

EVALUATION OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL WITHIN THE VICINITY OF AN INDUSTRIAL ESTATE, SANGO OTTA, NIGERIA

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ABSTRACT

Soil samples were collected at different locations in the vicinity of an industrial estate in Sango-Ota Ogun State, Nigeria. The polycyclic aromatic hydrocarbons (PAHs) were quantitatively and qualitatively analyzed using gas chromatography (GC) coupled with flame ionization detector (FID). The total concentration of thirteen PAHs ranged from 3.33 mg/kg to 34.00 mg/kg. The highest concentration of total PAHs was observed from sampling point Q, while the lowest concentration (3.33 mg/kg) was found in soil sample S. No value was recorded for samples H, J and M. The PAHs ratio was also calculated to know the source(s) of the pollution. Phen/An, Flu/Pyr, An/(Phen+An), Flu/(Flu+Pyr), BaA/(BaA+Chry). BaA/Chry ratios ranged from 0.00 -1.09, 0.35 -1.02, 0.48-1.00, 0.26 -1.00, 0.00 -0.81 and 0.00 -3.38, respectively. The calculated ratios showed that the source of pollution is majorly pyrogenic with minor contribution from petrogenic source which might have occurred as a result of industrial effluent from some industries, grass/wood and petroleum combustion, as well as vehicular emission in the studied area. In addition, low molecular weight PAHs (i.e. 3-rings) contributed 9.3%, while the high molecular weight PAHs (i.e. 4+5+6-rings) accounted for 91.7% to the total PAHs in the samples. The distribution largely supports pyrogenic source for PAHs in the area under study. In conclusion, point Q with the highest concentration of PAHs is the most polluted, while point S that has the lowest concentration of PAHs is the least polluted. The degree of pollution decreases with the distance away from the location of industries which establishes the fact that presence of the manufacturing industries contributed significantly to the PAHs pollution in the study area. However, it should be noted that pollution level at sampling points H, J & M were insignificant.

Keywords: PAHs, GC-FID, Soil, Pollution, Environment

Introduction

Environmental pollution has contributed a lot of damage to the life and normal health of people, over the last three decades. Industrialization and development of industrial zones in most developing countries have led to increase in the contamination of the environment by toxic and persistent organic and inorganic contaminants. Some industries accidentally or intentionally discharge toxic chemicals into the environment, contaminating drinking water sources, release toxins into air and reduce the soil quality. Polycyclic aromatic hydrocarbons (PAHs) are class of toxic and persistent organic compound that are commonly released by industrial processes into the environment. According to the United State Environmental Protection Agency (USEPA) toxic release inventory, industrial release of PAHs to the environment was about 4.9 million pounds in year 2000 while about 1.2 million was released in year 2010 into water and onsite landfill in the United State alone. PAHs refer to a large group of organic

compounds with more than two fused ring of benzene. PAHs are not produced for commercial use but are contained naturally in tar, creosote, mineral oil and coke and are also released by smoke and exhaust from incomplete combustion in industrial processes. PAHs belong to the group of priority pollutants have become a subject of great concern due to its carcinogenicity, mutagenicity and tetratogenicity [2]. They are found in the air, water, soil and recent marine sediments and can remain in the environment for months or years [1]. Certain industrial processes produce PAHs with characteristic distribution patterns due to their origins [9] including the metallurgical industries [10] and hydrocarbon spillage [11]. Atmospheric deposition after local and long range transport of PAHs due to emissions products from natural processes, such as forest fires and also as a result of human activity, such as production and processing of metals, coal, oil and gas are the main source of PAHs in soil. They are also present in car exhaust fumes, cigarette smoke and wood

