Distribution and the use of diagnostic ratios for source investigation in urban soils of the Yenagoa City, Bayelsa State, Nigeria

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Abstract. Yenagoa is a non-industrialized city. This work aims to investigate the distribution, content and source of the sixteen United State Environmental Protection Agency (USEPA) priority polycyclic aromatic hydrocarbons (PAHs) in urban soils of the Yenagoa, Bayelsa State, Nigeria. The PAH concentrations in the urban soil samples were performed using GC–MS method. The Swali market axis of the city had the highest concentration (ΣPAHs). The burden of low molecular weight (LMW) PAHs follows a decreasing order: Phenanthrene > acenaphthene>acenaphthylene>naphthalene>anthracene>fluorine and while the burden of high molecular weight (HMW) PAHs follows the decreasing order: Pyrene>Dibenzo (a,h)anthracene>indeno [1,2,3-cd]pyrene (IndP)>Chrycene>Fluoranthene>Benzo(a)anthracene>Benzo(k)fluoranthene>Benzo(b)fluoranthene. PAH fingerprint ratios for determining both petrogenic and pyrogenic (pyrolytic) PAH accumulation was employed. The Ph/An ratio for the soil samples were 2.49, 3.47, 0.613, 1.59, 1.99 and 2.44 respectively. This may be indicative of pyrogenic (pyrolytic) origin. Ind(1,2,3-cd)P and DbahA were high in the soils, this may indicate a major concern for carcinogenic risk and demands an urgent attention from policy makers and the government.

Keywords: PAHs, diagnostic ratios, soils, Yenagoa, Bayelsa state, Nigeria

1. Introduction
Crude oil reserves found here spurred petroleum production investors and allied industries and increased influx of people into the oil rich Niger Delta Region and consequently, the effect is generation of environmental pollutants that are not biodegradable, persistent and toxic such as polycyclic aromatic hydrocarbons (PAHs).

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment and can travel long distances from their sources [1], therefore separation of PAHs based on their origins poses a great challenge in environmental studies, especially when there are cumulative impacts on the environment from various sources of PAHs [9-10], each having adverse health effects. Therefore, there is a desperate need to evaluate and determine the sources of PAHs in the environment to enable proper monitoring and control of emissions into the environment. A chemical substance that has the tendency to contaminate either on its own or in combination with other substances or agent, any part of the environment is an environmental pollutant [11]. Persistent environmental pollutants stay longer in the environment. PAHs can be classified as being of petrogenic (petroleum) or pyrogenic (combustion) origins; they can also be classified as being of natural and anthropogenic origins. Anthropogenic PAHs, however, contribute the major proportion of PAHs in the environment [12-13].
Polycyclic aromatic hydrocarbons are very toxic and persistent environmental contaminants. This study was undertaken to assess the concentrations and possible sources of 16 PAHs (Polycyclic aromatic hydrocarbons) classified by the United State Environmental Protection Agency as priority pollutants include: naphthalene (Nap), acenaphthylene (Acep), acenaphthene (Acp), fluorine (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthen (FLR), pyrene (PYR), benzo[a]anthracene (B(a)A), chrysene (Chr), benzo[b]fluoranthene (B(b)F), benzo[k]fluoranthene (B(k)F), benzo[a]pyrene (B(a)P), dibenzo[a,h]anthracene (DaA), benzo[ghi]perylene (B(g)P), and indeno[1,2,3-cd]pyrene (InP). The study of polycyclic aromatic hydrocarbons (PAHs) distribution and assessment in urban soils of the Yenagoa metropolis has not been undertaken by previous workers. The main objective of the present study was to investigate the distribution of sixteen PAHs, as priority pollutants [14], in urban soils of the Yenagoa metropolitant city, Bayelsa State, Nigeria.

2. Materials and methods

2.1 Description of study/ sampling location

The study location for the research work is Yenagoa, with geographical coordinates of 5°02’N 6°20’E and 5.033°N 6.333°E, located at an elevation of about 1 meter above sea level. It has a land area of 706 km² and a population of 2.6 million inhabitants with a tropical monsoon climate and an average annual temperature of about 30°C. Six areas of the city were strategically chosen as sampling sites, the selected sites for sampling represent different dominant activities affecting the city environment (i.e. commercial, residential, religious, industrial, traffic and rural), and are spatially distributed over the Yenagoa city.

