

## Assessment of Polycyclic Aromatic Hydrocarbons (PAH) Concentration in Sediments and Soils around Ibadan, Southwestern Nigeria

<sup>1</sup>Ogungbuyi, P. I., <sup>2</sup>Obasi, R. A., <sup>3</sup>Abimbola A .F

<sup>1,2</sup>Ekiti State University, Ado-Ekiti, PMB 5363.Ekiti State Nigeria.

<sup>3</sup> Dept. of Geology, University of Ibadan, Nigeria.

### ABSTRACT

The concentrations of polycyclic aromatic hydrocarbons (PAHs) in sediments and surface soils under different land use patterns were studied using a High Performance Liquid Column-Fluorescence Detector (HPLC-FD) and Gas Chromatography-Mass Spectrometry (GC-MS) systems. Two sets of separate samples were collected. Set A involved ten surface soil samples and set B contained five top soil and two sediment samples. The results show that the sum of 15US Environmental Protection Agency (EPA) priority pollutant PAHs are present. The concentration of PAHs in the sediment and surface soils range from 1.68 to 919  $\mu\text{g kg}^{-1}$  and 1.76 to 2926.68  $\mu\text{g kg}^{-1}$  respectively. The results show also that the low molecular weights are more than the high molecular weight, and the calculated ratios of PHen/ANth, FLth/PYR, and FLth/(FLth+PYR) exceed the background values, all these suggest that the PAHs are more of petrogenic sources. These results show more of petrogenic origin than pyrogenic and others of mixed nature. The average PAH-homologue concentrations are 3 rings >4 rings >5 rings <6 rings > 2 rings. PAHs concentrations are higher in engine oil impregnated soil, incinerated soils and stream sediments as against a non - oil industrialized areas. Most of the PAHs like benzo[a] anthracene, chrycene, benzo [b] fluoranthene, benzo[ ghi] perylene have properties that are carcinogenic, toxic, mutagenic and teratogenic and are therefore dangerous to health. The public is advised not to take in food that are derived from such contaminated surface soils

**Keywords:** Assessment, petrogenic, pyrogenic, 15US EPA, health.

### 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are pollutants which are detrimental to the environment when they exceed the threshold limit. They are organic and widespread pollutants in the environment which are normally formed in combustion processes of carbonaceous materials at moderate or high temperatures and are found in soil, sediments, water and air (Harvey 1991). The role of PAHs in the environment is increasingly becoming an issue of global concern, especially their toxic nature to living organisms at excessive concentrations in soils, sediments and water. These media can be considered as very important ecological cross road in the environment. However this pollutant can also be in the environment from natural sources. Natural sources of PAHs include biosynthetic activity and natural fire. However, the major source of PAHs into the environment is anthropogenic which includes combustion from industrial and vehicle emissions, waste incineration and deposition of wet or dry atmospheric particulates (Wilson and Jones 1993). Many scholars have studied the effects of exposures to high level of pollutant mixtures containing PAHs. ( Menzie, at al., 1992) PAHs are potent atmospheric pollutants that have fused aromatic rings ( Fetzer, 2000). Most of the

studied areas are impregnated with either engine oil in the case of the mechanic workshop, or dump sites whose materials are regularly burnt. PAHs are lipophilic and they mix more easily with oil than water and this is why they are found primarily in soils, sediments and oily substances. It is a common sight to see burnt wood and fuel-related products in the metropolis. People unknowingly cultivate and produce food from the soils that are affected by polycyclic aromatic hydrocarbons and Glenn, (1995) says that these people run the health risk. Luch, (2005) states that some PAHs are known for their carcinogenic, mutagenic and teratogenic properties and they include benzo[a] anthracene, chrycene, benzo[k] fluorathene, benzo[a] pyrene, benzo[b] fluorathene, benzo[ghi] perylene and indeno[1,2,3-cd] pyrene. (C<sub>22</sub>H<sub>12</sub>). The study aims at assessing the concentration of these pollutants in suspected contaminated soils and sediments and their sources within the Ibadan metropolis.

