Distribution Pattern of Polyaromatic Hydrocarbons (PAHs) in Soils in the Vicinity of Fuel Stations in Abraka, Nigeria

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ABSTRACT: The concentration and pattern of carcinogenic polycyclic aromatic hydrocarbons (PAHs) were studied in top and bottom soil in the vicinity of fuel stations in Abraka Nigeria, using gas chromotograph (GC) Hawleth Packard 6890. Analysis of results show that sample $D(0.03979mg.kg^{-1})>C(0.01592mg.kg^{-1})>A(0.01155mg.kg^{-1})>B(0.00325mg.kg^{-1})>E (0.00191mg.kg^{-1})$. Investigation also reveals that all tested samples are contaminated, with mean values ranging between $0.000207\pm0.00026mg.kg^{-1}$ and $0.002123\pm0.00303mg.kg^{-1}$. Similarly, spearmen's rank correlation coefficient (SRCC) of sample points At/Ab (0.99), Bt/Bb (0.99), Ct/Cb (0.98), Dt/Db (0.96) and Et/Eb (0.98) show a high and positive correlation between contaminants from top and bottom soil in each sample point. Molecular ratio analyses also show that petroleum origin is the chief source of PAHs contamination in all samples except in the control that is characterized with pyrogenic and petrogenic source. @JASEM

Key words: PAHs, soil Contamination, Abraka.

Polyaromatic hydrocarbons (PAHs) are group of organic compound that consist of fused aromatic rings and do not contain heteroatoms or carry substituents, (Fetzer, 2007). PAHs occur in oil, coal and tar deposites and are produced as byproducts of fossil fuel or biomass combustion. PAHs are also found in foods such as: cereals, oils and fats, vegetables and charred broiled meat/fish, (Brandley, *et.al*., 1988 and Azza, 2005). These multi-benzenoid ringed compounds have received considerable attention in recent years through ecological and ecotoxicological research because some have been identified as potent carcinogen, mutagen and teratogen (US-DHHS, 1995; Marr, *et.al*., 1999; Berko, 1999; FSA 2002, and CCMA, 2008). The extent of accumulation in soil and toxicity of PAHs in organism is affected by environmental factors such as: soil organic carbon, soil structure and particle size distribution, microbial population and physical and chemical properties of PAHs (Wilson and Jones, 1993).

Properties like lipophilicity, low water solubility and adsorption to particulate organic matter makes them a potentially toxic group of environmental contaminants, (Micias-Zomora, *et.al*., 2002). They may be eliminated or transformed to even more alkylated or substituted toxic derivatives through biotic or abiotic process such as sulfonation, nitration, microbial or photo oxidation (Gaga 2004). The prevalent mechanism of PAHs toxicity to invertebrates is narcosis which results in the degradation of cell membrane. This degradation can result in mild toxic effects or mortality depending upon exposure. Some PAHs also demonstrate photo activated toxicity which could cause mortality at very low concentrations of PAHs but require direct exposure of organism to ultraviolet (Uv) radiation in sunlight. The Uv radiation causes the chemical bonds in the PAHs to excite and form high energy radicals which speedily oxidize the tissue of exposed organism. Therefore, the objective of this research is to evaluate the concentration and pattern of distribution of PAHs in the study area.

MATERIALS AND METHODS

Study Area: The study area is located between latitude 5^o45^1 and 5^o50^1N and longitude 6° and 6^o15^1E. According to UNDP (2006), the rainfall pattern is the characteristics of the rainforest zone with mean annual rainfall of 3000mm. Temperature are high and fairly constant throughout the year. Average monthly temperature for the warmest months (February to April) ranged from 28^oC to 33^oC while the average monthly temperature for the coolest months (June – September) ranged between 21^oC and 23^oC.

Sampling: Samples were collected in the month of June and July 2009. All sample containers were thoroughly washed with laboratory grade phosphate detergent and thereafter rinsed with de-ionized water. The containers were then heated at 400^oC for about 30 minutes until dryness. Using a quadrant technique, composite samples were collected from each sample station at 0 – 30cm using a soil auger. Sample extraction and fractionation were done as recommended by OIEWG, (1999).

