

SPATIAL VARIATION AND DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL

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ABSTRACT. An investigative study on polycyclic aromatic hydrocarbons (PAHs) in soils of different sampling stations in Effurun metropolis and its environs of the Niger Delta Area of Nigeria was carried out with gas chromatography mass spectrometry (GC-MS). Among the 16 US EPA priority PAHs determined, pyrene was observed to be the most abundant compound at all sites (20 %), followed by fluoranthene (14 %), phenanthrene (12 %), chrysene (10 %) and benzo(ghi)perylene (6 %). High concentrations of pyrene could be attributed to anthropogenic source such as industrial and vehicular emissions. On the other hand, naphthalene, acenathalene and anthracene accounted for 3.2 %, 1.6 %, and 1.1 %, respectively. The observed trend: Refinery > Ekpan > Enerhen > Water Resources > Alegbo > Ugborikoko > Ugboroke could be attributed to the density of industrial and commercial activities in each area. Clear differences in the total PAH between urban/industrial and rural areas were observed. The results showed that PAH levels in soils from heavily industrial sites were higher in concentrations to the effect that Refinery locations were comparatively higher than all other locations. The higher levels of PAHs observed in the Refinery location are clear indications of combustion emissions and gas flaring from fractionating towers.

KEY WORDS: Polycyclic aromatic hydrocarbons (PAHs), Soil poolution, Niger Delta Area (Nigeria)

INTRODUCTION

In the strictest definition, polycyclic aromatic hydrocarbons (PAHs) are composed of “two or more fused aromatic (benzene) rings”. They are group of chemicals that are formed during incomplete burning of coal, oil, gas, wood garbage, or other organic substances such as tobacco and charbroiled meat. PAH usually occur naturally, but they can be manufactured as individual compounds for research purposes. As pure chemicals, PAH generally exist as colourless, white, or pale yellow-green solids. They have a faint, pleasant odour. PAH have been found in at least 585 of the EPA’s 1350 national priorities list of hazardous waste sites. PAH may be divided into two groups, depending upon their physical and chemicals properties: low molecular weight PAH containing three or fewer aromatic rings and high-molecular weight PAH containing more than three aromatic rings.

PAHs are most often found in environmental samples as a minute fraction of a complex mixture of hydrocarbons in the environment and providing information on the extent of oil weathering and degradation. Petrogenic (related to crude oil and its products) PAHs characteristically have a greater percentage of alkyl PAH compared to parent compounds while pyrogenic (generated by high temperatures) PAHs tend to have a predominance of parent compound PAH compared to alkyl PAH.

Soil systems seem to be the important repository for atmospheric PAHs [1]. Once deposited, they can reside for longer than 20 years [2] and accumulation may lead to contamination of food

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chains [3]. However, PAHs are not static and recalcitrant. They are subject to redistribution and transformation processes. Leaching of PAHs may be more significant where there is ground contaminated with solvents. Therefore, a wide investigation for soil contamination with PAH is needed to avoid any food production risk and to restrict the deleterious effect of these contaminants on the ecosystem.

PAH concentration in soil correlate significantly with the corresponding levels in air [4], house dust [5], urban street dust [6] and plants [7]. Therefore, PAH determination in soil may provide important information on the environmental pollution state.

The extent of soil pollution by PAHs also depends on factors such as the cultivation and use of the soil, its porosity, its lipophilic surface cover, and its content of humic substances [8]. There is a correlation between the organic content of a soil and the PAH concentration. The deposited PAHs are accumulated mainly in the humus layer of soil [9-11]. Extremely high PAH concentrations were found in the soil near an American plant where animal by-products and brewer's yeast had been processed [12].