### 2. STUDY AREA

Ibadan metropolis is located between longitudes 3<sup>o</sup> 15' - and 4<sup>o</sup> 00'E and latitudes 7<sup>o</sup> 15' and 7<sup>o</sup> 30'N. Ibadan, capital of Oyo State in Nigeria is the largest city in West Africa, with a total area of 3080km<sup>2</sup>, and density of 250km<sup>2</sup>.It enjoys the characteristic West African

Monsoon Climate marked by a distinct seasonal shift in the wind pattern. The area is influenced by the moist maritime South –West monsoon winds while the dry season occurs usually from November to February. The mean annual rainfall for Ibadan is between 1250mm and

1290mm while the mean annual temperature is about 26.6°C (Oluwande,1977; Onianwa and Egunyomi,1983; Oguntoyinbo,1986). There are three major landform units that dominate Ibadan metropolis namely, plains, hills, and river valleys.

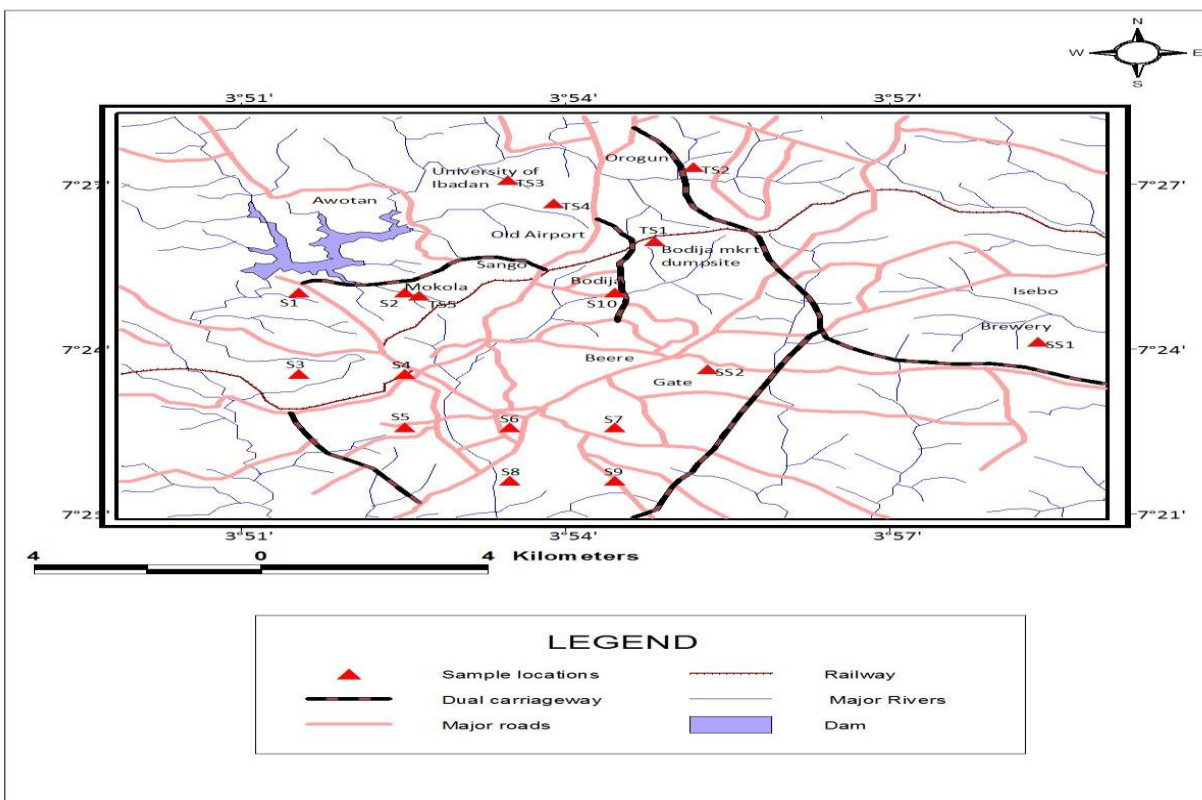


Fig :1 Map showing sample locations

## 2.1 Sample Locations

Ten (10) soil samples (composite from fifty sampling sites) were collected systematically within the densely populated area of Ibadan metropolis (Fig 1). Seven (7) out of the ten samples (5 topsoils and 2 sediments) were collected from areas suspected to be contaminated. (Table 1). The topsoils and the sediments are dried at room Temperatures for some days. All foreign objects like roots and gravel sized materials were picked and separated from the dried samples. They were then disaggregated in a porcelain mortar and later sieved through < 65µm polythene sieve to remove coarse particles like stones, roots and other debris to have a homogenized fraction before geochemical analysis. The mortar was washed with water and air dried for each sample to avoid contamination with other samples. The homogenized samples were then sent to the Activation Laboratories for analysis.