smoke. PAH accumulation over a long period of time can lead to contamination of groundwater and food chains as determined in the inner tissues of various vegetable species and in root of crops [4] in their growing environment and in the industrial area of Thessaloniki in Greece. They can also be deposited on earth surface where they can persist for some period of time based on geographical and climatic conditions [8]. Humans may be exposed to PAHs via the air, water and food [3]. In addition, humans may be exposed dermally, orally and by inhalation of PAH residues present in soil, particularly in the industrial area. Consequently, it is important to assess the risks posed by PAHs in soil at such sites so that the risk on health can be reduced to an acceptable level. The commonly used chemical risk assessment paradigm entails identification and characterization of a chemical hazard, which is then compared with an estimate of human exposure to the chemical, in order to assess the risk posed. Numerous studies on soil pollution by PAHs in Nigeria have been reported. However, most previous studies have concentrated on crude oil rich Niger Delta region. At present limited data is available on the contribution of non-petroleum based industries on the increasing burden of PAHs in the Nigerian environment, therefore, this study was conducted to assess the level, distribution and identify the possible sources of PAHs within an industrial estate in Sango-Otta, Ogun state Nigeria.

Materials and Methods Description of study area and sample collection

Sango -otta is one of the fastest growing urban communities in Ogun State south west Nigeria. It is located between latitude 6° 30'N – 6° 50'N and longitude 3° 02'E – 3° 50'E with an elevation of about 53m above the sea level. An industrial estate which hosts different pharmaceutical companies, aluminum rolling mills, chemical plant, paints and manufacturing of electrical appliances are concentrated within the community. The map of Nigeria showing the location of Ogun state is shown in Fig. 1.0. Soil samples were collected within the vicinity of the industrial estate at different locations (Fig. 1) with stainless steel spade. The position of the sampling point were recorded with GPS (Global positioning system) and longitude and latitude were reported. The samples were taken at about 0-15 cm at an interval of 50 m from each other. The samples were composited from five sub-samples and a minimum of two composited samples from each location. The samples were wrapped with aluminum foil paper, stored in a metal box and transported to the laboratory. The samples were air-dried, ground and sieved with a 200 µm sieve after which they were wrapped properly with an aluminum foil and kept at 4

°C prior to analysis. The total organic carbon (TOC) in the samples was determined using Walkley Black method [17].

Extraction and Quantification of PAHs

The air dried soil samples were extracted according to USEPA (Ultrasonic Method 3550C). 10 g of dried soil sample mixed with anhydrous sodium sulphate (1:1) was ultrasonically extracted with 50 mL of dichloromethane for 20 minutes and centrifuge for 10 minutes, and repeated three times. Elemental sulphur was removed by the addition of small amount of copper tuning.