The concentrations of individual PAH in soil resulting mainly from motor vehicle exhaust usually range between 1 and 2000 $\mu\text{g}/\text{kg}$. It has been reported that PAHs may accumulate preferentially on the surfaces of soil aggregates preferential flow paths [13]. The PAH content of soil often decreased with increasing depth [10, 7, 14]. This corroborated later findings by other authors [15] which hypothesised that the gradients of PAH concentrations in aggregates are caused by higher inputs of PAHs from the atmosphere or above-lying soil horizons, transported along preferential flow paths in contact with aggregate surfaces, compared with sources by leaching, volatilization and degradation

Although a considerable amount of research has been performed on the atmospheric occurrence of PAHs, distribution and fate in soil. There are no published data on the typical levels of PAHs, their persistence and degradation, their behavior in soil-plant systems and their mobility from the soils in Nigeria. Owing to the fact that some PAHs have been classified as carcinogenic substances, it is imperative to determine their levels in soils of different environment and their spatial distribution evaluated.

This research work covers studies on the spatial distribution of PAHs in soils of seven different sampling stations in Effurun metropolis of Uvwie Local Government Area of Delta State in Nigeria.

EXPERIMENTAL

Description of study area

Uvwie Local Government Area is one of the 25 local Government areas in Delta State with its administrative headquarter at Effurun. Apart from Warri, Effurun is the next busiest, industrial and highly commercial city in the state. In facts records shows that 60 % of the companies that are stated to operate in Warri, actually have their base and operation in Uvwie. From the national population commission, Uvwie Local Government Area has a total population of about 145,045 people with household capacity of about 34,099. The total geographical area of the local Government is 95.157 sq km with a population density of about 1524.

The study area was divided into sampling stations to ensure an effective coverage of the entire area study and to enable respective sample collection, aimed at providing data that are reflections of the environment. The sampling stations were chosen to reflect urban, sub-urban, and rural settlement depending on the human population density and the level of commercial/ industrial activities.

The entire study area was delineated into 7 sampling stations as follows: Enerhen, Refinery, Water Resource, Ugborikoko, Ugboroke, Ekpan, and Alegbo. With respect to different anthropogenic activities, the sampling stations were further classified into the following activity

sites: Industrial, Market, Traffic Junctions and Roadsides. The map of the study area which includes the sampling locations is shown in Figure 1.

Sampling, handling and pre-treatment

Sampling was done between the month of October 2003 and September 2004. Sampling was limited to soil samples only. The exact geographic co-ordinates for each sampling point per location were obtained with the aid of Global Positioning System, GPS GERMIN 12 and were reflected in the area of study map shown in Figure 1.