Analysis: Final extracts after re-concentration using a rotary evaporator was packed in a 2 ml GC vials and analyzed with a Gas Chromatograph (GC), Hawlett-Packard 6890. GC column conditions: Column made up of 5% PMS (100/120 mesh) coated with 3% OV-17 paced in a 1.8 x 2 mm ID glass column with Helium carrier gas at 40 mL/min flow rate. Column temperature head at 100^oC for 4 min, then programmed at $8^oC/min$ to a final hold at 280^oC. H_2 and Air gas were used to light up the FID. Quantification of the PAHs was accomplished using a seven-point, external standard curve (APHA, 1998). The standard curves were linear, with correlation

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coefficients for the investigated PAHs ranging between 0.997 and 0.999. No internal standards were however, employed in the quantification using the GC: soil samples, having being dried with anhydrous Na_2SO_4 were extracted with a mixture of dichloromethane (DCM) and acetone, thereafter solvent-exchanged with hexane. Clean-up and fractionation was done using silica gel permeation chromatography.

RESULTS AND DISCUSSIONS

The PAHs levels and pattern of distribution in the study area from both top and bottom soil are presented in Table 1. Investigation reveals that all tested samples have been contaminated with these priority pollutants, with mean values ranging from 0.000207 ± 0.00026mg.kg^{-1} to 0.002123 ± 0.00303mg.kg^{-1}.

Similarly, the total PAHs values in each sample point ranged between 0.00082mg.kg^{-1} and 0.06298mg.kg^{-1}. Also, the total mean concentration level of these POPs in the study area show that D(0.03979mg.kg^{-1})

> C(0.01592 mg.kg^{-1}) > A(0.01155 mg.kg^{-1}) > B(0.00325 mg.kg^{-1}) > E(0.00191 mg.kg^{-1}). The observed high concentration level of these contaminants at sample points D and C could be attributed to the fact that storage and sales of petroleum products are done in open drums and tanks. While sample station A and B are modern fuel stations were storage and sales of petroleum products are done through underground tanks and pipes respectively. Analysis of results show that there is high concentration of HPAHs and high concentration of total PAHs in top soil than bottom soil as shown in figure 1 below. The distribution pattern between top and bottom soil could be related to environmental degradation (microbial and wood-rotting fungi) processes of PAHs in soils (Wilson and Jones, 1993; Sims and Overcash, 1983). Similarly, the computed Spearman's Rank Correlation Coefficient (SRCC) of sample points At/Ab (0.99), Bt/Bb (0.99), Ct/Cb (0.98), Dt/Db (0.96) and Et/Eb (0.98), show a high and positive correlation between contaminants from top and bottom soil in each sample point.

Table 1: Mean Concentration values of Polycyclic Aromatic Hydrocarbons (PAHs) from top and bottom soil in the study area (mg.kg^{-1} dry weight)

PNAs	Mw	Ring	At	Ab	Bt	Bb	Ct	Cb	Dt	Db	Et	Eb
Naphthalene (Nap)	128.2	2	0.00011	0.00003	0.00003	0.00002	0.00007	0.00002	0.00721	0.00075	0.00002	0.00002
Acenaphthylene (Acy)	152.2	3	0.00123	0.00004	0.00051	0.00008	0.00008	0.00026	0.00781	0.00089	0.00021	0.00002
Acenaphthene (Ace)	154.2	3	0.00325	0.00002	0.00004	0.00001	0.00009	0.00028	0.00067	0.0056	0.00007	0.00001
Fluoren (Flu)	166.2	3	0.00023	0.00201	0.00002	0.00002	0.00072	0.00083	0.00731	0.00071	0.00001	0.00001
Phenathrene (Phe)	178.2	3	0.00031	0.00001	0.00001	0.00004	0.00049	0.00072	0.00041	0.00004	0.00002	0.00002
Anthrecene (Ant)	178.2	3	0.00327	0.00091	0.00007	0.00001	0.00215	0.00145	0.00152	0.00046	0.00004	0.00003
Fluoranthene (Flt)	202.3	4	0.00021	0.00011	0.00004	0.00001	0.00027	0.00007	0.00047	0.00032	0.00081	0.00041
Pyrene (Pyr)	202.3	4	0.00212	0.00022	0.00186	0.00082	0.00087	0.00616	0.00487	0.00112	0.00007	0.00002
Chrysene (Chr)	228.3	4	0.00211	0.00001	0.00031	0.00002	0.00029	0.00003	0.00024	0.00639	0.00014	0.00001
Benzo (a) anthracene (B[a]A)	228.3	4	0.00014	0.00005	0.00004	0.00005	0.00073	0.00003	0.00456	0.00038	0.00002	0.00001
Benzo (a) pyren (B[a]P)	252.3	5	0.00121	0.00005	0.00007	0.00002	0.00007	0.00002	0.00324	0.00007	0.00045	0.00003
Benzo (b) fluoranthen (B[b]F)	252.3	5	0.00025	0.00021	0.00006	0.00003	0.00004	0.00002	0.00785	0.00088	0.00057	0.00001
Benzo (k) fluoranthene (B[k]F)	252.3	5	0.00137	0.00003	0.00009	0.00003	0.00082	0.00002	0.00521	0.00034	0.00008	0.00004
Benzo (ghi) perylen (B[ghi]P)	267.0	6	0.00078	0.00023	0.00066	0.00057	0.00891	0.00133	0.00628	0.00241	0.00005	0.00003
Indeno (123-cd) Pyren (I[123cd]P)	276.3	6	0.00012	0.00002	0.00027	0.00018	0.00029	0.00011	0.00081	0.0072	0.00041	0.00014
Dibenzo (a,h) anthracen (D[ah]A)	278.4	6	0.00242	0.00001	0.00049	0.00001	0.00456	0.00003	0.00452	0.00056	0.00003	0.00001
Total			**0.01913**	**0.00396**	**0.00457**	**0.00192**	**0.02045**	**0.01138**	**0.06298**	**0.01660**	**0.003**	**0.00082**