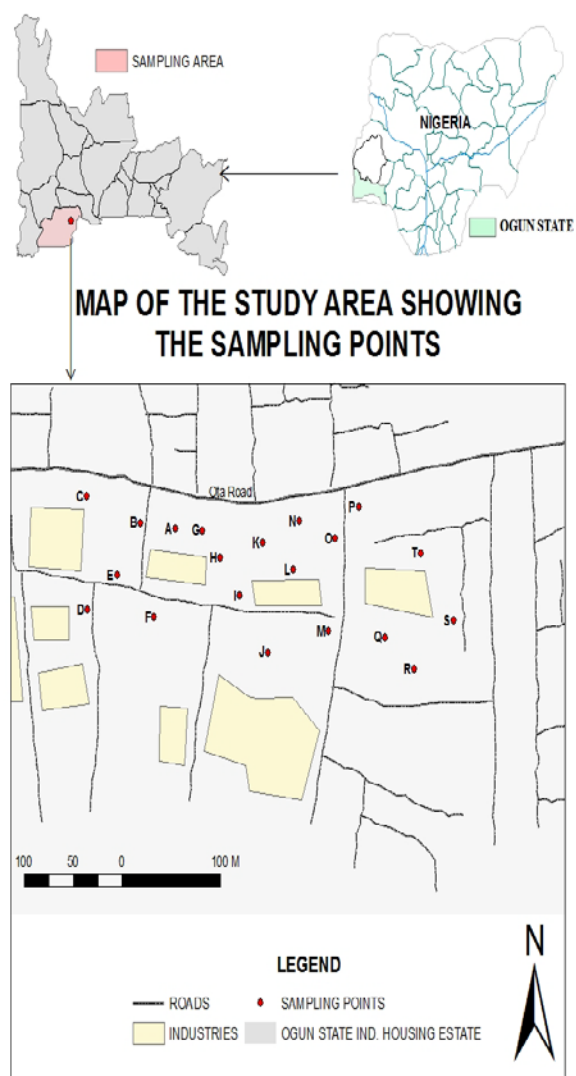


Figure 1: Map of the Nigeria showing the location of Sango Ota and an insert of the sampling point

The concentrated extract was transferred to column (30 cm X 10 mm i.d.) packed with silica gel/alumina (4:1). The column was pre-eluted with 30 mL of hexane before loading the sample. The concentrated extract was separated into saturate, aromatic (PAHs) and polar fractions by using 30 mL of n-hexane, 30 mL of n-hexane / dichloromethane (2:3,v/v) and 30 mL of methanol respectively. The PAH fraction was subjected to gas chromatographic analysis. The identification and quantification of the 16 priority PAHs compounds were carried out using gas chromatography HP 5890 powered with HPCMEM software with flame ionization detector (GC-FID) based on the retention times compared to that of external PAHs standards. These compounds were naphthalene, acenaphthylene, acenaphthene, flourene, phenanthrene, anthracene, fluoranthene, pyrene, benzo (a) anthracene, chrysene, benzo (b) fluoranthene, benzo (k) fluoranthene, benzo (a) pyrene, dibenz (a,h) anthracene, benzo (g,h,i) perylene and indeno (1,2,3,cd) pyrene. Aliquot of PAH fraction was injected into a GC-FID. The separation was effected on 30 cm X 0.25 mm i.d., HP-5 fused silica column using nitrogen as carrier gas. The oven temperature ramped at 100 °C (2 min hold) followed by 280 °C for 16 min at 10 °C/min, then 300 °C for 4 min and 10 °C/min. For quality control two methods blanks (solvents) were also analyzed along with the samples. The concentrations of PAHs in the method blanks are below the method detection limit.

Results and Discussion

Total organic carbon (TOC) is a direct measure of the samples organic richness and the values are presented in fig. 2. The result shows that the samples contains significant amount of organic matter one of which is polycyclic aromatic hydrocarbon (PAHs). The thirteen PAHs concentration and distribution in the soil samples are given in table 1. The sum of which is defined as PAHs ranged from 3.33 mg/kg to 34.00 mg/kg with the average value of 7.46 mg/kg. The sampling point and the coreesponding coordinate is recorded in Table 2. The highest concentration of \sum 13PAHs was recorded in the soil samples from Point Q, no value was recorded for point H,J and M and the highest concentration recorded at this location might resulted from diffuse pollution sources from combustion products which are transfer to soil by wet or dry deposition. The lowest concentration of the 13 PAHs was recorded at sampling point S. It was observed that as distance increases from the vicinity of the industrial estate, there is decline in PAHs concentrations establishing the fact that the industrial discharge contributed significantly to pollution level in the area under study [18]. 7, 12-

Dimethylbenz[a] anthracene that was present in almost every sample is a highly potent carcinogen that is activated by microsomal enzymes to a diol epoxide metabolite that binds covalently to DNA in mammalian cells, leading ultimately to tumor induction. Its presence in the samples can be attributed to the presence of aluminium/iron/steel production industries in the study area [10].