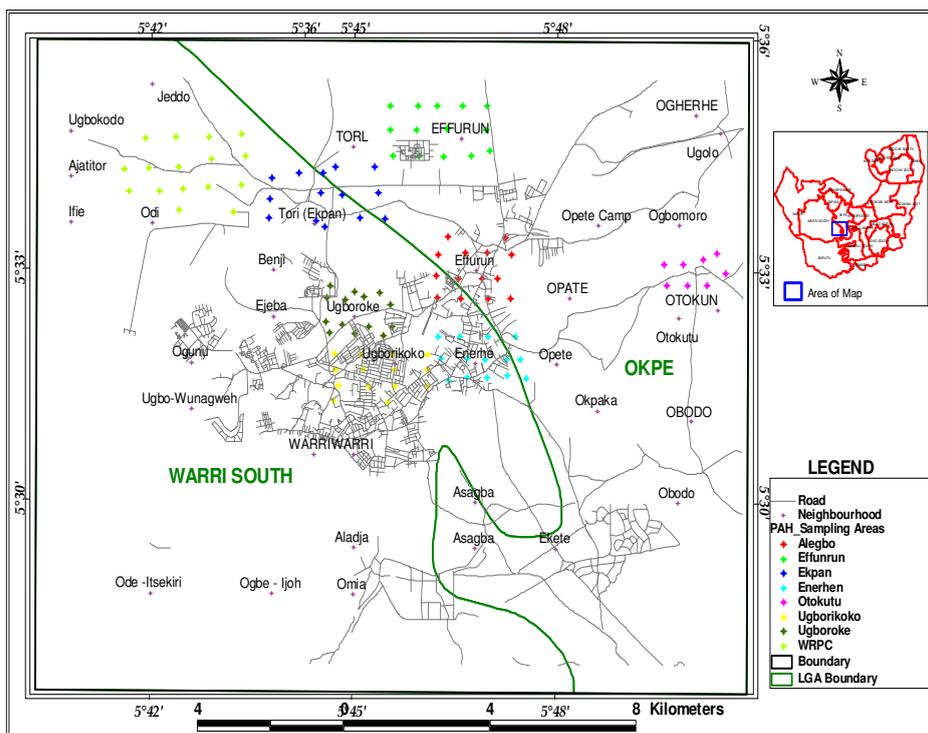


Figure 1. Map of study area, source: designed with ESRI Arc View GIS (version 3.3) software using sampling points coordinates as input.

A total of 108 soil samples were collected from the seven sampling stations. Averages of six (composite) samples were collected per station. The choice of sampling points was guided by the level of activities. At each sampling location, soil samples were taken from various points at depth 0-15 cm using soil auger. This depth was chosen because 0-15 cm constitutes the feeding zone for most arable crops. Beyond this zone, plant utilizes the soil mostly for anchorage. Soil samples on collection were stored in appropriate pre-labelled sampling bags. They were stored in aluminium foil bags. Quality assurance/quality control forms an integral part of the sampling process. Sample chain of custody forms were used for the registration and tracking of samples from the field to the laboratory. The soil auger and homogenizing bucket were constantly cleaned after each composite sampling. Aluminium foil sheet lining the bucket and disposable

hand-gloves were also changed after each composite sample. The soil samples in aluminium bags were kept on ice-chips placed in coolers immediately after collection. In the laboratory, the samples were kept in the freezer prior to laboratory analysis.

Analysis

A 50:50 solvent mix of acetone and methylene chloride was prepared. About 10.00 g aliquot of a well-mixed sample was weighed into a solvent rinsed beaker. Fifty millilitres of the solvent mix was added to the samples and spiked with 1 mL of the surrogate mix. Sample was placed in the sonicator and sonicated for 15 min at 70 °C. Ten grams of anhydrous sodium sulfate were added to the sample until a clear extract developed. The extract solvent was poured into a round bottom flask. Extraction was repeated once more with an additional 50 mL of solvent mix, sonicated and the beaker allowed to settle before being decanted into the same round bottom flask. The solvent was concentrated, hexane-exchanged and reconcentrated to 1 to 2 mL. The sample extract was fractionated into the aliphatic and aromatic fractions using silica gel columns. The columns were packed with 10.00 g of 100-200 mesh silica gel pre-condition (baked) at 105 °C over night. The silica was mixed with hexane to form slurry.

Instrumental parameters

Gas chromatography operating procedure

Instrument type. Gas Chromatography Mass Spectrometer System HP6890 series and 6890 plus was used. The basic GC parameters for the analysis of polynuclear aromatic hydrocarbon were follows: injector temp: 250 °C; initial temp: 100 °C; temp rate 1:4 °C/min, final temp: 310 °C; detector temp: 300 °C; detector type: flame ionization detector; column type: high performance capillary column HP-5, cross linked PH ME siloxane 1909IJ-413; film thickness: 0.25 um, length: 30 mL; phase ratio: 320 column ID: 0.32 mm; carrier gas: helium; inlet mode: splitless; linear velocity: 30 cm/sec.; FID condition: hydrogen: 35 mL/min; air 350 mL/min.; data acquisition system: computerized system for collecting, storing and processing detector output.

Calibration

The instrument was always calibrated before sample analysis by injecting 1 µL of a series of PAH standards. A five-point calibration curve was prepared using the PAH standard mixture that was commercially obtained. The concentration range of the curve was 2.0 µg/mL to 20 µg/mL. The response factor (RF) was calculated for each component of the PAH mixture standard using the area response and the amount of standard material. The relative standard deviation percentage (% RSD) of the RF was calculated for each component across the calibration curve. The value was never in excess of 30 % for the curve to be deemed valid. The average respond factor for the weight ranges were calculated and used for sample quantification.

