

Full Length Research Paper

Characterization and distributions of aliphatic and polyaromatic hydrocarbons in soils of oil sand deposits area of Ondo State, Nigeria

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The concentration, distribution profile and possible sources of n-alkanes and polycyclic aromatic hydrocarbons in the soil of oil sand deposits in Ondo Southwest Nigeria were investigated to determine the present level of contamination prior to exploitation of the oil sand deposits. Surface soil samples (0-15 cm) were collected from Ilubinrin, Agbabu and Oloda communities. The level and distribution of polyaromatic hydrocarbons and n-alkanes in the soil samples were analyzed using gas chromatography coupled with a flame ionization detector. The mean concentrations of polycyclic aromatic hydrocarbons (PAHs) in the soil of Agbabu, Ilubinrin, and Oloda were 36.07 ± 1.61 , 16.09 ± 0.76 and 10.04 ± 0.55 $\mu\text{g}/\text{kg}$ and the mean concentrations of identified, resolved n-alkanes were 14.03 ± 0.55 , 22.38 ± 0.99 and 30.37 ± 1.20 mg/kg , respectively. The odd-numbered alkanes were dominant in Agbabu and Ilubinrin, while the even numbered alkanes are dominant in Oloda. The distribution of total combustion specific PAHs was higher in most of the area than the non-combustion specific PAHs and the highest percentage of total carcinogenic PAHs was 28, 33 and 45% in Oloda, Ilubinrin, and Agbabu, respectively. The studied area was not polluted with PAHs, but there was evidence of PAH's accumulation in the soil. Various n-alkanes and PAHs ratios were obtained to identify the possible sources of PAHs and n-alkanes. Mixed sources of pyrogenic and petrogenic PAHs were discovered with predominant pyrolytic sources due to combustion of wood, biomass, and bitumen seepage.

Key words: Polycyclic aromatic hydrocarbons, oil sand, diagnostic ratio, aliphatic hydrocarbons, bitumen.

INTRODUCTION

Mining and exploitation of natural resources have posed environmental, social and economic problems to many

communities in developing countries. Nigeria has abundant mineral resources, including solid minerals

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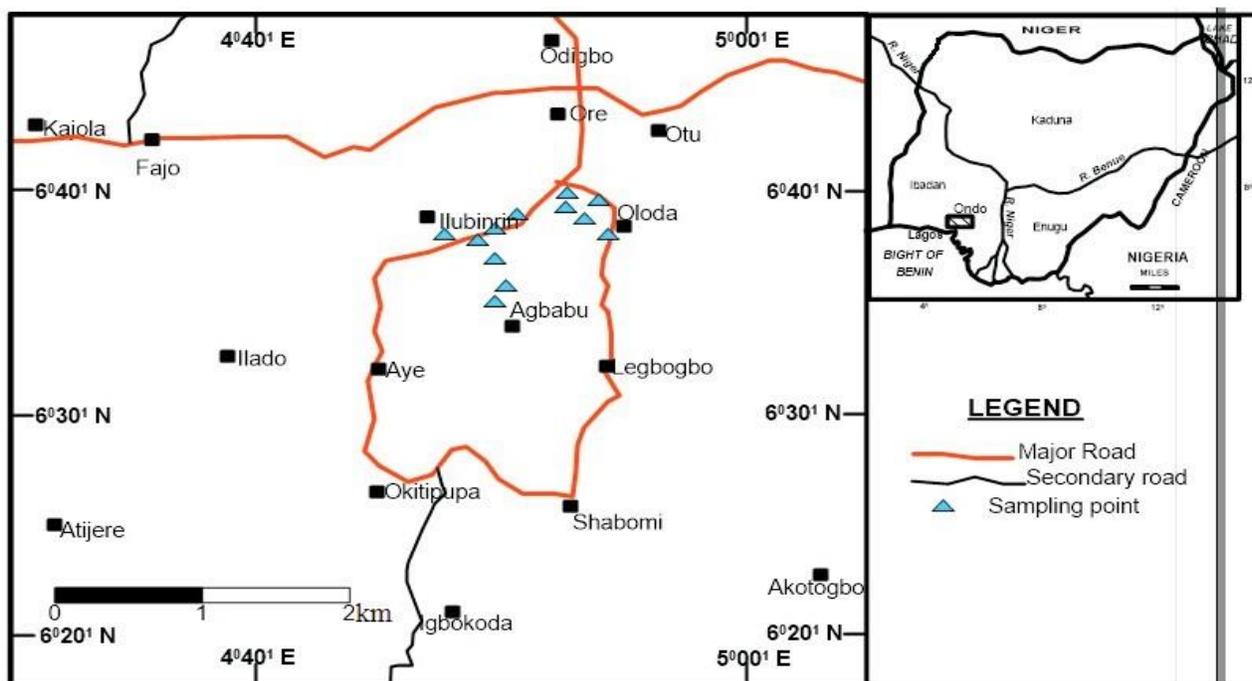