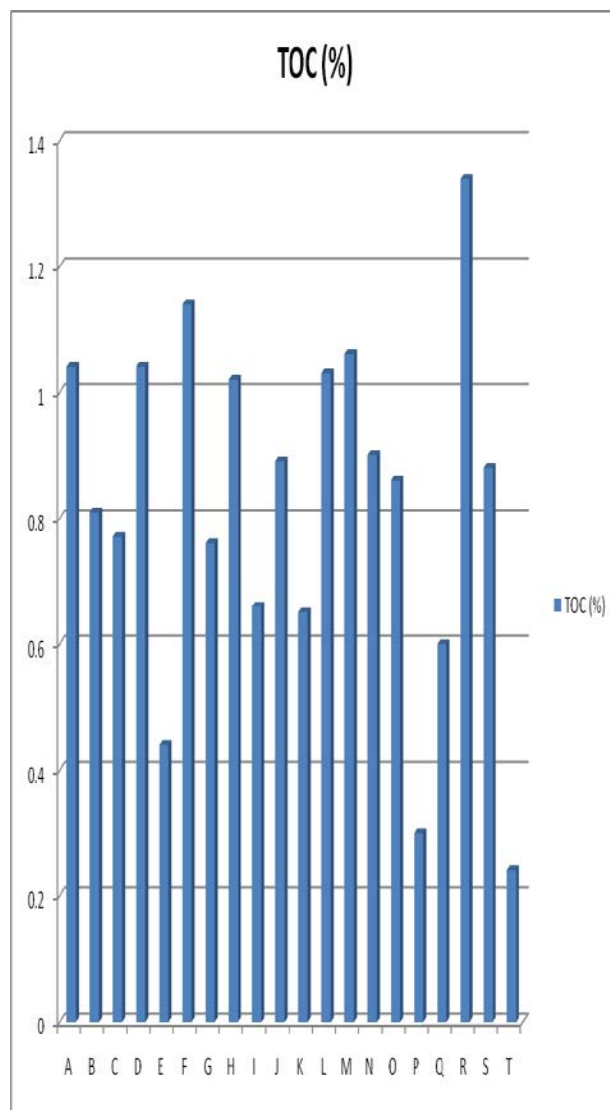


Figure 2: Distribution of TOC in the soil samples in the vicinity of the Sango-Ota industrial estate

Table 1: Concentration of PAHs (mg/kg) in the soil in the vicinity of sango-ota industrial estate

PAH s/ SMP	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
Nap	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ace	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Acep	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Flo	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.328	ND	ND	ND
Phe	0.39	ND	0.44	ND	ND	0.42	0.37	ND	0.48	ND	0.40	0.38	ND	0.38	0.37	ND	0.69	0.38	0.45	0.38
Ant	0.44	ND	0.50	0.40	ND	0.43	0.41	ND	0.51	ND	0.43	0.41	ND	0.43	0.40	ND	0.85	ND	0.41	0.42
Fluo	0.45	ND	0.51	0.41	ND	0.44	ND	ND	0.52	ND	0.43	0.44	ND	0.42	0.41	ND	0.61	ND	ND	0.41
Pyr	0.99	0.83	0.50	0.62	ND	0.91	1.06	ND	0.51	ND	ND	1.24	ND	0.75	ND	ND	0.62	ND	0.75	1.02
BcP	0.92	0.31	0.11	0.64	2.89	0.77	0.34	ND	1.17	ND	0.76	0.79	ND	0.38	0.96	2.88	1.57	0.34	0.59	0.85
BaA	0.89	1.29	ND	1.63	2.11	ND	0.57	ND	0.37	ND	ND	2.17	ND	3.57	ND	ND	0.55	1.92	ND	ND
Chr	0.77	1.45	1.10	0.39	1.29	0.59	1.34	ND	1.04	ND	0.59	0.59	ND	2.12	0.49	0.95	1.46	1.57	0.35	0.51
7,12DBaA	0.92	0.75	0.70	0.80	0.72	0.88	0.75	ND	1.01	ND	0.87	0.89	ND	0.70	0.73	0.71	2.69	0.75	0.79	0.83
BjF	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.46	ND	ND	ND
BeP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.32	ND	ND	ND
3MC	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	21.86	ND	ND	ND
DaiP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DahA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	11.91	ND	ND	ND	ND	ND	ND
Total	5.78	4.63	4.85	4.88	6.10	4.45	4.83	ND	5.61	ND	3.47	6.91	ND	20.68	3.36	4.54	34.00	4.96	3.33	4.42