Quantification

The concentration of each analyte and hydrocarbon range in a sample was determined by calculating the amount of analyte or hydrocarbon range injected, from the peak response, based upon the analyte/internal standard response ratio. The contribution from the solvent front and the surrogate compound were excluded from the total area of the sample.

Soil sample concentration ($\mu\text{g/g}$)

$$C_f = \frac{\text{Area}(p) \times R_f \times V_f \times D_f \times 1000}{W_i}$$

where C_f = final sample concentration ($\mu\text{g/L}$), $\text{Area}(p)$ = measured area of peak (peaks), W_i = initial weight extracted (g dry weight), V_f = final extract volume (mL), D_f = dilution factor of sample or extract, R_f = response factor from the calibration standard calculation.

RESULTS AND DISCUSSION

The mean concentrations of PAH components in soils at the described sampling stations are given in Table 1, while their spatial variation along sampling location is shown in Figure 2. The highest total PAH concentration was observed in the Refinery location ($45.9 \pm 2.70 \mu\text{g/g}$), while the Ugboroke location, which is predominantly residential, gave the lowest mean value of $3.83 \pm 0.18 \mu\text{g/g}$. These values were however higher than that obtained from the control location, Otokutu, which had mean concentration of $0.035 \pm 0.003 \mu\text{g/g}$. Total PAHs concentration increased markedly in the order of Refinery > Ekpan > Enerhen > Water Resources > Alegbo > Ugborikoko > Ugboroke > Otokutu (control). This order of ranking could be attributed to the density of industrial and commercial activities in each area. Clear differences in the total PAH between urban/industrial and rural areas were observed. This is in agreement with the report of the study on the concentrations and source characterization of polycyclic aromatic hydrocarbons in pine needles from Korea, Mexico, and United States [16]. Furthermore, the results also agree with the findings of a similar study, that increasing industrialization and vehicular traffic associated with the population growth in metropolitan areas can be responsible for increased PAH concentrations [17].

Low molecular weight PAHs (LPAH) are the 2–3-rings PAHs, while the high molecular weight PAHs (HPAH) are the 4–6-rings PAHs. The summation of low molecular weight PAH (ΣLPAH) and that of high molecular weight PAH (ΣHPAH) had similar trend with the total PAH concentrations along the sampling locations. The ranges of concentrations of total PAHs observed in the sampling areas are much higher than other remote or rural locations [18]. Comparatively, they are lower than soils of Hong Kong [19] and that of Shantou, China [20]. The ΣHPAH in all the locations except the control were quite higher than the ΣLPAH . The study areas are notable for high vehicular traffic and petroleum refinery activities. The high levels of HPAH are characteristics of emissions from fossil fuel combustion [21, 22].

Except for WRPC, the values obtained for naphthalene in the other sampling stations were lower than $0.91 \mu\text{g/g}$ dry weight reported for Wales [23]. However, the concentration obtained at WRPC compared favourably to results reported for Korean soils: $0.024 \mu\text{g/g}$ dry weight [24] and China soils: $0.028 \mu\text{g/g}$ dry weight [25]. The lowest naphthalene concentration at Otokutu could be considered as the background levels, as Otokutu is a rural setting devoid of the prevalent urban and industrial activities in Effurun metropolis. The relatively high value obtained for Ekpan compared to other sampling locations could be attributed to the influence of the activities of the refinery which is its nearest neighbour. For phenanthrene, the mean concentrations were higher than $0.021 \mu\text{g/g}$ dry weight reported for Korean soils [24] and $0.019 \mu\text{g/g}$ dry weight Beijing soils [25]. The values observed for acenaphthylene in the study area, was higher than that reported for Birmingham United Kingdom: $0.009 \mu\text{g/g}$ (dry weight, dw) and Tokushima Japan: $0.004 \mu\text{g/g}$ (dw) [26].