Figure 1. Map of Ondo State showing sampling area.

and fossil fuel. The fossil fuel consists principally of crude oil, coal, and bituminous sand. The Nigerian oil sands region is one of the largest natural bitumen deposits in the world with an estimated 30 to 40 million barrels and potential bitumen recovery of about four billion barrels (Adegoke et al., 1991). Despite the economic importance of these resources, there is growing concern over the environmental and health risks that could result from contaminants released during mining, exploration, refining, and transportation of these resources (Ite et al., 2013). PAHs and n-alkanes are ubiquitous in the environment and released through different anthropogenic activities and natural sources (Wilckle, 2000). Polycyclic aromatic hydrocarbons (PAHs) and n-alkanes accumulate in soil from atmospheric deposition, seepage from natural sources, biogenic sources and discharge of wastes. Petrogenic sources and pyrogenic sources are the main anthropogenic sources of PAHs (Inengite et al., 2010). Identifying the impact of oil sand industrial activities on the ecosystem requires knowledge of the background level and pre-development concentration of contaminants in environmental media (Wiklund et al., 2012). Previous studies on the Nigerian oil sand regions focused on the geology, mineralogy (Egunyomi and Olatumile, 2010) and methods of processing with limited studies on the pre-development level of potential contaminants in the area. Therefore, this study describes the level, distribution pattern and sources of hydrocarbons (n-alkanes and PAHs) in soil of selected communities within the Nigerian

oil sand deposit belt.

MATERIALS AND METHODS

Site description

The Nigerian oil sands region stretches across Edo, Ondo to Lagos State covering about 140 km. The area falls within the Afowo formation and the Araromi shale of the eastern part of the Dahomey basin. The area is composed of sandstone impregnated with bitumen. Okosun (1990) described the stratigraphic settings of the basin. Three different communities with the largest reported oil sand deposits, namely Oloda, Agbabu and Ilubirin were selected for the study. These communities are small villages surrounded by scattered farm settlements and forest. Oil sand outcrops and seepage of liquid bitumen from the subsurface are seen in the area, contaminating soil and farmland, surface and groundwater. Figure 1 shows the map of Ondo State displaying the selected communities.

Sampling and sample preparation

Soil samples were collected from locations close to the oil sand deposits from three selected communities. Samples were collected between February and March, 2015. Soil sampling stations were established at 100 m × 100 m away from the deposit and each other. Ten soil samples were randomly collected from different points within each sampling station and composite. Soil samples (0-15 cm) were collected into pre-cleaned glass containers with a calibrated soil auger, wrapped with aluminum foil, covered and composite. The composite sample was homogenized and air-dried. Four composite soil samples were collected at the study areas. The air dried samples were ground with a pestle and mortar, and sieved

Table 1. Mean concentration of n-alkanes in the soil of Oloda, Ilubinrin and Agbabu (mg/kg, dry weight).