D-Not Detectable; SMP-Sample; PAHs-Polycyclic Aromatic Hydrocarbons; Nap-Naphthalene; Ace-Acenaphthylene; Acep-Acenaphthene; Flu- Fluorene; Phe- Phenanthrene ; Ant-Anthracene; Fluo-Fluoranthene; Pyr-Pyrene; BcP-Benzo(c)Phenethrene; BaA-Benzo(a)Anthracene; Chr-Chrysene; 7,12DBaA-7,12-Dimethylbenzo(a)anthracene;BjF-Benzo(j)fluoranthene;3MC-3-Methylcholanthrene;DaiP-Dibenzo(a,i)Pyrene;DahA-Dibenzo(a,h)Anthracene

A marked distribution pattern of the PAHs concentration in soil was shown in table 2 and fig. 3 with predominance of 4, 5, and 6 rings. The 3-rings PAHs accounted for approximately 9.3 %, 4-rings PAHs accounted for approximately 62.1%, 5-rings PAHs accounted for 2.2%, and 6-rings accounted for 26.5%, however, no 2 ring PAHs was observed. It is the 4-rings that have the highest concentrations (62.1%) which

includes: fluoranthene, pyrene, benzo(c)phenanthrene, benzo(a)anthracene, 7,12-dimethylbenzo(a) anthracene and chrysene. While the 5-rings has the lowest concentration (2.2 %) such as benzo(j)fluoranthene, benzo(e)pyrene, benzo(a)pyrene and benzo(k)fluoranthene. These results show that the source of PAH are mainly pyrogenic with minor contribution from petrogenic source [18- 20].

Table 2: Relative Distribution Pattern (mg/kg) and (%) Composition of Individual PAHs in soil within the vicinity of sango-ota industrial estate

Sample	3-rings	4-rings	5-rings	6-rings	LMW/HMW
A	0.83	4.94	ND	ND	0.17
B	ND	4.63	ND	ND	0.24
C	0.93	3.92	ND	ND	0.09
D	0.40	4.48	ND	ND	ND
E	ND	7.00	ND	ND	0.24
F	0.86	3.59	ND	ND	0.19
G	0.77	4.06	ND	ND	ND
H	ND	ND	ND	ND	0.21
I	0.99	4.63	ND	ND	ND
J	ND	ND	ND	ND	0.31
K	0.82	2.64	ND	ND	0.13
L	0.79	6.13	ND	ND	ND
M	ND	ND	ND	ND	ND
N	0.82	7.95	ND	11.91	0.04
O	0.77	2.60	ND	ND	ND
P	ND	4.54	ND	ND	ND
Q	1.87	7.49	2.79	21.86	0.06
R	0.38	4.58	ND	ND	0.08
S	0.86	2.47	ND	ND	0.35
T	0.81	3.62	ND	ND	0.22
Sum	11.88	79.26	2.79	33.77	
%	9.30	62.07	2.18	26.45	

ND –Not detectable

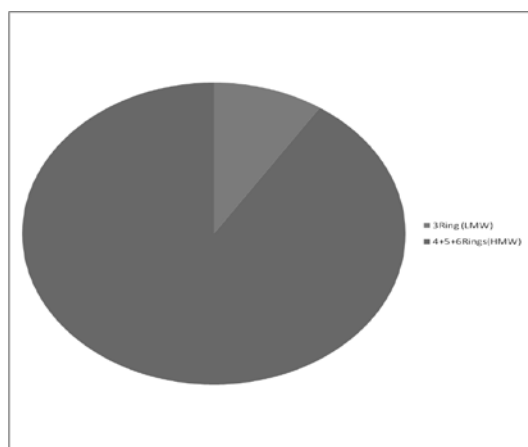


Figure 3: Relative Distribution of low molecular weight (LMW) and high molecular weight (HMW) PAHs in soil within the vicinity of Sango-Ota