Table 1. Mean concentration of PAHs at each sampling location (mean \pm standard deviation).

PAH components ($\mu\text{g/g-dry wt}$)	Enerhen	Refinery	Ekpan	Effurun Water Res
Naphthalene (Naph)	0.035 \pm 0.002	2.103 \pm 0.101	0.865 \pm 0.003	0.052 \pm 0.002
2-Methyl Naphthalene (2MNaph)	0.064 \pm 0.004	2.539 \pm 0.810	0.531 \pm 0.002	0.268 \pm 0.030
Acenaphthylene (Any)	0.085 \pm 0.121	0.898 \pm 0.003	0.575 \pm 0.210	0.057 \pm 0.004
Acenaphthene (Ane)	0.158 \pm 0.001	0.767 \pm 0.002	0.591 \pm 0.023	0.036 \pm 0.005
Florene (Flo)	0.216 \pm 0.004	0.970 \pm 0.021	0.605 \pm 0.004	0.115 \pm 0.080
Phenathrene (Phe)	0.916 \pm 0.022	6.275 \pm 0.910	2.745 \pm 0.002	0.803 \pm 0.005
Anthracene (Anth)	0.122 \pm 0.001	0.526 \pm 0.003	0.219 \pm 0.006	0.058 \pm 0.002
Σ LPAH	1.596 \pm 0.155	14.078 \pm 1.850	6.131 \pm 0.250	1.389 \pm 0.128
Fluoranthene (Fluo)	2.635 \pm 0.048	6.045 \pm 0.002	2.878 \pm 0.463	0.974 \pm 0.005
Pyrene (Pyr)	2.342 \pm 0.329	10.446 \pm 1.201	3.017 \pm 0.004	2.627 \pm 0.005
Benzo(a)anthracene (BaA)	0.435 \pm 0.003	0.553 \pm 0.003	0.464 \pm 0.002	0.363 \pm 0.002
Crysen (Chry)	1.911 \pm 0.030	4.685 \pm 0.320	1.716 \pm 0.202	0.694 \pm 0.004
Benzo(b)fluoranthrene (BbF)	0.697 \pm 0.092	2.068 \pm 0.110	0.718 \pm 0.004	0.333 \pm 0.001
Benzo(k)fluoranthrene (BkF)	0.629 \pm 0.040	2.277 \pm 0.002	0.659 \pm 0.007	0.281 \pm 0.004
Benzo(a)pyrene (BaP)	0.908 \pm 0.002	0.731 \pm 0.202	0.562 \pm 0.000	0.354 \pm 0.031
Indeno(1,2,3-cd) perylene (IcdP)	1.001 \pm 0.032	0.812 \pm 0.023	0.595 \pm 0.002	0.114 \pm 0.010
Dibenzo(ah)anthracene (DahA)	0.744 \pm 0.043	1.982 \pm 0.232	0.744 \pm 0.050	0.937 \pm 0.037
Benzo(ghi) perylene (BghiP)	0.963 \pm 0.032	2.260 \pm 0.111	0.725 \pm 0.005	0.948 \pm 0.001
Σ HPAH	12.265 \pm 0.651	31.859 \pm 2.206	12.078 \pm 0.739	7.625 \pm 0.100