Fig. 1. Map of study area showing sampling sites
Table 1: Table showing sampling sites, coordinates and description

| Sampling sites         | Coordinates         | Description of Location                                      |
|------------------------|---------------------|---------------------------------------------------------------|
| Azikoro express way    | 4.8900°N, 6.2960°E  | Petrol Station and Major road NNPC filling station area       |
| Swali road             | 4.9186°N, 6.2673°E  | Market activities                                             |
| MelfordOkilo Road      | 4.9421°N, 6.2739°E  | Office Complex Government House Area.                         |
| Tombia round about     | 4.9975°N, 6.2628°E  | Anthropogenic activities                                      |
| Opolo market           | 4.9490°N, 6.3359°E  | Market                                                        |
| Opolo round about      | 4°56'22''N,6°20'14''E | Anthropogenic activities.                                    |

2.2 sampling/sample preparation
The sampling sites were divided into six sub-areas, namely Azikoro express way, Melford Okilo Road, Swali Road, Opolo Roundabout Expressway, Tombia Roundabout, and Opolo market. In each of the sub-areas, three soil samples were selected randomly from each site and homogenized into a composite sample. The first batch of samples at Azikoro expressway (flyover area), Melford Okilo Road (Government House), Swali (market area) were collected on 14th November 2018, the top-soil using a hand auger at a depth of 0–15 cm. While on the 16th of March 2019, the second samples collected at Tombia Roundabout, Opolo main Road (market) and Sani Abacha Expressway (Opolo Roundabout). A total of nine soil samples were made into three different composite samples, after the removal of the exposed surface. The composite samples were sieved using a 1mm stainless steel sieve. The sampling and sample preparation was done according to the procedure previously described [2].

2.3 Sample extraction
One gram of each sample was carefully weighed into a dried organic free and pre-cleaned glass vials. Ten milliliters (10 ml) of 8 ml n-hexane and 2 ml dichloromethane in a ratio 4:1 was added to the sample. The sample was placed in an organic flask shaker at 200 osc/min for 60 minutes. The sample was then left in the vials at laboratory room temperature to concentrate for a minimum of 24 hours. The extract was filtered using a funnel and filter paper into an extraction bottle. The extract was stored in a dry organic free, pre-cleaned glass vial with Teflon rubber caps for analysis.

2.4 Sample analysis
Analysis was done using Gas Chromatography-Mass Spectroscopy (GC-MS). 1 μl of the concentrated sample was injected by means of exmire micro syringe through rubber septum into the column. Separation occurs as vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column by a flame ionization detector FID. Identity of PAHs in the samples was confirmed by the retention time and abundance of quantification/confirmation ions in the authentic PAHs standards. Fourteen priority PAHs were quantified using the response factors related to the respective internal standards based on five-point calibration curve r individual compounds. In this study, the concentrations of PAHs were corrected for the surrogate standard recoveries, and are expressed on a dry-weight (dw) basis.

2.5 PAHs source identification
The diagnostic ratio method for identifying PAHs source involves comparison of ratios of frequently found PAHs pairs. They allow to distinguish between PAH pollution originating from petrogenic (liquid fuels spills), pyrolytic (combustion of fuels) and burning biomass or coal sources [8].

Table 2: Some diagnostic ratios values for particular pollution emission sources

| Diagnostic ratio | Petrogenic | Fuel combustion | Coal, grass, wood burning |
|------------------|------------|-----------------|--------------------------|
| ANT/(ANT + PHE)  | < 0.1      | > 0.1           | -                        |
| FLA/(FLA + PYR)  | < 0.4      | 0.4 – 0.5       | > 0.5                    |
| BaA/(BaA + CHR)  | <0.2       | > 0.35          | 0.2 – 0.35               |

ANT – anthracene; BaA – benzo[a]anthracene; CHR – chrysene; FLA – fluoranthene; PHE – phenanthrene; PYR – pyrene

3. Results and discussion
The sixteen PAHs recommended as priority pollutants by the U.S. Environmental Protection Agency [14] were determined in urban soil samples. From the analyses of the extracts, PAHs were found at all the sampling sites. A total of fourteen of the targeted EPA priority polycyclic aromatic hydrocarbons (PAHs) were quantified in surface urban soil from Yenagoa city, Bayelsa State, Nigeria and are presented in Table 2. The results were read as the detection limit on the gas chromatogram for individual PAHs in microgram per liter and these are converted to milligram per kilogram (mg/kg). The minimum detection limit for GC-MS used in the analysis on the chromatogram was 1 × 10⁻³ mg/kg.

