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DISTRIBUTION AND SOURCE APPORTIONMENT OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN DIFFERENT ENVIRONMENTAL MATRIX

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ABSTRACT

The levels, distribution and in relation to their sources, sixteen polycyclic aromatic hydrocarbons (PAHs) were investigated in surface water and soil samples around the Kokori oil Field, Nigeria, using gas chromatograph (GC). Hawlett Packard 6890. It was observed that all tested samples have been contaminated with PAHs with different levels ranging from 0-1.0468mgL^{-1} with total mean value of 9.491mgL^{-1} for water sample, while soil samples mean values ranged between 0 and 0.001145mg/kg with total mean concentration of 0.006mg/kg. The percentage distribution of low PAHs/high PAHs and ratio analysis show that their sources are petrogenic and pyrogenic but dominated with petrogenic PAHs. The Spearman's rank correlation coefficient (0.99) between the water and soil sample for the contaminants studied is high and positive.

INTRODUCTION

Polycyclic Aromatic hydrocarbon (PAHs) are group of persistent organic pollutants (POPs) which have two or more fused benzonoid rings and no element other than carbon and hydrogen (Henner *et al.,* 1997). According to CCME (2008), PAHs composition in contaminated environmental samples is useful in delineating between different anthropogenic source especially in urbanized, industrialized areas. Sources of unsubstituted PAHs are grouped as – kinetically - favoured: those preferentially produced through combustion processes (ie., pyrogenic PAHs); thermodynamically-favoured: PAHs which are energetically stable over long period of time and tending to dominate in more mature environmental/geological compartments such as crude oil or coal deposites (i.e, Petrogenic PAHs); and PAHs derived directly from plant products and synthesized at least in part, through biologically mediated processes. Soclo *et al*. (2000) stated that petrogenic contamination of various environmental matrix is characterized with the dominance of low molecular weight PAHs (LPAHs), while pyrogenic contamination is dominated with high molecular weight PAHs (HPAHs).

Sixteen PAHs have been listed as priority pollutants by US-EPA (Watts, 1997), these priority pollutants have received considerable local and global attention through ecological and ecotoxicological research (US-DHHS, 1995; Berko, 2002; Wcislo, 1998; Okoro, 2005; FSA, 2002; Azza, 2005; CCME, 2008) because of their genotoxic, carcinogenic and/or mutagenic properties (Marr et al., 1999). The extent of accumulation in soil, and toxicity of PAHs in organism is affected by environmental factors such as organic matter, 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 (Macias-Zamora *et al.,* 2002). They may be eliminated or transformed to even more alkylated or substitute toxic compound through biotic or abiotic processes such as sulfonation, nitration or photo-oxidation (Gaga, 2004).

Source identification, levels and distribution of PAHs in different environmental compartments is of great importance for the effective control of PAHs pollution. Therefore, this study is geared towards source identification and distribution of PAHs in surface waters and soil in the study area.

MATERIALS AND METHODS

Study Area

The study area falls within the Kokori oil-Field and is located between latitude 6° 02' to 6° 05'N and longitude 5° 36' – 5° 42'E. The oil wells have been in operations for over 30 years Emoyan *et al* (2008). The study area covers an approximate area of $2km^2$ with access road made of asphalt connecting various oil well heads. Well 13, 34, and 35 are in a fenced land measuring about 200 sq feet, well 14 36 and 37 in a fenced land measuring 200sq feet. Anthropogenic activities in the area include: oil/gas extraction (with oil well-heads and flow station), and peasant agriculture. 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°C to 33°C while the average monthly temperature for the coolest months (June – September) ranged between 21°C and 23°C.

Sampling: Soil samples were collected in the month of June, July, August and September 2007. All sample containers were thoroughly washed with laboratory grade phosphate detergent and thereafter rinsed with deionized water. The containers were then heated at 400°C for about 30 minutes until dryness. Using a quadrant technique, composite samples were collected from each sample station at 0 – 15cm using a soil auger. Samples were transferred from sample station in container with ice chest and stored £4°C for 7 days before extraction. Sample extraction and fractionation were done as recommended by OIEWG, (1999).

Water Samples: Composite water samples were collected in the month of June, July, August and September 2007. Water sample were collected in a litre amber glass bottle with Teflon-lined screw cap that had previously been washed with chromic acid and rinsed thoroughly with deionized water, 5ml of 1:1 HCl acid was added and cooled to about 4°C before analysis (APHA, 1998).

Analysis

The water samples for PAHs analysis were extracted with methylene chloride, dried with anhydrous Na_2SO_4 and solvent-exchanged into hexane. Clean-up and fractionation was done using silica gel permeation chromatography. 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 held at 100°C for 4 min, then programmed at 8°C/min to a final hold at 280°C. 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 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. Final extracts were similarly analyzed using the same described GC and same conditions.