Total PAH	13.861 \pm 0.794	45.937 \pm 2.697	18.210 \pm 0.915	9.012 \pm 0.639
PAH components ($\mu\text{g/g-dry wt}$)	Ugborikoko	Ugboroike	Alegbo	Otokutu
Naphthalene (Naph)	0.131 \pm 0.010	0.091 \pm 0.011	0.038 \pm 0.004	0.001 \pm 0.000
2-Methyl Naphthalene (2MNaph)	0.166 \pm 0.001	0.085 \pm 0.002	0.081 \pm 0.002	0.001 \pm 0.000
Acenaphthylene (Any)	0.045 \pm 0.005	0.028 \pm 0.001	0.034 \pm 0.000	0.001 \pm 0.002
Acenaphthene (Ane)	0.055 \pm 0.011	0.035 \pm 0.000	0.031 \pm 0.002	0.001 \pm 0.000
Florene (Flo)	0.078 \pm 0.040	0.084 \pm 0.002	0.083 \pm 0.012	0.001 \pm 0.000
Phenathrene (Phe)	0.673 \pm 0.003	0.398 \pm 0.001	1.021 \pm 0.020	0.012 \pm 0.001
Anthracene (Anth)	0.057 \pm 0.001	0.031 \pm 0.060	0.097 \pm 0.001	0.002 \pm 0.001
Σ LPAH	1.205 \pm 0.071	0.752 \pm 0.077	1.385 \pm 0.041	0.019 \pm 0.004
Fluoranthene (Fluo)	0.956 \pm 0.022	0.428 \pm 0.020	1.148 \pm 0.002	0.002 \pm 0.000
Pyrene (Pyr)	0.941 \pm 0.027	0.529 \pm 0.044	1.275 \pm 0.003	0.002 \pm 0.001
Benzo(a)anthracene (BaA)	0.245 \pm 0.006	0.109 \pm 0.032	0.393 \pm 0.001	0.001 \pm 0.000
Crysen (Chry)	0.638 \pm 0.002	0.337 \pm 0.004	0.680 \pm 0.032	0.002 \pm 0.001
Benzo(b)fluoranthrene (BbF)	0.225 \pm 0.004	0.153 \pm 0.002	0.338 \pm 0.002	0.002 \pm 0.000
Benzo(k)fluoranthrene (BkF)	0.246 \pm 0.003	0.140 \pm 0.041	0.295 \pm 0.003	0.002 \pm 0.000
Benzo(a)pyrene (BaP)	0.323 \pm 0.000	0.266 \pm 0.003	0.441 \pm 0.006	0.001 \pm 0.001
Indeno(1,2,3-cd) perylene (IcdP)	0.171 \pm 0.010	0.114 \pm 0.001	0.330 \pm 0.004	0.001 \pm 0.001
Dibenzo(ah)anthracene (DahA)	0.508 \pm 0.005	0.520 \pm 0.040	0.707 \pm 0.003	0.002 \pm 0.000
Benzo(g,h,i) perylene (BghiP)	0.377 \pm 0.044	0.478 \pm 0.031	0.843 \pm 0.141	0.002 \pm 0.000
Σ HPAH	4.630 \pm 0.123	3.074 \pm 0.218	6.450 \pm 0.197	0.017 \pm 0.004
Total PAH	5.836 \pm 0.298	3.827 \pm 0.183	7.834 \pm 0.413	0.035 \pm 0.003