n-alkane	Sampling site		
	Oloda	Ilubinrin	Agbabu
C8	ND	ND	ND
C9	ND	ND	ND
C10	ND	ND	ND
C11	ND	ND	0.045
C12	0.001	0.001	0.114
C13	0.505	0.610	2.027
C14	0.587	1.031	1.81
C15	1.300	2.968	3.679
C16	1.393	2.308	3.245
C17	0.912	2.023	2.814
C18	1.157	1.487	2.191
C19	0.912	2.295	2.139
C20	1.032	2.069	2.088
C21	1.202	0.617	1.116
C22	1.605	1.861	2.513
C23	0.988	2.023	2.225
C24	0.704	0.364	0.988
C25	1.136	1.894	2.112
C26	0.409	0.635	0.904
C27	0.046	0.059	0.131
C28	0.084	0.093	0.193
C29	0.033	0.033	0.026
C30	0.023	0.012	0.011
THC	14.029	22.383	30.371
SD	0.552	0.99	1.20
Σ even HC	6.995	9.861	14.057
Σ Odd HC	7.034	12.522	16.314
MH	C22	C15	C15
CPI	1.01	1.26	1.16
CPI2	1.07	1.36	1.24
Σ (TCH)/Q ₆	10.07	9.70	9.36

THC: n-alkane total concentration; CPI₁: carbon preference index calculated as $\Sigma C_9-C_{29}/\Sigma C_8-C_{30}$; CPI₂: carbon preference index calculated as $\Sigma C_{13}-C_{25}/\Sigma C_{12}-C_{24}$; MH: Major hydrocarbon; Σ Odd HC: sum of odd numbered alkane; Σ even HC: sum of even numbered alkane; SCL/LCL: ratio of short chain to long chain alkanes. ND: Not detected.

through a 2 mm sieve and kept in brown bottles before analyses

Extraction and instrumental analysis

The air-dried soil samples were extracted according to USEPA method 3550C-ultrasonic extraction. The concentrated extract was fractionated into aliphatic, aromatic (PAHs) and polar fractions by eluting with of n-hexane, n-hexane/dichloromethane (2:3 in v/v) and methanol, respectively. The identification and quantification of PAHs and n-alkanes were performed with an Agilent 7890A Gas chromatograph (GC) with a flame ionization detector (FID). The GC was equipped with an HP5 fused silica capillary column (30 m x 0.25 mm internal diameter with 0.25 μ m film thickness). Helium gas was used as the carrier gas at a flow rate of 1 ml/min and nitrogen was used as the makeup gas. Fractioned extract (1 μ l) was injected in a splitless mode. The GC oven temperature was programmed as follows: for the aliphatic fraction, the oven temperature was

programmed from 60°C held for 2 min and ramped at 6°C min⁻¹ to 300°C and held for 20 min. For PAHs analysis, the oven temperature was programmed from 60°C (held for 2 min) to 180°C at a rate of 30°C min⁻¹, from 180 to 250°C at a rate of 5°C min⁻¹ and from 250 to 330°C at a rate of 15°C min⁻¹ (held for 8 min). The USEPA 16 priority PAHs and C₈-C₃₀ standard mix were analyzed using the same instrumental conditions. Identification of n- alkanes and PAHs compounds was based on a comparison of samples retention times with that of the reference standard mix and quantification was performed with five points external calibration method.