RESULTS AND DISCUSSION

The results in Table I and II show that all tested samples have been contaminated with PAHs with different levels ranging from 0 – $1.0468mgL^{-1}$ with a total mean value of $9.491mgL^{-1}$ for water samples. While soil samples mean values ranged between 0 and 0.001145mg/kg with a total mean concentration of 0.006mg/kg. Similarly, Flu recorded the maximum mean concentration of $1.0468mgL^{-1}$ while B[a]P recorded the lowest mean concentration of $0.2309mgL^{-1}$ for water samples. Also, Nap recorded the maximum mean concentration of 0.001145mg/lg while B

[a]P recorded the lowest mean concentration of 0.00000517mg/kg for soil samples. It is possible that B[a]P undergo environmental degradation than other PAHs, hence the low level recorded in both matrix.

Table I: Mean Concentration of PAHs (mgl^{-1}) for water samples in the study area

S/N	PNAs	Mw	Ring	Range	X/S	P. Value
1	Naphthalene (Nap)	128.2	2	0-1.42	0.8634±0.5172	>0.05
2	Acenaphthylene (Acy)	152.2	3	0.215-1.215	0.9011±0.4145	>0.05
3	Acenaphthene (Ace)	154.2	3	0-1.186	0.7428±0.4979	>0.05
4	Fluoren (Flu)	166.2	3	0-1.525	1.0468±0.4673	>0.05
5	Phenathrene (Phe)	178.2	3	0-1.213	0.8714±0.5057	>0.05
6	Anthrecene (Ant)	178.2	3	0-1.561	0.8421±0.5824	>0.05
7	Fluoranthene (Fla)	202.3	4	0-1.152	0.6594±0.5245	>0.05
8	Pyrene (Pyr)	202.3	4	0-1.253	0.4918±0.5570	>0.05
9	Chrysene (Chr)	228.3	4	0.017-1.212	0.4745±0.5260	>0.05
10	Benzo (a) anthracene (B[a]A)	228.3	4	0.015-1.514	0.4950±0.6020	>0.05
11	Benzo (a) pyren (B[a]P)	252.3	5	0.11-1.121	0.2309±0.3732	>0.05
12	Benzo (b) fluoranthen (B[b]F)	252.3	5	0-1.451	0.3938±0.5639	>0.05
13	Benzo (k) fluoranthene (B[k]F)	252.3	5	0-1.251	0.2956±0.4377	>0.05
14	Benzo (ghi) perylen (B[ghi]P)	267.0	6	0-1.512	0.3753±0.5107	>0.05
15	Indeno (123-c) Pyren (I[123-cd]P)	276.3	6	0-1.612	0.5411±0.6814	>0.05
16	Dibenzo (a,h) anthracen (D[ah]A)	278.4	6	0-1.515	0.2660±0.5106	>0.05

Table 2: Mean Concentration of PAHs (Mg/kg) for soil samples in the study area

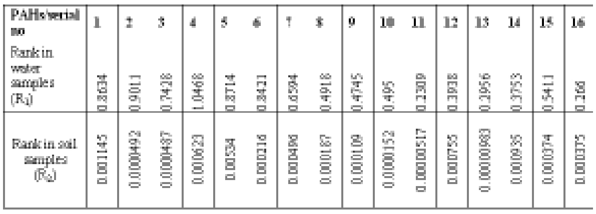
S/N	PNAs	Mw	Ring	Range	X/S	P. Value
1	Naphthalene (Nap)	128.2	2	0-0.00685	0.001145±0.002795	>0.05
2	Acenaphthylene (Acy)	152.2	3	0-0.0014	0.0000492±0000604	>0.05
3	Acenaphthene (Ace)	154.2	3	0-0.000141	0.0000487±0.0000518	>0.05
4	Fluoren (Flu)	166.2	3	0-0.000224	0.000623±0.0000849	>0.05
5	Phenathrene (Phe)	178.2	3	0-0.000296	0.000534±0.000119	>0.05
6	Anthrecene (Ant)	178.2	3	0-0.00113	0.000216±0.000451	>0.05
7	Fluoranthene (Fla)	202.3	4	0.0000108-0.00222	0.000496±0.000859	>0.05
8	Pyrene (Pyr)	202.3	4	0-0.000515	0.000187±0.00257	>0.05
9	Chrysene (Chr)	228.3	4	0-0.000633	0.000109±0.0000257	>0.05
10	Benzo (a) anthracene (B[a]A)	228.3	4	0-0.000046	0.0000152±0.0000235	>0.05
11	Benzo (a) pyren (B[a]P)	252.3	5	0-0.000031	0.00000517±0.0000127	>0.05
12	Benzo (b) fluoranthen (B[b]F)	252.3	5	0-0.00259	0.000755±0.001188	>0.05
13	Benzo (k) fluoranthene (B[k]F)	252.3	5	0-0.000059	0.00000983±0.0000241	>0.05
14	Benzo (ghi) perylen (B[ghi]P)	267.0	6	0-0.00365	0.000935±0.001544	>0.05
15	Indeno (123-c) Pyren (I[123cd]P)	276.3	6	0-0.001145	0.000374±0.000465	>0.05
16	Dibenzo (a,h) anthracen (D[ah]A)	278.4	6	0-0.001145	0.000375±0.000467	>0.05