Benzo(g,h,i)perylene, a six member ring PAHs, highly associated with vehicular emissions was detected in samples from all sampling locations. The result obtained in order of magnitude were as follows: Refinery > Enerhen > Water Resources > Alegbo > Ekpan > Ugboroike > Ugborikoko > Otokutu. Apart from the refinery, the influences of vehicular emissions were observed in the trend across the other sampling locations. The variation of Benzo (g, h, i) perylene across the sampling location is shown in Figure 2. The results were similar to that reported for industrial and recreational area in former Soviet Union [27].

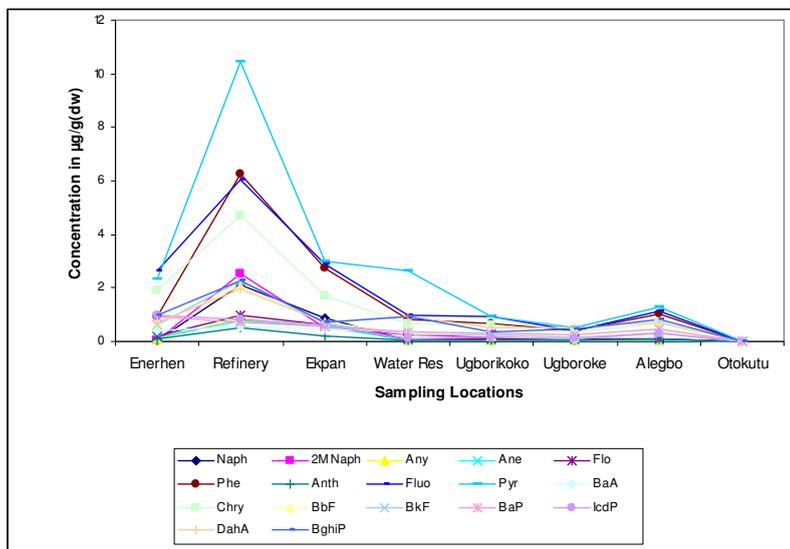


Figure 2. Spatial variation of PAHs along sampling locations.

In general, pyrene was observed to be the most abundant compound at all sites (20 %), followed by fluoranthene (12 %), phenanthrene (12 %), chrysene (10 %) and benzo(g,h,i)perylene (6 %). The concentration of pyrene could be attributed to anthropogenic sources such as industrial and vehicular emissions. On the other hand, naphthalene, acenaphthalene, and anthracene accounted for 3.2 %, 1.6 %, and 1.1 %, respectively. The profile of the component PAHs are shown in Figure 3.

The potential sources of polycyclic aromatic hydrocarbons in the study area could be attributed to both industrial and commercial activities. Some of the industrial activities includes gas flaring from refinery, effluents from the refinery and petrochemical plant, spill from the Pipeline and Product Marketing Company (PPMC) depot, spill from pipelines that pass through the city, spill and indiscriminate dumping of used lubricating oils, exhaust fumes from power generating plants. This is not limited to industrial activities but also include banks and residential quarters as well as hotels. The emissions from power generating plants can not be undermined as epileptic power supply from the National Electric Power Authority has compelled both residents and the industrial establishment to seek alternatives power sources to keep their businesses going.

Major commercial activities that stand as potential source of PAH in the environment of the study area are vehicular emissions due to high traffic density, and also the number of motor parks that are distributed across the length and breadth of the area. The activities in auto-mechanic workshops, filling (petrol) stations also lead to the spills of used oils, and other petroleum products to the environment. The poor waste management accounting for several waste dumps in every nook and crannies of the area is also potential source.