RESULTS AND DISCUSSION

Characterization and spatial distribution of n-alkanes

Table 1 shows the distributions of n-alkanes in soil samples

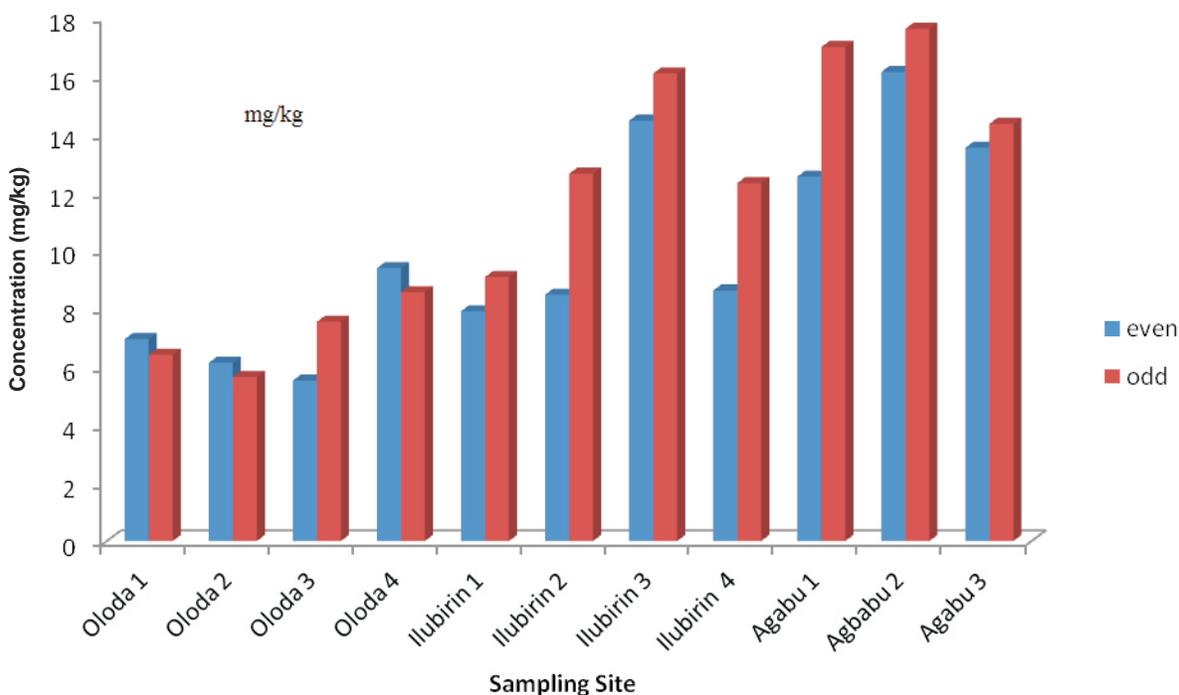


Figure 2. Distribution of even and odd-numbered alkanes in soil of Oloda, Ilubirin, and Agbabu.

from the oil sand deposit region of Ondo State, Nigeria at different sampling locations. The spatial distribution of *n*-alkane varies significantly between the sampling locations. The total mean concentrations of *n*-alkanes in Oloda (14.03 ± 0.55 mg/kg dry weight), Ilubirin (22.38 ± 0.99 mg/kg dry weight) and Agbabu (30.37 ± 1.20 mg/kg dry weight) were lower than the Nigerian EGASPIN intervention concentration (50.00 mg/kg dry weight) and the Oklahoma Department of Environmental Quality Limit (50.00 mg/kg) (Fagbote and Olanipekun, 2010). This is comparable to the total concentration of *n*-alkanes recorded in soil of other communities, outskirts of Beijing, China (0.60-39.92 mg/kg) Port Harcourt, Nigeria (16.74-2025 mg/kg) (Olajire et al., 2007) observed lower concentration of total *n*-alkane in soil within the vicinity of the Agbabu oil sand deposit (0.422-2.289 mg/kg); lower concentrations were also recorded around a petroleum industrial park in China (0.576-1.202 mg/kg) (Teng et al., 2015). The soil is characterized by *n*-alkanes ranging from C_{12} - C_{30} with the highest concentrations of n - C_{15} and the absence of light chains *n*-alkanes between C_8 and C_{11} (Table 1). The highest *n*-alkane concentrations between C_{15} and C_{25} in the entire sampling locations (Table 1) suggested pollution from biogenic or heavy hydrocarbon sources. The total sum of odd numbered alkane; 7.034, 12.52 and 16.31 mg/kg were higher than the even number alkanes; 6.995, 9.861 and 14.06 mg/kg in Oloda, Ilubirin and Agbabu. Odd numbered alkanes were dominant at all the sampling stations in Ilubirin and Agbabu. However, there was spatial variation in the spatial