Investigation into sources of PAHs have used the molecular ratio of some specific hydrocarbons (Soclo *et al.,* 2002; Yunker *et al.,* 2000; Lin *et al.,* 2005, Emoyan *et al.,* 2008) from the calculated molecular ratio of Ant/178, 0.005; Fla/Fla+Pyr, 0.006; Flu/Pyr, 2.13; Phe/Ant, 1.03 and Chr/B[a]A, 0.96 for water samples, and Ant/178, $2x10^{-6}$; Fla/Fla+Pyr, 0.73; Flu/Pyr, 3.33; Phe/Ant, 2.47 and Chr/B[a]A, 7.17 for soil samples reveal that the levels and distribution of these priority pollutants in the environmental matrix are characterized by pyrogenic and petrogenic sources. However, results show that LPAHs (PAHs with 2 and 3 ring) recorded 44.5% in the water samples. Similarly, LPAHs and HPAHs in the soil samples accounted for 50% and 50% respectively, this show that the sources of these POPs in the studied compartments are of petrogenic dominance. The high percentage of HPAHs in the soil samples could be attributed to fractions from bush burning and other anthropogenic activities.

The percentage distribution of Genotoxic (Gen)/Carcinogenic (Car) PAHs (Chr, B[a]A, B[a]P, B[k]F, B[ghi]P, 1[123-cd] P and D[ah]A and other PAHs (Nap, Acy, Ace, Flu, Phe, Ant, Fla and Pyr (WHO/IPCS, 1998) in the study area accounted for 32.4% and 67.6% respectively in the water sample while 33.3% and 66.7% was recorded for Gen/ Car and other PAHs in the soil samples. The results for both environmental compartments studied show that there is high concentration of other PAHs in the study area.

The high concentration distribution of LPAHs in the water samples as shown in Table I and II reveal that LPAHs are water soluble with low affinity for particulate adsorption, similarly the high percentage concentration of Gen/Car PAHs observed in the soil sample could be attributed to their affinity for particulate adsorption (Mackey *et al.,* 1992 and CCME 2008). Also, analysis of results show that the large differences between the total mean concentration in soil (0.006mg/kg) and water samples (9.49mgL^{-1}) could be attributed to degradation processes by microbial and wood-rotting fungi, volatilization and leaching of LPAHs in soil (Staffan, 2003). However, the computed Rank correlation coefficient of 0.99 in Table III show that there is a high, positive rank correlation between the mean concentration of the 16 PAHs analyzed in water and soil samples.

Table 3: Spearman's Rank Correlation coefficient Between Water and Soil Samples for 16 PAHs Analyzed



PAHs/serial no	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Rank in water samples (R_1)	0.8634	0.9011	0.7428	1.0468	0.8714	0.8421	0.6594	0.4918	0.4745	0.495	0.2309	0.3938	0.2956	0.3753	0.5411	0.266
Rank in soil samples (R_2)	0.001145	0.0000492	0.0000487	0.000623	0.00534	0.000216	0.000496	0.000187	0.000109	0.0000152	0.00000517	0.000755	0.00000983	0.000935	0.000374	0.000375

The observed mean concentration of PAHs in soil samples could be strongly sorbed to organic matter and undergo "aging" making them relatively unavailable for degradation processes. These processes of sorption and 'aging' though limit the degradability of these contaminants, but at the same time reduces the toxicity of the soil PAHs by lowing the fraction available for uptake by living organisms

(Weissenfels *et al.,* 1992; Alexander, 1995), thereby posing a long-term environmental threat to living organisms.

Conclusion

Comparison of data generated from the analysis of sixteen PAHs listed as priority pollutant from water and soil samples show that the study area is contaminated with these POPs. Analysis of results also reveal that the sources of these contaminants is pyrogenic and petrogenic but however dominated with petrogenic PAHs. The rank correlation coefficient is also high and position between water and soil sample for the contaminants analyzed.

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