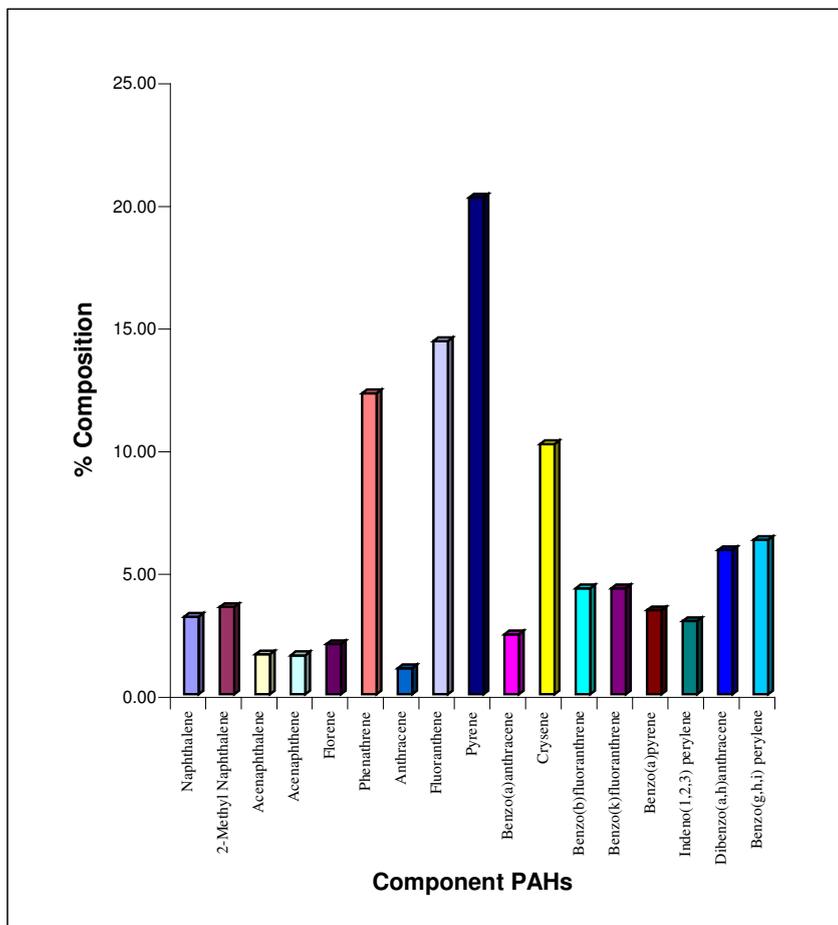


Figure 3. Profile of PAH species in Surface Soils of study area.

The spatial distribution of total PAHs in the soil was clearly observed in the contour map of total concentrations of PAHs with respect to the refinery (Figure 4). This was obtained with the aid of the Arc View Geographic Information System (GIS) (version 3.3) using the concentrations data at each sampling points as input with regards to their geographic coordinates values. The various contour lines depicting densities that are equivalent of concentration ranges defined in the map legend. The areas in the map that are lighter in shades corresponds to low concentrations of PAHs which is typical of most rural areas, while areas with darker or intense shades are representative of higher concentrations of PAHs. The concentrations of all PAHs in the soils tended to decline with increasing distance from the Refinery locations which was similarly reported in the study of temporal trends and distribution of PAHs in soils of Mosco [28].

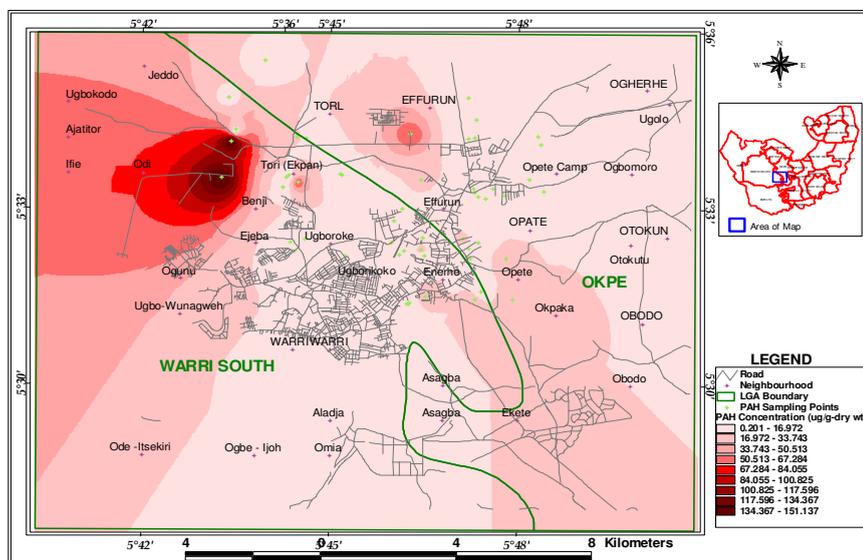


Figure 4. Contour map of total PAHs concentrations in soil of the study area.

CONCLUSIONS

The total soil PAH concentration in each location is influenced by the kind of anthropogenic activities. The study showed that PAH levels in soils from industrial sites were higher in all the locations, followed by markets, road junctions and roadside. The PAH concentration in soils from residential areas were the least. This could be attributed to the influence of industrial activities on the levels of pollutants in the environment. The higher levels of PAHs observed in the Refinery location are clear indications of combustion emissions and gas flaring from fractionating towers.

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