

POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) AND POLYCHLORINATED BIPHENYLS (PCBs) IN SOILS OF AGBABU, NIGERIA

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Abstract:

Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were investigated in soils of Agbabu, Nigeria. PAHs in the samples were quantified using gas chromatograph - mass spectrometer, while gas chromatograph - flame ionization detector was used for PCBs analysis. The maximum sum of concentrations of PAHs (Σ PAH) was 0.07 ± 0.036 ppm in the dry season, and 0.69 ± 0.19 ppm in the rainy season. Apart from three stations in both seasons where PAHs were not detected, other Σ PAH concentrations obtained were higher than $1-10 \mu\text{g}/\text{kg}$, indicating anthropogenic sources. Most of the PAH concentrations obtained were within the expected limits for a rural environment. However, in the rainy season, 0.20 ± 0.04 ppm for Benzo(b)fluoranthene, 0.21 ± 0.05 ppm for Benzo (g, h, i) perylene and 0.32 ± 0.04 ppm for Indenol (1, 2, 3 - cd) pyrene exceeded the expected limit. In the dry season, there was no significant relationship ($r^2 = 0.002$) between mean concentrations and percentage soil organic carbon while there was significant correlation ($r^2 = 0.57$) in this relationship in the rainy season. The predominance of 4 - 6 ring PAHs and the ratios between pairs of individual PAHs showed that the PAHs were from pyrolytic sources. No PCB congener was detected in the samples investigated.

Key Words: Agbabu Nigeria, Polycyclic aromatic hydrocarbons, Polychlorinated biphenyls, soils

Introduction

Bitumen was discovered at Agbabu, Nigeria over a hundred years ago, preceding the discovery of oil by over 50 years. The probable reserve of bitumen and heavy oil in the entire Nigerian belt is about $120 \times 4.3\text{km}$ (Adegoke and Ibe, 1982; Oboh et al., 2006).

Agbabu is a village of about 8, 611 inhabitants in Ondo State, south-west, Nigeria; in the coordinates of $E004^{\circ}48-49^{\circ}$ and $N06^{\circ}34-36^{\circ}$ (Figure 1). Farmers at Agbabu area deal mainly in cash crops such as cocoa and kolanut; and food crops such as yam and plantain. In Nigeria, there are two seasons: rain (April to September) and dry (October to March).

Polycyclic aromatic hydrocarbons (PAHs) contain complex chemicals which include carbon and hydrogen with a fused ring structure, containing at least two benzene rings (Sexton et al., 2011). PAHs have been documented to cause several health problems (Hati et al., 2009). Some PAHs and their derivations are highly toxic. Their mutagenic or carcinogenic properties are the main risk to human health (Prycek et al., 2007). Bitumen contains very small quantities of PAHs at 4 – 6 condensed rings which are not bioavailable. The effects of PAHs on human health depend on the concentration, type and extent of exposure.

PCBs belong to a class of organic compounds having a basic chemical structure, which include two benzene (biphenyl) molecules and between 1 and 10 chlorine atoms substituted on each of the benzene molecules (ATSDR, 2001). There are 209 congeners of PCBs; there are no known natural sources of PCBs. The major sources of PCBs in Nigeria include importation of electrical transformer oils and other anthropogenic activities such as agriculture, discharge of industrial wastes into rivers and incineration (Adeyemi et al., 2009). Studies on both human and laboratory manuals provide strong evidence of the toxic potential of exposure to PCBs (Zaborski et al., 2011). The health effects include liver, thyroid, dermal and ocular changes, reduced birth weight, reproductive toxicity and cancer (Adeyemi et al., 2009).