## 3. ANALYTICAL PROCEDURES

Analytical procedures involved extraction, separation and analyses of the samples using High Performance Liquid

Chromatography (HPLC) –Fluorescence Detector (FD) in the laboratory. PAHs in the soils are extracted using Soxhlet extraction. 5g of freeze-dried sample are filtered in a porous cellulose thimble (25×70 mm) and placed in a Soxhlet extractor. The extractor is then fitted to a 100 mL flask containing 60 mL dichloromethane. The extraction is performed for 24 hrs. The PAHs are mixed with 50 mL dichloromethane in a 500 mL brown glass bottle with Teflon lined caps and the mixture was shaken on a rotary shaker (200 rpm) at 25 °C. Thereafter, 20 mL of the dichloromethane layer is transferred to a 100 mL in the flask. All the extracts in the round bottom flask are dried by rotary evaporation. The residues are then dissolved in 2 mL of cyclohexane while 0.5 mL of the solute is transferred and purified with a silica gel column (8×220 mm) and washed with a mixture of 1:1 of hexane and dichloromethane. The first 1 mL of eluate is discarded because it contained non-polar saturated hydrocarbons and is less retained than PAHs by silica gel. The second 2-mL aliquot of eluate is collected, dried by sparging with N<sub>2</sub> and then redissolved in 1 mL acetonitrile for HPLC determination. The first set of samples collected is analysed using Gas Chromatography-Mass Spectrometry.

### 3.1 Quantification of PAHs

Quantitative analysis of the soil and sediments extracts is performed by using the high performance liquid chromatography (HPLC). 15 US Environmental Protection Agency (USEPA) priority PAHs analyzed are Naphthalene (Na), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (An), Fluoranthene (FluA), Pyrene (Pyr), Benzo[a]anthracene (BaA), Chrysene (Chry), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Benzo[a]pyrene (Bap), Dibenz[a,h]anthracene (DBA), Benzo[g,h,i]perylene (BghiP), and Indenol[1,2,3-cd]pyrene (IP) (EPA1984). Acenaphthylene was excluded from this study due to its low fluorescence properties. The total PAHs concentration is regarded as the sum of the concentration of 15 PAHs for each collected sample. In order to understand PAH species the Low Molecular Weight (LMW) containing 2-4 ring and High Molecular Weight (HMW) containing 5-6 ring are also determined. The Shimadzu Class-VP HPLC system equipped with a fluorescence detector (RF-10AXL), a gradient pump (LC-10AT) and a reversed phase column C18 (Varian ChromSpher 5 PAH, 250×4.6 mm) was used for the determination of PAHs in the soils and sediments. An external standard mixture was used for quantification of the 15 PAHs.

### 3.2 Quality Control

The detection limit of the HPLC method for the 15 PAHs was in the range of 0.12  $\mu\text{g g}^{-1}$  to 1.57  $\mu\text{g kg}^{-1}$ . Method blanks (solvent) and spiked blanks (standards of EPA610 PAH mixture, LA 96245, Supelco, USA spiked into soil) were extracted and analyzed as described above. The recoveries and the relative standard deviations of this method for 15 PAHs were in the range of 74 to 110% and 0.53 to 0.57%, respectively. Results of blanks extracted under the same conditions were below detection limits and analytical results were without recovery ratio correction. Data were analyzed using known standard and current used geochemical software package and statistical SPSS software.

## 4. RESULTS AND DISCUSSION

### 4.1 Results

Table 2 shows the result of PAH analysis for (5) soils and (2) sediments samples collected from suspected contaminated sources. The result shows that all the data analyzed are above the detection limits. The samples were collected from areas suspected to be contaminated with oil related products and others with different pollutants. For example the value of naphthalene in the soil, ranges from 103.9  $\mu\text{g/kg}$  in Ts3 (university farmland) to