Table 3: The concentrations of PAHs (mg/kg) in urban soils

| sample code | Swa | Fly | GOH | TOM | MAO | RAO | Rings | Class of PAH |
|-------------|-----|-----|-----|-----|-----|-----|-------|--------------|
| Naphthalene | 0.021 | 0.008 | 0.007 | 0.009 | 0.013 | 0.209 | 2 | LMW |
| Acenaphthylene | 0.105 | 0.035 | 0.019 | 0.019 | 0.006 | 0.335 | 3 | LMW |
| Acenaphthene | 0.375 | 0.043 | 0.197 | 0.020 | 0.025 | 0.026 | 3 | LMW |
| Fluorene | 0.029 | 0.022 | 0.010 | 0.016 | 0.033 | 0.043 | 3 | LMW |
| Phenanthrene | 0.513 | 0.023 | 0.016 | 0.020 | 0.013 | 0.015 | 3 | LMW |
| Anthracene | 0.205 | 0.007 | 0.027 | 0.013 | 0.006 | 0.006 | 3 | LMW |
| Fluoranthen | 1.129 | 0.008 | 0.115 | 0.054 | 0.024 | 0.015 | 3 | LMW |
| Pyrene | 5.364 | 0.162 | 2.745 | 0.037 | 0.027 | 0.070 | 4 | HMW |
| Benz(a)anthracene | 0.939 | 0.031 | 0.814 | 0.035 | 0.092 | 0.023 | 4 | HMW |
| Chrysene | 1.373 | 0.033 | 0.212 | 0.010 | 0.019 | 0.025 | 4 | HMW |
| Benzo(b)Fluoranthene | 0.087 | 0.033 | 0.205 | 0.048 | 0.064 | 0.011 | 5 | HMW |
| Benzo(k)Fluoranthene | 0.075 | 0.002 | 0.010 | 0.137 | 0.196 | 0.026 | 5 | HMW |
| Indeno(1,2,3-cd)pyrene | 2.836 | 0.356 | 1.722 | 0.225 | 0.112 | 0.019 | 6 | HMW |
| Dibenz(a,h)anthracene | 2.064 | 4.000 | 1.932 | 1.614 | 0.533 | 0.680 | 6 | HMW |
| ∑PAHs | 15.114 | 4.761 | 8.033 | 2.257 | 1.164 | 1.503 | 6 | HMW |
| Mean | 1.080 | 0.340 | 0.574 | 0.161 | 0.083 | 0.107 | 6 | HMW |
From the results, Benzo(a)Pyrene and Benzo(g,h,i)Perylene were below the detection limits for all the sampling locations. The results showed that pyrene had the highest concentration at Government House, with a value of 2.745 mg/kg followed by Dibenzo(a,h)anthracene with a value of 1.932 mg/kg, and indeno (1,2,3–cd) pyrene as 1.722 mg/kg. The total PAHs content at government house soil was 8.033 mg/kg. For Azikoro flyover area the total concentration was found to be 4.742 mg/kg, the three dominant PAHs were in this order; Dibenzo(a,h)anthracene > indeno(1,2,3–cd)pyrene > pyrene with concentrations of 4.00 mg/kg, 0.356 mg/kg and 0.1615 mg/kg respectively. At Swali location, the total concentration in the soil was 15.114 mg/kg with pyrene had the highest concentration of 5.364 mg/kg, indeno (1,2,3–cd)pyrene, dibenzo(a,h)anthracene with a concentration of 2.836 mg/kg each, Chrysene with a concentration of 1.373 mg/kg, fluoranthene 1.1289 mg/kg. For Tombia the total concentration was 2.257 mg/kg, the dominant PAHs in this area were Dibenzo(a,h)anthracene (1.614 mg/kg), indeno(1,2,3–cd)pyrene (0.224 mg/kg), Benzo(k)fluoranthene (0.1368 mg/kg), fluoranthene (0.0539 mg/kg), Benzo(b)fluoranthene (0.047 mg/kg). For Opolo market, the total concentration was 1.164 mg/kg, the dominant PAHs were Dibenzo(a,h)anthracene (0.533 mg/kg), Benzo(k)fluoranthene (0.196 mg/kg), indeno (1,2,3–cd)pyrene (0.1162 mg/kg), Fluoranthene (0.0539 mg/kg), Benzo(b)fluoranthene 0.0479 mg/kg). At Opolo roundabout, the total concentration was 1.671 mg/kg, the dominant PAHs were Dibenzo(a,h)anthracene (0.679 mg/kg), Naphthalene(0.209 mg/kg) and acenaphthylene (0.335 mg/kg). These results were in agreement with those reported [7]. It was further revealed that the individual PAH levels within Yenagoa were low for two ringed PAHs naphthalene and three ring acenaphthylene and acenaphthen and high for five rings Dibenzo(a,h)anthracene in soil samples. This may be attributed to the fact that the five ringed PAHs are persistent and non-biodegradable.

From the results, PAH levels in Yenagoa were high at some specific locations which follows sequence: Swali (15.114 mg/kg) > Government House (8.033 mg/kg) > Flyover area (4.742 mg/kg) respectively. Furthermore, PAHs present potential carcinogenic risks to residents [2]. Benzo(g,h,i)Perylene was below the detection limit. Ind and DbahA were also high in soils. Soil is the primary steady reservoir and sinks for PAHs in the terrestrial environment, because PAHs are readily absorbed by organic matter in soil and difficult to degrade [3].