distribution of the odd and even numbered alkane within the sampling station in Oloda (Figure 2). The dominance of even numbered alkane is commonly observed in bitumen and oil derived from carbonate or evaporate rock (Ficken et al., 2000; Fagbote and Olanipekun, 2012), even-numbered alkanes dominant the *n*-alkanes in Oloda 1, 2 and 4 while odd number alkanes were predominant in Oloda 3. This suggested a significant petrogenic input of *n*-alkanes in the soils of Oloda. The nC_{17} *n*-alkane is considered as a typical indicator of hydrocarbons from algae (Zegouagh, 1998). The nC_{17} is high in all the sampled soil; this indicates a significant input of petrogenic source of *n*-alkanes in the soil. The carbon preference index, CPI shows the relative contribution of *n*-alkanes from biogenic and anthropogenic sources. A CPI_1 indicates the relative contribution of *n*-alkane from natural (biogenic) sources and a CPI_1 shows anthropogenic (petroleum) sources. The values of CPI_1 for the whole range of hydrocarbon, $CPI_1 (\sum(C_9-C_{29})/(\sum(C_8-C_{30}))$ in the soil of Oloda (1.01), Ilubirin (1.26) and Agbabu (1.16) were about 1 (Table 1). This indicated that the main sources of *n*-alkane in the soil were from anthropogenic activities and not from natural biogenic sources. The CPI in the range of nC_{13} - nC_{25} 1.0 indicated petrogenic sources of normal alkane (Vladimir et al., 2012). The $CPI_2 (\sum(C_{13}-C_{25})/(\sum(C_{12}-C_{24}))$ in the soil of the studied areas is shown in Table 1. The CPI_2 values in the soil of the study areas ranged from 1.1 to 1.4. The ratio of total *n*-alkanes to *n*- C_{16} is less than 15 for petroleum-contaminated soil. The value of $\sum(THC)/n-C_{16}$ in the area

Table 2. Mean Concentration of PAHs in soil of Agbabu, Oloda and Ilubinrin (Mean±SD µg/kg, dwt)

PAHs	Abbreviation	Oloda	Ilubinrin	Agbabu
Naphthalene	NA	0.607±0.21	2.552±0.81	3.032±0.92
Acenaphthylene	Ant	0.903±0.26	1.335±0.34	1.722±0.61
Acenaphthene	Ace	0.924±0.27	1.815±0.60	2.497±0.51
Fluorene	Fl	1.585±0.80	1.736±0.34	2.949±0.54
Phenanthrene	Ph	0.880±0.81	0.655±0.70	1.962±0.58
Anthracene	Anth	1.612±0.18	1.584±0.42	4.845±1.74
Fluoranthene	Flu	0.639±0.37	0.723±0.20	1.787±0.67
Pyrene	Py	0.072±0.02	0.342±0.31	1.166±0.51
Benzo(a)anthracene	BaA	0.095±0.04	0.560±1.05	2.099±1.07
Chrysene	Chr	1.128±0.33	1.375±0.57	5.133±2.04
Benzo(b)fluoranthene	B(b)F	1.076±0.50	1.964±0.54	0.798±0.46
Benzo(k)fluoranthene	B(k)F	0.056±0.02	0.404±0.16	5.141±1.68
Benzo(a)pyrene	B(a)p	0.333±0.10	0.428±0.54	1.395±0.69
Indeno(1,2,3cd)pyrene	Icdp	0.080±0.03	0.450±0.54	1.051±0.38
Dibenzo(a,h)anthracene	DahA	0.047±0.02	0.153±0.22	0.426±0.41
Benzo(g,h,i)perylene	Bghip	0.009±0.01	0.013±0.00	0.063±0.34
TPHA	-	10.043±0.55	16.087±0.76	36.069±1.61
LPAH	-	6.510±0.41	9.676±0.62	17.010±1.11
HPAH	-	3.530±0.44	16.410±0.59	19.060±1.80
COMPAH	-	4.432 (44%)	7.271 (45%)	19.798 (55%)
CPAHs	-	2.814 (28%)	5.334 (33%)	16.045 (45%)

TPHA: Total sum of 16EPA priority PAHs; LPAH: low molecular weight PAHs; HPAH: high molecular weight PAHs; COMPAH: sum of combustion specific PAHs; CPAHs: sum of carcinogenic PAHs.

was greater than 15. The ratios showed that petroleum input of *n*-alkane was evident in the areas. The ratio of short chain to long chain alkanes (SCC/LCC) less than 1 usually represents *n*-alkanes produced by higher plants, marine animals, and sedimentary bacteria. SCC/LCC values close to 1 suggest that *n*-alkanes are mainly from petroleum and plankton sources and SCC/LCC values greater than 2 often show the presence of fresh oil (Wang et al., 2006). Petroleum distillates have the SCC/LCC value smaller than one (Wang and Fingas, 2005). The ratio of SCC/LCC (Table 1) in the soil samples were greater than one suggesting an anthropogenic source of *n*-alkanes.