206.67  $\mu\text{g/kg}$  in Ts1 (dump site), and from 148.68  $\mu\text{g/kg}$  in stream sediment to 161.61  $\mu\text{g/kg}$  in the dump site of motor parts respectively. Acenaphthene content is high in both the soil (2926.68  $\mu\text{g/kg}$ ) and sediments (919.29  $\mu\text{g/kg}$ ). The total contents of the 15PAHs in the samples show that the lowest concentration value of **955.18  $\mu\text{g/kg}$**  is found in the farmland of the university while the highest value of 9833.99  $\mu\text{g/kg}$  is from the mechanic workshop areas of the metropolis. The high concentration of the PAHs in the mechanic workshop areas is attributed to the indiscriminate discharge of petroleum and engine oil products in those areas. PAHs values also range from 1.76 to 2926.68  $\mu\text{g/kg}$  for soils and 1.68 to 919.29  $\mu\text{g/kg}$  for sediments. It can be seen from Table 2 that PAHs concentrations in soils and sediment are obviously different, the  $\sum\text{PAHs}$  for samples Ts2 and Ts4 (9833.99 and 3459.65  $\mu\text{g/kg}$ ) respectively are higher than that in SS1 and SS2 (1729.08  $\mu\text{g/kg}$  and 1561.89  $\mu\text{g/kg}$ ) respectively.

Table 3 shows the result of samples collected from the densely populated areas of the Ibadan metropolis. The area has low vehicular movement and less industrial activities. The result also shows that all the data analysed are below the detection limit (background values) an indication that no impregnation of oil-related product or pyrolytic related contaminant in the areas have occurred. The statistical descriptive analysis to determine whether significant differences existed between sediment and soil  $\sum\text{PAH}_{15}$  levels with respect to the land use was calculated as shown in Table 4

It is observed that most of the values obtained from some locations are predominantly of low molecular weight (LMW) PAHs especially those that have ring structures that fall from 2-ring to 4-ring. The 3-ring structures PAHs are dominant while Benzo[b]fluoranthene to Indenol[1,2,3-ed]pyrene with 5-ring and 6-ring respectively are of high molecular weight (HMW) as shown in Table 4. However, the data show that the concentrations of PAHs in the samples are in the order of 3-ring > 4-ring > 5-ring > 6-ring > 2-ring as shown in the PAH-homologue maximum.  $\sum\text{PAHs}$  values reveal that the concentrations of PAHs are influenced by the environmental domain or land use. The type of land use influences the PAH concentrations and accumulation pattern in soils (Wilcke 2000). The concentrations of PAHs in the soils and sediment of the different land use / environmental domains show this relationship, urban area > dumpsite > effluent discharge > farmland. The PAH homologues concentration in topsoil and sediments are shown in Figs.2 and 3. The Fig.2 shows that acenaphthene has the highest concentration of  $\sum\text{PAH}_{15}$  in TS2 (sample from the mechanic village) followed by SS2 and this is considered to be contaminant by US EPA (1985).