Where n = 2, t = top soil, b = bottom soil

A lot of molecular ratio of specific hydrocarbons have been used for the investigation of sources of PAHs in different environmental martrix (Soclo, *et.al*; 2002, Yunker, *et.al*; 2002; Lin, *et.al*; 2005, Emoyan, *et.al*; 2008, Azza, 2006 and Linzhong and Jing 2004). These ratios were calculated for this study in Table II. In this way, source analysis were achieved with results showing petroleum origin as the chief source of PAHs contamination in all samples except in the control point (E) that is characterized with pyrogenic and petrogenic PAHs.

The ease of volatilization and leaching of LPAHs due to high vapour pressure and Henry's law constant of these contaminant could account for the low concentration level of LPAHs over HPAHs except at sample point A as shown in Table III. Similarly, their solubility in aqueous environment could have reduced their concentration in the study area.

Conversely, sorption and "aging" (Hatzinger and Alexander 1995; Loehr and Webster, 1996; Weissenfels, *et.al*., 1992 and Allard, *et.al*., 2000)

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could account for the high concentration level of HPAHs in the study area.

The total mean PAHs level of 0.014481mg.kg^{-1} of the study area is higher than 0.00522mg.kg^{-1} of other study in the Niger Delta (Emoyan, *et.al.*, 2008).

The observed high concentration of these priority pollutants in the study area could cause the contamination of groundwater as a result of leaching through soil, especially when mobile organic solvent accompany PAHs or when channel are present in the soil (Bedient, *et.al.*, 1984; Sloof, *et.al.*, 1989).

Table 2: Selected Ratios of PAHs Isomers Pairs for soil at the study area (mg.kg^{-1})

Ratio	Sample station					Source identification	
	A	B	C	D	E	Crude oil, petrol, diesel and vehicle emission	Wood, soot, bush burning cool and wood
Ant/178 (*Gaga, 2004*)	11^{-5}	22^{-7}	10^{-5}	55^{-6}	19^{-7}	<0.1	>0.1
Flt/flt+pyr (*Gaga, 2004*)	0.12	0.02	0.04	0.12	0.92	<0.5	>0.5
B[a]A/228 (*Gaga, 2004*)	14^{-6}	19^{-7}	16^{-6}	11-5	65^{-8}	<0.35	>0.35
1[123[d]p/11+B[ghi]p (*Azza, 2006*)	0.12	0.27	0.04	0.15	0.88	<0.2	>0.5
Flu/pyr (*Azza, 2006*)	095	0.05	0.22	1.00	0.20	<1.0	>1.0
Phe/Ant (*Lizhong and Jing,* 2004)	0.08	0.75	0.33	0.23	0.5	<10	>10
LPAHs/HPAHs (*Soclo, et. al., 2000*)	1.22	0.16	0.29	0.55	0.15	>1.0	<1.0

Conclusion: Comparison of data generated from the sample station reveals that there is high concentration of PAHs in top soil than in bottom soil. Also, fuel stations were storage and sales of petroleum products are done in open tanks and drums contribute more to the contamination of the study area with these organic pollutants. The Department of petroleum resources (DPR) should as a matter of concern lease with environmental research institutes in other to ascertain the concentration and effect of these POPs in the environment so as to determine appropriate sites to locate fuel stations. Secondly, DPR should disband all fuel stations carrying out storage and sales of petroleum products in surface tanks and drums respectively. Since this operation release higher level of PAHs onto the environment.

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