Distribution and concentration of PAH in soil

Table 2 shows the average concentration and distribution of the US EPA priority PAHs in the soil of Oloda, Ilubinrin and Agbabu. The average concentration of PAHs (16PAHs) in the soil of Agbabu, Ilubinrin and Oloda was 36.069±1.61, 16.087±0.76 and 10.043±0.55 µg/kg, respectively. The total average concentration of PAHs in the soil was higher than the average concentration of PAHs (0.07±0.036 µg/kg) earlier reported in the soil of Agbabu (Fagbote and Olanipekun, 2010) and the endogenous concentration (1-10 µg/kg) resulting from plant synthesis,

anthropogenic input results in value of total PAHs greater than 10 µg/kg (Olajire and Brack, 2005). The total PAHs concentration in the soil samples was comparable to the concentration of PAHs in some of the communities (Odiabidi (367 µg/kg) and Ahoada (168 µg/kg)) hosting crude oil deposits in the Nigeria Niger Delta reported by Ana et al. (2009). Maliszewska-Kordybach (1996) classified soil contamination based on the total concentration of PAHs (16PAHs) as non-contaminated (200 µg/kg), weakly contaminated (200-600 µg/kg), contaminated (600-100 µg/kg) and heavily contaminated (1000 µg/kg). The soil of Agbabu, Ilubinrin and Oloda was non-contaminated but there is increasing accumulation of PAHs in the soil of the area from anthropogenic activities. The proportion of combustion specific PAHs in Agbabu, Oloda and Ilubinrin was 55, 44 and 45% of the total mean PAHs concentrations, respectively. The ring size distribution of PAHs in the soil is as shown in Figure 3. The results showed that all ring sizes of PAHs were present in the soil samples with an increasing order of 3>4>5>2>6-ring PAHs in all the studied sites.

The International Agency for Research on Cancer, IARC, has identified seven PAHs as priority carcinogens. The sum of the seven identified carcinogenic PAHs (benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd) pyrene and benzo (k)fluoranthene) were 2.814,