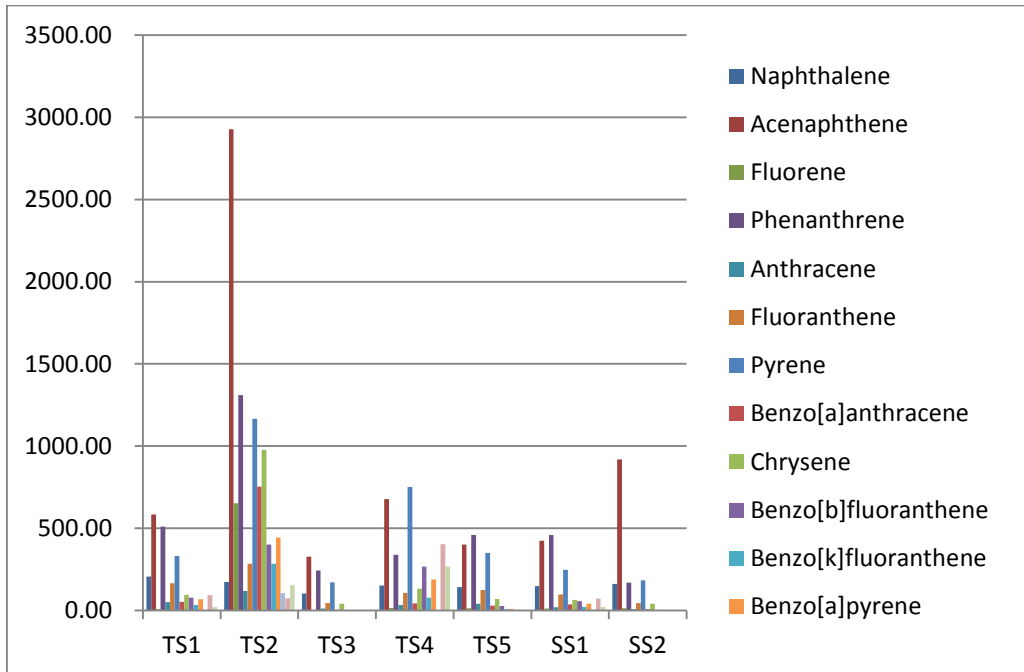


Fig. 2 PAH-homologues in soils and sediments with different utilization pattern

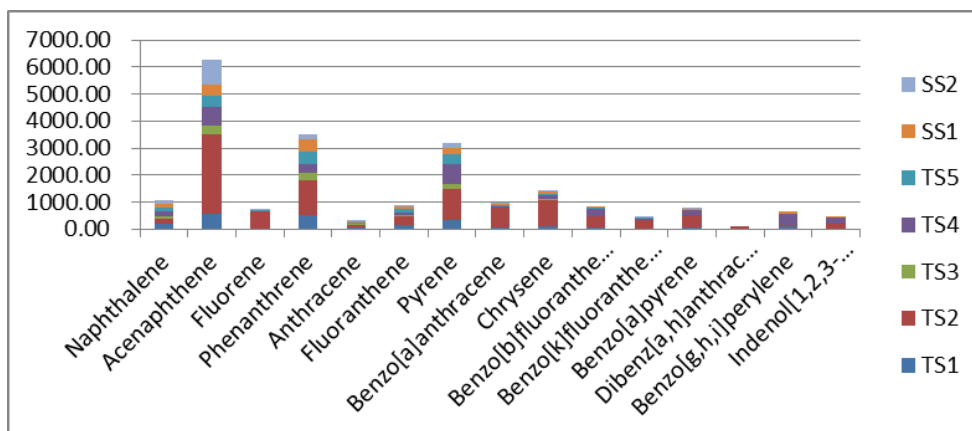


Fig. 3 PAHs concentration in soil and sediments samples

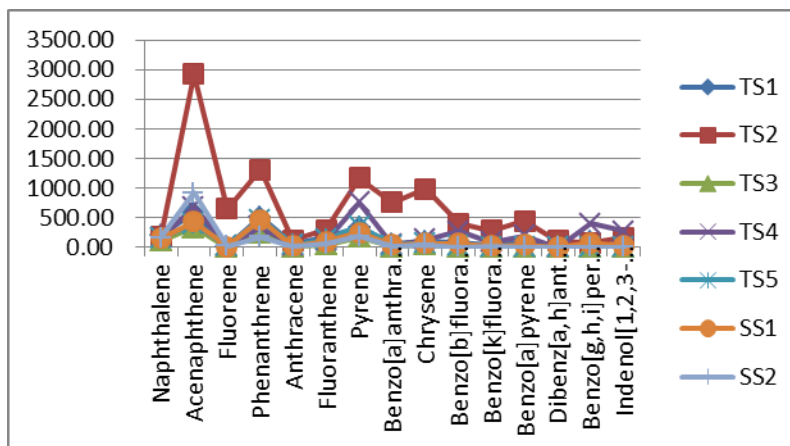


Fig. 4 PAHs concentrations in soils and sediments samples of the selected targeted area



## 4.2 Source Identification

Some other generalizations concerning sources of PAHs are also available using several different PAHs ratios. Petrogenic contamination is characterized by the predominance of the lower-molecular-weight (LMW) PAHs (2-3 benzenoid rings) which have high volatility and are easily transported from one source areas to another. The HMW PAHs with heavier weight have low volatility and minimal transport. LMW PAHs are usually of petrogenic origin while, the high-molecular-weight (HMW) PAHs 4-6 benzenoid ring dominate in the pyrolytic (Bernner et al.1990; Wise et al.1988).In this study the LMW are more than the HMW which suggest petrogenic origin. Petrogenic sources of PAHs contain mostly light molecular weight and are generated from geochemical alteration of organic matter from petroleum spills, coal fired plants and municipal sewage treatment facilities whereas PAHs with 4-6 benzenoid rings are generated mainly through incomplete combustion of organic matter at temperatures usually above 400<sup>o</sup>c over a short time of interval.).