Source diagnostic ratios

The source diagnostic indices are calculated from interpretative PAH concentration and presented in table 3 and were used to indicate source of the PAHs [18, 19, 20]. Phe/Ant ratio ranged from 0.80 to 1.08 which is generally less than 10 in the samples therefore indicating pyrogenic origin. Flou/Pyr, Ant/Ant + Phe and BaA/ Chr ratios ranged from 0.35 to 1.03, 0.26 to 1.00 and 0.35 to 1.68 respectively. Majority of the samples have Flou/Pyr, BaA/ Chr ratios greater than 1 and Ant/Ant + Phen greater than 0.10 which largely support pyrogenic source with minor contribution from petrogenic source. BaA/ BaA+ Chr and Flou/ Flou + Pyr ranged from 0.62 to 0.81 and 0.26 to 0.51 respectively. BaA/ BaA+ Chr and Flou/ Flou + Pyr ratios greater than 0.35 and 0.50 respectively reflected major contribution from pyrogenic source. The LMW/HMW ratio in all the samples is less

than 1 (0.04-0.35) which reflects substantial contribution from pyrogenic source. Fig. 4 also showed that the main

source of PAHs in the study area is mainly pyrogenic with contribution from petrogenic source.

Table 3: Source Diagnostic Ratios of PAHs in soil within the vicinity of sango-ota industrial estate

SAMPLE	Phe/Ant	Fluo/Pyr	Ant/Ant + Phe	Fluo/Fluo + Pyr	BaA/BaA + Chr	BaA/Chr
A	0.90	ND	ND	0.32	0.54	1.16
B	ND	ND	ND	ND	0.47	0.89
C	0.89	1.03	0.53	0.51	0.00	0.00
D	0.00	0.65	1.00	0.39	0.81	4.23
E	ND	ND	ND	ND	0.62	1.64
F	0.97	0.48	0.50	0.32	0.00	0.00
G	0.90	ND	0.53	ND	0.30	0.43
H	ND	0.45	0.53	ND	ND	ND
I	0.93	1.02	0.52	0.51	0.26	0.35
J	ND	ND	ND	ND	ND	ND
K	0.93	ND	0.52	ND	ND	ND
L	0.94	0.35	0.52	0.26	0.79	3.38
M	ND	ND	ND	ND	ND	ND
N	0.89	0.56	0.53	0.36	0.63	1.68
O	0.92	0.41	0.52	1.00	0.00	0.00
P	ND	ND	ND	ND	ND	ND
Q	0.80	0.98	0.56	0.50	0.27	0.38
R	ND	ND	ND	ND	0.55	1.22
S	1.09	ND	0.48	ND	ND	ND
T	0.91	0.41	0.53	0.29	ND	ND