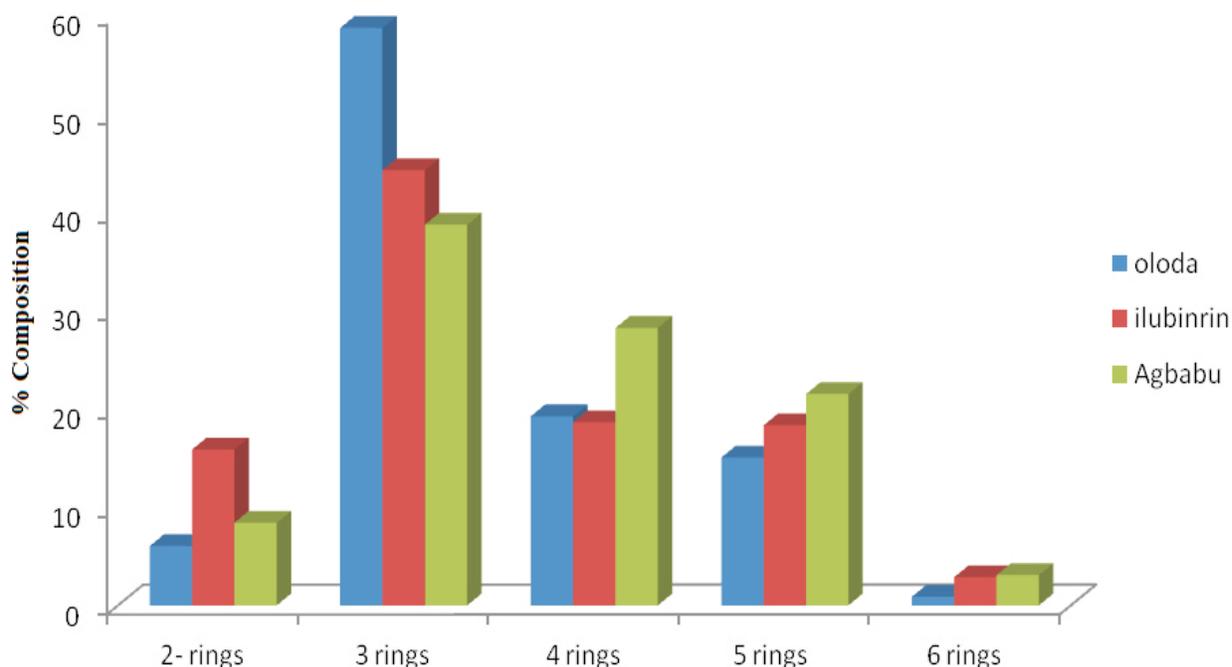


Figure 3. Ring size distribution of PAHs in soil of Agbabu, Oloda and Ilubinrin.

Table 3. Diagnostic ratios of PAHs in Agbabu, Ilubinrin and Oloda soil.

Sampling point	Diagnostic ratio							
	Phen/An	Flu/Pyr	Bap/chr	Na/Ace	An/Phen+An	Flu/Flu+pyr	BaA/BaA+Chr	Inp/Inp+Bghip
Oloda 1	0.37	12.1	0.14	0.00	0.73	0.92	0.13	0.90
Oloda 2	0.68	10.48	0.38	0.84	0.59	0.91	0.34	0.86
Oloda 3	0.58	5.97	0.37	1.21	0.63	0.85	0.35	0.92
Oloda 4	0.78	6.39	0.38	0.88	0.56	0.86	0.35	0.91
Ilubinrin 1	0.26	0.99	0.23	1.15	0.79	0.50	0.19	0.99
Ilubinrin 2	0.42	1.86	0.34	1.34	0.71	0.65	0.18	0.95
Ilubinrin 3	0.44	7.68	0.37	2.00	0.69	0.88	0.29	0.87
Ilubinrin 4	0.45	1.41	0.61	1.33	0.68	0.58	0.32	0.91
Agbabu 1	0.37	1.40	0.36	1.49	0.72	0.58	0.25	0.94
Agbabu 2	0.38	1.51	0.25	1.23	0.72	0.60	0.18	0.97
Agbabu 3	0.47	1.82	0.18	0.91	0.68	0.65	0.14	0.89

5.333 and 16.045 $\mu\text{g}/\text{kg}$ in Oloda, Ilubinrin and Agbabu accounting for 28, 33 and 45% of the total mean PAHs concentration in the soil (Table 2). Highly toxic and class 1 carcinogen benzo(a)pyrene was detected in all the samples. The mean concentration of benzo(a)pyrene in soil of Agbabu, Ilubinrin and Oloda was 1.395 ± 0.69 , 0.428 ± 0.50 and 0.333 ± 0.10 ig/kg , respectively, thus posing high risk to the community despite the low concentration of PAHs recorded in the area when compared with other crude oil host communities in the Niger Delta.

Identification of sources of PAHs in the soil

Anthropogenic sources of PAHs are due to petrogenic and combustion input, PAHs derived from petrogenic sources are characterized by the predominance of low molecular weight PAH (LPAHs) (Emoyan et al., 2015), while PAHs from combustion sources are characterized by a higher proportion of high molecular weight PAHs (HPAHs). Low-temperature combustion of biomass also results in the formation of LPAHs (Kumar and Kothiyal, 2012). Low molecular weight PAHs are classified as 2 to 3 ring PAHs

and high molecular weight PAHs as 4 to 6 rings PAHs (Mathieu and Friese, 2012). The total sum of low molecular weight PAHs (LPAH) were higher than the high molecular weight PAHs (HPAH) in Oloda and Ilubinrin accounting for 65 and 60% of the total PAHs concentrations (Table 2), the abundance of LPAH could have originated from the outcrop of bitumen sand deposits and from the combustion of biomass. The PAHs pattern at Agbabu was dominated by high molecular weight PAHs (52% of the total PAHs concentration in Agbabu). The ratio of LPAH/HPAH can be used to differentiate different PAHs sources, the values of LPAH/HPAH were 1.85, 0.59 and 0.89 in Oloda, Ilubinrin and Agbabu, respectively. LPAH/HPAH less than 1 is an indication that PAHs in Ilubinrin and Oloda are mostly from combustion sources (Kumar and Kothiyal, 2012).