Table 5 shows the ratio of LMW and HMW. It is taken that when the standard value for LMW/HMW ratio is less than unity (<1) , it indicates a pyrogenic source and when the ratio is greater than unity (>1) , it suggests petrogenic sources. (Baumard et al.,1998) .The result in Table 5 shows that most ratios are greater than unity and are therefore of petrogenic origin. The origin and composition of PAHs are different for sediments and surface soils from different environments

Phenanthrene/anthracene ratio is used to distinguish between petrogenic and pyrogenic sources of PAH (Baumard et al.1998). Phenanthrene/anthracene ratio (PHEN and ANT) are two structural isomers with different physicochemical properties. PHEN/ANTH isomer ratio is temperature dependent and decreases with increasing temperatures. Phenanthrene is thermodynamically more stable than Anthracene. PHEN/ANTH ratios have been attributed to the slow maturation of petroleum at low temperatures. (Cardellicchio et al.2007). By contrast pyrolysis of organic matter at high temperatures generates PAHs characterized by a low PHEN/ANTH (<10) and the slow thermal maturation of organic matter in petroleum is characterized by much higher PHEN /ANT ratio (>10).

Yunker et al.,(2000) state that when the ratio of IPYR/IPYR +BPERY is less than 0.20, it indicates a petrogenic origin of the soil, and when it is between 0.20-0.50, it is of a mixed origin that is ( combustion and petrogenic), and when the value is greater than 0.50 (>0.50), the origin becomes pyrogenic.(Table 6). Yunker et al., (2002) further state that when B[a]ANT/B[a]ANT+CHERY ratio is less than 0.2 (<

0.2), it indicates a petrogenic source and between 0.32 and 0.35 shows mixed source and greater than 0.35 (> 0.35), it becomes petrogenic. Based on this, the PAHs value for surface soil is 0.16 an indication of petrogenic source while the sediment value is 0.28 indicating combustion source which means liquid fuel that originates from vehicle and crude oil combustion.

Similarly, the fluoanthene/pyrene ratio (FLTH/PYR) is often used to distinguish between pyrolytic and petrogenic sources (Neff et al.,2005). FLTH is less thermodynamically stable than PYR and a predominance of FLTH over PYR is characteristic of pyrogenic source. In petroleum derived PAHs PYR is more abundant compared to FLTH ( Budzinski, et al., 1997) Ratios of FLTH/PYR for the study area are in the range of 0.14—0.50 for the soil and 0.25—0.39 for the sediments (Table 8a).

Table 8b reveals that the ratio of FLTH/(FLTH/PYR) is 0.22 for the topsoil and 0.24 for stream sediment an indication of petroleum sources. Generally, it is observed that the concentration of pyrene is higher than that of fluoranthene in all the samples, therefore the point source for the PAHs is petroleum derived. (Budzinski et al., 1997).These ratios infer that the main source of PAHs in these samples is petrogenic. This establishes the evidence of the presence of PAHs within the Ibadan and environs. People are therefore advised to avoid eating food that are derived from the soils and sediments impregnated with contaminants

## 5. CONCLUSIONS

Accumulation of PAH in topsoils and sediments is investigated in some areas of Ibadan Southwestern Nigeria. The sum of 15 PAHs concentration range from 1.68 to 919 µg kg for topsoil and 1.76 to 2926.68 µg kg for sediment. The lower molecular weight (LMW) makes up the largest proportion of all the PAHs while the high molecular weight (HMW) shows **ing** the lowest concentration. The higher concentration of PAHs is found in sediment and soils collected from dump site and mechanic village. The sources of the PAH into the environment are mainly petrogenic.

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**Table: 1 Description of sample location and nature of contamination**

Sample number	Sample type	Location (Target Site)	Nature of Contamination	Coordinate
TS 1	Soil	Dumpsite, Bodija Market	Top edge incineration facility	003° 54.872'E, 07° 25.973'N
TS2	Soil	Mechanic workshop, Orogun	Indiscriminate discharge of engine oil	003° 54.872'E, 07° 25.973'N
TS3	Soil	University of Ibadan, faculty of Agriculture farmland	Common farm with fertilizer	003° 58.513'E, 07° 24.096'N
TS4	Soil	Student Union Shopping mall, University of Ibadan	Diesel/petrol electricity power generators	003°53.485'E, 07° 27.116'N
TS5	Soil	Garri industry dumpsite heating, Mokola	Domestic heating with wood to generate charcoal	07° 24.961' 003° 52.636'
SS1	stream sediment	NBL Brewery factory New Gbagi ,Ife Road	Discharge of effluent into stream	07°24 .096' 003° 58.513'
SS2	stream sediment	Araromi Motor spare part workshop. Agodi-Gate	Dumping of used motor spare parts into the streams	07° 23.583' 003° 55.374'