Higher, (4–6) rings PAHs were more predominant than the lower ringed PAHs (2 and 3) rings, which is indicative of PAHs having pyrogenic origin. The probable human carcinogen
PAHs includes BaA, BaP, Bflas, Chry, and InP[4, 5] reported that increasing molecular weight with increasing carcinogenicity of the heavier PAHs. The major PAH contaminants of concern (COCs) in soils were identified in the assessment, which were benz[a]anthracene, benzo[a]pyrene (BaP), benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene [6].

3.2 PAHs diagnostic ratio
PAHs diagnostic ratios were calculated from the results and are presented in Table 4. The results of the diagnostic ratios of PAHs revealed that Ant/Ant+Phe for soil samples were: government house(0.61) had the highest, Opolo market(0.22) with the lowest ratio; This indicates that PAHs for all the sampling sites; Government house, Swali, flyover, Tombia, Opolo market, and Opolo roundabout were of combustion origin (ratios > 0.1).

Table 4. The diagnostic ratio calculated for all the study sites

| sample code | ANT/(ANT + PHE) | FLA/(FLA + PYR) | BaA/(BaA + CHR) | Phe/Ant | HMW/LMW PAHs |
|-------------|-----------------|-----------------|-----------------|--------|---------------|
| SWA         | 0.286146        | 0.173862        | 0.406124        | 2.494717 | 7.564322      |
| FLY         | 0.223694        | 0.045216        | 0.484013        | 3.470383 | 7.564322      |
| GOH         | 0.619802        | 0.0403          | 0.793449        | 0.613419 | 7.564322      |
| TOM         | 0.384877        | 0.596234        | 0.784307        | 1.598232 | 7.564322      |
| MAO         | 0.334146        | 0.467048        | 0.82591         | 1.992701 | 7.564322      |
| RAO         | 0.290179        | 0.17214         | 0.481632        | 2.446144 | 7.564322      |

Fluo/Fluo + Pyr values as follows: Government House (0.0403), flyover site (0.045) and Tombia(0.59) respectively. This indicates that Opolo market with a ratio of 0.47 is of liquid fossil fuel combustion origin (range of ≥ 0.4 and ≤ 0.5), while for Government House, Swali, flyover and Opolo roundabout are of petroleum source (ratios <0.4), and for Tombia (0.59) was likely of grass, wood and coal combustion sources (ratios > 0.5). These findings are in agreement with those [8].

The BaA/BaA+Chry ratio as follows: Swali market (0.40) had the least ratio, Government House (0.79) had the highest ratio, this indicates that all the sampling locations were of combustion origin (> 0.35). The results of PAH diagnostic ratio revealed that the soils of the Yenagoa city were of petroleum (petrogenic), combustion (pyrogenic), and grass/wood/straw combustion sources, the pyrogenic combustion sources had the dominant ratio indicates that PAHs in Yenagoa city soil samples were mostly of pyrogenic origin. The EPA has classified the following seven PAH compounds: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene as probable human carcinogens [14]. These were detected at high concentrations for each soil sample which may be detrimental to human health. The total observed PAHs concentration 32.981 mg/kg in the soil samples was above the critical level of 4.00 mg/kg recommended by WHO for soils at Government House area. Swali and flyover locations were moderate, while Tombia, Opolo roundabout and Opolo market were also above the acceptable minimal level of 0.1 mg/kg as recommended by the US EPA for each sample site. When these harmful compounds are inhaled or ingested by man, they could be harmful. [8] reported that there may be potential synergy between PAH compounds with different biological targets.
4. Conclusion

This study was carried out to investigate the distribution, content and diagnose the source emission of the sixteen USEPA priority polycyclic aromatic hydrocarbons (PAHs) in urban soils of the Yenagoa city, Bayelsa state, Nigeria. Six LMW PAHs: naphthalene, acenaphthylene, acenaphthene, fluorene, Phenanthrene, anthracene, and eight HMW PAHs: Fluoranthene, pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Pyrene, Dibenz[a,h]anthracene were found, among them are the major PAH contaminants of concern (COCs) in soils were identified in the assessment, which are benz[a]anthracene, benzo[a]pyrene (BaP), benzo[b] fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h] anthracene, and indeno[1,2,3-c,d]pyrene. Polycyclic aromatic hydrocarbons (PAHs) diagnostic ratios are powerful and versatile tools in identifying PAH pollution emission sources. The major anthropogenic sources in the study areas were of pyrogenic origin. The pyrogenic sources were combination of vehicular emissions, grass/wood combustion and petroleum combustion. The concentrations of PAHs were relatively high; when compared to the USEPA permissible limits in soil which is 0.1mg/kg.

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