The ratio of phenanthrene to anthracene (Phe/An) and fluoranthene to pyrene (Flu/Pyr) are used to identify PAHs sources. Combustion of organic matter at high temperature generates PAHs characterized by Phe/An 10 and slow decomposition of organic matter lead to higher Phe/An 10 (Wang et al., 2014). The values of Phe/An in Oloda, Iluninrin and Agbabu (Table 4) were less than 10 indicating pyrolytic sources of PAHs in the soil. The ratio of Flu/Pyr less than 1 is characteristics of petrogenic origin and greater than 1 is the characteristics of pyrolytic origin, the values of Flu/Pyr in the entire study area were greater than 1, indicating pyrolytic sources of PAHs. The ratio of anthracene to the sum of anthracene and phenanthrene ($\text{Ant}/(\text{Ant}+\text{Phe})$), can also be used to identify PAHs sources. The ratio of $\text{Ant}/(\text{Ant}+\text{Phe})$ 0.1 indicates PAHs sources to be of petroleum sources while $\text{Ant}/(\text{Ant}+\text{Phe})$ 0.1 indicates combustion sources of PAHs (Budzinski et al., 1997), the $\text{Ant}/(\text{Ant}+\text{Phe})$ ratios in Agbabu, Oloda and Ilubinrin were greater than 0.1 (Table 3), confirming that combustion products were the predominant PAHs sources in the studied areas.

Also, the ratio of benzo(a)anthracene to benzo(a)anthracene+chrysenes ($\text{B(a)A}/(\text{B(a)A}+\text{Chyr})$) in Ilubinrin and Agbabu showed a mixed source of pyrogenic and petrogenic origin. The ratio of $\text{B(a)A}/(\text{B(a)A}+\text{Chyr})$ greater than 0.2 indicates petroleum sources and between 0.20 and 0.35 indicate mixed sources while values greater than 0.35 indicates pyrolytic sources (Yunker et al., 2002). The ratio of fluoranthene to the sum of fluoranthene and pyrene ($\text{Flu}/(\text{Flu}+\text{Pyr})$) could differentiate petroleum combustion sources from other types of combustion sources. Olajire and Brack (2005) and Inengite et al. (2010) suggested that the ratio of $\text{Flu}/(\text{Flu}+\text{Pyr})$ 0.4 indicates petroleum combustion sources, values between 0.4 and 0.5 indicate pyrogenic, while 0.5 indicate combustion of coal, grasses, and woods. The $\text{Flu}/(\text{Flu}+\text{Pyr})$ ratios in Ilubinrin (0.50-0.88), Agbabu (0.58-0.65) and Oloda (0.85-0.92) were greater than 0.5, thus suggesting that the PAHs in the soil samples likely originated from pyrogenic sources derived from the combustion of wood and grasses. Also, it is presumed that the ratio of indeno(1,2,3cd)-pyrene ($\text{Ind}/\text{Ind}+\text{BghiP}$)

less than 0.2 indicates petroleum sources. ($\text{Ind}/\text{Ind}+\text{BghiP}$) in the range of ≥ 0.2 and ≤ 0.5 indicates petroleum combustion sources and >0.5 as grass, wood and coal combustion sources. The ratios of $\text{Ind}/\text{Ind}+\text{BghiP}$ were greater than 0.5 in the entire study area confirming that burning of wood and grasses are the major sources of pyrogenic PAHs in the entire study area.

Conclusion

The concentrations and origin of PAHs and *n*-alkanes in the soil of selected communities in the oil sand region of Nigeria were reported. The level of PAHs are below the regulatory standard value and the area is classified as unpolluted by PAHs, but the accumulation of PAHs and *n*-alkane in the soil was observed. Analysis of diagnostic ratios and molecular indices reveals that anthropogenic activities and seepage of bitumen from the bitumen deposit are the major sources of *n*-alkane and PAHs in the soil of the area. The *n*-alkanes in the soil are predominately from petrogenic sources from the oil sand deposit sites while the PAHs are from mixed petrogenic and pyrogenic sources with predominant input from the combustion of wood and grass. The observed values of *n*-alkanes and PAHs will serve as useful baseline data for monitoring and assessment when exploration begins.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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