**Table:2 PAHs analysis for soil and sediment samples for the seven samples in a targeted area**

	PAHs conc. (ug/kg) Soils					Sediments (ug/kg)		detection limit
	TS1	TS2	TS3	TS4	TS5	SS1	SS2	
Naphthalene	206.67	174.64	103.97	152.28	143.60	148.68	161.61	1.57
Acenaphthene	583.64	2926.68	328.42	677.92	401.88	425.28	919.29	0.86
Fluorene	7.93	652.56	n.d.	16.81	15.00	11.63	13.96	0.33
Phenanthrene	510.92	1311.22	244.63	339.00	460.16	459.64	170.05	0.76
Anthracene	50.86	118.83	11.52	33.00	42.27	20.06	9.08	0.24
Fluoranthene	166.97	285.09	45.92	107.24	125.01	97.33	46.22	0.78
Pyrene	332.08	1166.50	172.72	752.43	350.44	247.21	183.23	0.42
Benzo[a]anthracene	52.66	754.42	4.98	43.62	29.07	37.47	9.30	0.25
Chrysene	96.55	978.01	41.26	132.56	71.33	64.81	42.28	0.49
Benzo[b]fluoranthene	78.29	402.15	n.d.	267.28	27.35	57.63	n.d.	0.8
Benzo[k]fluoranthene	33.12	284.21	1.76	78.98	9.45	21.73	5.19	0.12
Benzo[a]pyrene	69.72	444.43	n.d.	188.56	10.67	41.75	1.68	0.23
Dibenz[a,h]anthracene	n.d.	105.69	n.d.	n.d.	n.d.	n.d.	n.d.	0.42
Benzo[g,h,i]perylene	93.28	74.26	n.d.	403.07	n.d.	73.38	n.d.	0.82
Indenol[1,2,3-cd]pyrene	23.02	155.30	n.d.	266.90	n.d.	22.49	n.d.	0.61
Total 15 PAHs	2305.72	9833.99	955.18	3459.65	1686.24	1729.08	1561.89	

n.d. ;below the detection limit

Table: 3 Result of samples from densely populated and non-industrialized areas of Ibadan

PAH screen duplication %	TS1	TS2	TS3	TS4	TS5	TS6	TS7	TS8	TS9	TS10	matrix spike%	
										recovery	recovery	
Naphthalene	<15	<15	<15	<15	<15	<15	<15	<15	<15	117	117	
Acenaphthylene	<15	<15	<15	<15	<15	<15	<15	<15	<15	131	128	
Acenaphthene	<15	<15	<15	<15	<15	<15	<15	<15	<15	127	119	
Fluorene	<15	<15	<15	<15	<15	<15	<15	<15	<15	129	122	
Phenanthrene	<15	<15	<15	<15	<15	<15	<15	<15	<15	124	119	
Anthracene	<15	<15	<15	<15	<15	<15	<15	<15	<15	125	118	
Fluoranthene	<15	<15	<15	<15	<15	<15	<15	<15	<15	129	121	
Pyrene	<15	<15	<15	<15	<15	<15	<15	<15	<15	149	151	
Chrysene	<15	<15	<15	<15	<15	<15	<15	<15	<15	147	134	
Benzo(a)anthracene	<15	<15	<15	<15	<15	<15	<15	<15	<15	161	136	
Benzo(b)fluoranthene	<15	<15	<15	<15	<15	<15	<15	<15	<15	141	149	
Benzo(k)fluoranthene	<15	<15	<15	<15	<15	<15	<15	<15	<15	159	155	
Benzo(a)pyrene	<15	<15	<15	<15	<15	<15	<15	<15	<15	214	202	
Indeno(1,2,3-cd)pyrene	<15	<15	<15	<15	<15	<15	<15	<15	<15	189	189	
Dibenzo(a,h)anthracene	<15	<15	<15	<15	<15	<15	<15	<15	<15	229	215	
Benzo(ghi)perylene	<15	<15	<15	<15	<15	<15	<15	<15	<15			
SSTD% Recovery	82	101	117	16	115	146	117	101	128	127	119	138

