from PAH Distribution in Sediments. *Journal of Environmental Management*, 91: 328-335.

[19] Emoyan, O.O. (2014). Quantification and distribution characteristics of Polycyclic Aromatic Hydrocarbons (PAHs) in soil Profiles of Western Delta, Nigeria. *JORS Journal of Environmental Science, Toxicology and Food Technology*, 8 (3) 1. 31-39.

[20] Benlahcen, K.T., Chaoui, A., Budzinski, H., Bellocq, J. and Garrigues, P.H. (1997). distribution and sources of Polycyclic Aromatic Hydrocarbons in some Mediterranean coastal sediment. *Marine Pollution Bulletin*, 34: 298-305.

[21] Magi, E., Bianco, R., Ianni, C. and Di Carro, M. (2002). Distribution of Polycyclic Aromatic Hydrocarbons in the sediments of the Adriatic sea. *Environmental Pollution*, 119: 91-98.

[22] Lizhong, Z. and Wang, J. (2004). Pattern and sources of Polycyclic Aromatic Hydrocarbon pollution in sediment of Hangzhou, China. *Organohalogen Compounds*, 66: 291 – 296.

[23] Azza, Z. (2006). Levels of Polyaromatic Hydrocarbons in Egyptian vegetables and their behaviour during soaking in oxidizing agents solution. *World Journal of Agricultural Sciences*, 2 (1): 90-94.

[24] Emoyan, O.O., Agbaire P.O. and Peretieto-Clarke B.O. (2008). Distribution and speciation of Polyaromatic Hydrocarbons (PAHs) in soil around oil wells heads in Delta State, Nigeria. *Proceedings of the 31st International Conference of the Chemical Society of Nigeria*, 762-771.

[25] Kanaly, R.A. and Harayama, S. (2000) Biodegradation of High-molecular-Weight Polycyclic Aromatic Hydrocarbons by Bacteria. *Jnrnl. Bacteriol*, 182: 2059-2067.

[26] Oleszczuk, P. and Baran, S. (2003). Degradation of individual Polycyclic Aromatic Hydrocarbons (PAHs) in soil polluted with aircraft fuel. Institute of Soil Science and Environmental Management, University of Agriculture. *Polish Journal of Environmental Studies*, 12 (4): 431-437.

[27] Mackay, D., Shiu, W.Y. and Ma, K.C. (1991). Illustrated handbook of physico-chemical properties and environmental fate for organic chemicals: Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins and Dibenzofurans. Boca Raton Publishers, pp. 367.

[28] Manoli, E., Samara, C., Konstantinou, I. and Albanis, T. (2000). Polycyclic Aromatic Hydrocarbons in the Bulk Precipitation and Surface Waters of Northern Greece. *Chemosphere*, 41:1845-1855.

[29] Earl, N., Cartwright, C.D., Horrocks, S.J., Worboys, M., Swift, S., Kirton, A., Askan, A.U., Kelleher, H. and Nancarrow, D.J. (2003). Fate and transport of selected contaminants in the soil environment. Draft Technical Report P5-079/TR1. Environmental Agency, Bristol, pp. 182.

[30] Liu, Y., Chen, L., Huang, Q.H., Li, W.Y., Tang, Y.J., Zhao, J.F., Liu, Y., Chen, L., Huang, Q.H., Li, W.Y. (2009). Source apportionment of Polycyclic Aromatic Hydrocarbons (PAHs) in surface sediments of the Huangpu River, Shanghai, China. *Science of the Total Environment*, 407: 2931–2938.