ND = Not Detectable

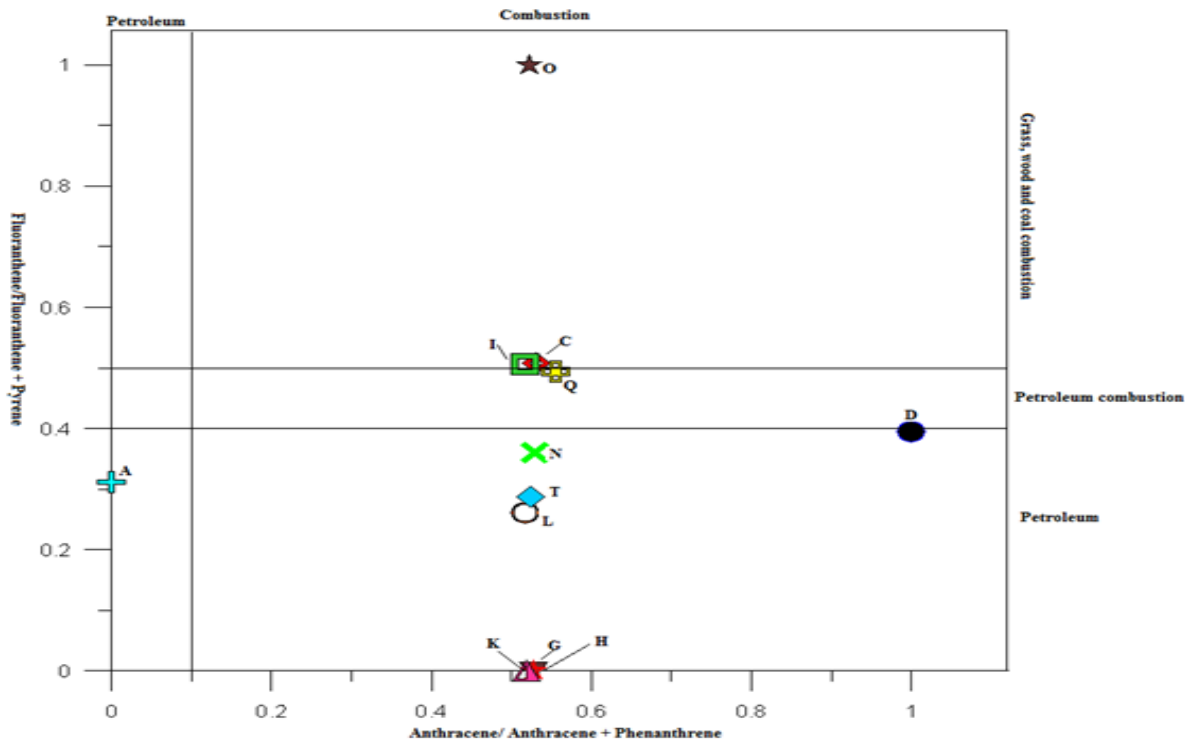


Figure 4: PAHs Source identification (Petrogenic vs. Pyrogenic) in soil in the vicinity of sango-ota industrial estate

Comparism of PAHs levels from other parts of the globe

From table 2, the sum of the concentrations 13 PAHs ranged from 3.33 mg/kg to 34.00 mg/kg. The levels of 13 PAHs in the soil samples were within the range reported for soils from polluted area in the Niger Delta [19, 21]. The total concentration of 13 PAHs in soils from the industrial zones in Korea, ranged from 109-178 mg/kg. Surface soils from the outskirts of Beijing, China, contained total concentrations of 16PAHs (16 priority pollutants proposed by the United States Environmental Protection Agency) ranging from 16 to 3884 mg/kg with a mean value of 1347 mg/kg [21]. The concentration of 7,12DiBenzo (a) anthracene, the most carcinogenic PAHs in the present study, ranged from 0.71 mg/kg to 2.69 mg/kg with a mean value of 0.91 mg/kg. The soil studied in this work can be regarded as being moderately polluted.

Conclusion

This work investigated the distribution of polycyclic aromatic hydrocarbons (PAHs) in the soil samples collected from an industrial Estate Sango Otta in Ogun state, Nigeria. The level of individual PAHs can be associated with their sources, through the use of specific PAHs ratios which provide more unique distribution for the sources. The high concentration of the PAHs was recorded in soil samples from sample Q with the value 34.00 mg/kg which indicate that it is the most polluted site among the ones investigated.

The PAHs concentration in the soil decreased with increasing distance from the industrial area. The potential source of the PAHs based on this study is majorly pyrogenic such as coal and biomass combustion and industrial discharge with minor contribution from petrogenic source e.g. exhaust from vehicles and electricity generating set. Pollution status of this study area can be regarded as being moderate presently; however serious attention must be paid to indiscriminate discharge of industrial waste particularly from the aluminum/steel manufacturing industry in the study area to forestall further pollution.

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