Table 4: Statistical description of the 15 PAHs

PAH	Ring structure	Minimum	Maximum	Mean	Std. Deviation	Weight
Naphthalene	2-ring	103.97	206.67	155.9214	31.29065	LMW
Acenaphthene	3-ring	328.42	2926.68	898.0729	916.02429	
Fluorene		7.93	652.56	119.6483	261.09033	
Phenanthrene		170.05	1311.22	499.3743	378.90465	
Anthracene		9.08	118.83	40.8029	37.74147	
Fluoranthene		45.92	285.09	124.8257	82.59445	
Pyrene	4-ring	172.72	1166.50	457.8014	369.09837	
Benzoanthracene		4.98	754.42	133.0743	274.53728	
Chrysene						
Benzofluoranthene	5-ring	27.35	402.15	166.5400	161.77448	HMW
Benzokfluoranthene		1.76	284.21	62.0629	101.43885	
Benzoapyrene		1.68	444.43	126.1350	169.90190	
Dibenzanthracene	6-ring	105.69	105.69	105.6900	.	
Benzoghiperylene		73.38	403.07	160.9975	161.64258	
Indeno123cdpyrene		22.49	266.90	116.9275	117.90004	



PAH- homologue			
2-ring	103.97	206.67	155.92
3-ring	515.48	5009.29	1554.55
4-ring	264.88	3184.02	2919.53
5-ring	30.79	1130.79	354.74
6-ring	201.56	775.66	383.62

**Table 5 Diagnostic ratio of PAHs (after Baumard et al.1998; Wise et al.1988; Bernner et al.1990)**

PAHs Ratio	value	Interpretation
PHen/ANth	< 10	Pyrogenic source
PHen/ANth	> 10	Petrogenic source
LMW/HMW	< 1	Pyrogenic
LMW/HMW	>1	Petrogenic source
Pyr>Flth FLth>PYr		Petrogenic Pyrogenic
FlIth/PYR	>1	Pyrogenic source
PYR/FLth	<1	Petrogenic source
BaA/(BaA +Chr)	<0.2	Petrogenic source
IPy/(IPy +BPer)	>0.5	pyrogenic source
IPy/(IPy +BPer)	<0.2	Petrogenic source

**Table: 6 Ratios of different PAHs homologues**

Ratio	TS1	TS2	TS3	TS4	TS5	SS1	SS2
IPY/IPY+BPER	0.2	0.68	ND	0.4	ND	0.23	ND
BaA/BaA+Chr	0.35	0.44	0.11	0.25	0.29	0.37	0.18
Lth/FLth+Pyr	0.3	0.2	0.21	0.12	0.26	0.28	0.2
PHEN/ANTH	0.05	11.03	21.24	10.27	10.89	22.91	18.73

**Table 7: Ratio of Phen/Anth**

	TS1	TS2	TS3	TS4	TS5	SS1	SS2
Phenanthrene	510.92	1311.22	244.63	339.00	460.16	459.64	170.05
Anthracene	50.86	118.83	11.52	33.00	42.27	20.06	9.08
Ratio Phen/Anth	10.05	11.03	21.24	10.27	10.89	22.91	18.73

**Table 8a: Ratio of FLth/PYr**

	TS1	TS2	TS3	TS4	TS5	SS1	SS2
Fluoranthene	166.97	285.09	45.92	107.24	125.01	97.33	46.22
Pyrene	332.08	1166.50	172.72	752.43	350.44	247.21	183.23
Ratio FLth/PYr	0.50	0.24	0.27	0.14	0.36	0.39	0.25

**Table 8b: Ratio of FLth/ (FLth+PYr)**

	TS1	TS2	TS3	TS4	TS5	SS1	SS2
Fluoranthene	166.97	285.09	45.92	107.24	125.01	97.33	46.22
Pyrene	332.08	1166.50	172.72	752.43	350.44	247.21	183.23
FLth+PYr	499.05	1451.59	218.64	859.67	475.45	344.54	229.45
FLth/ (FLth+PYr)	0.33	0.20	0.21	0.12	0.26	0.28	0.20