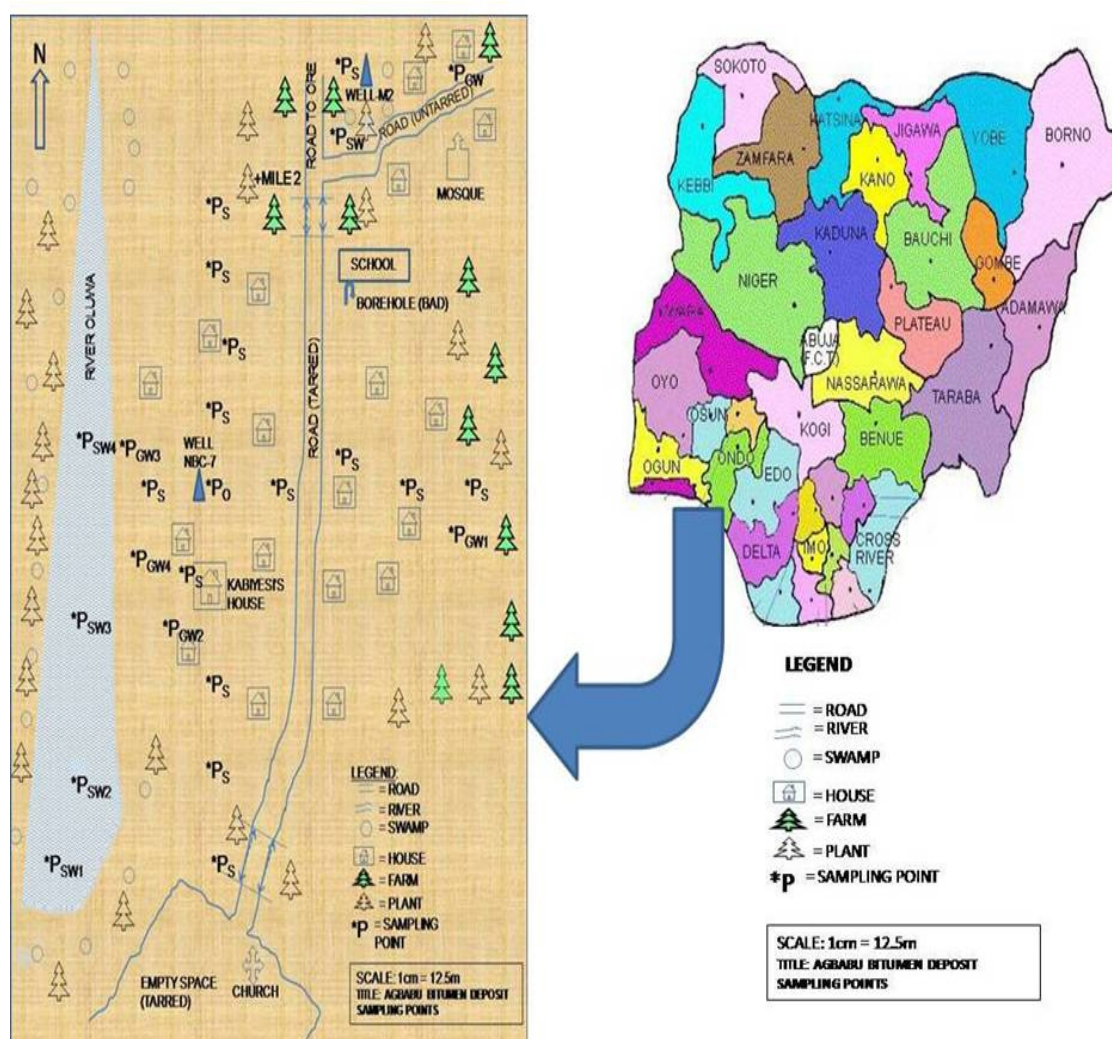


Figure 1: Map of Nigeria showing Agbabu sampling points

Distribution of PAHs in water and soil samples from the vicinity of Agbabu bitumen field has been studied using GC-FID (Abass et al., 2007). n-Alkanes distribution in soil and water samples collected near Agbabu bitumen field of south-western, Nigeria has been reported by Olajire et al. (2008). Evaluation of the status of heavy metals pollution of sediments of Agbabu bitumen deposit area, Nigeria has been investigated (Fagbote and Olanipekun, 2010a). Levels of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in sediments of bitumen deposit impacted area have also been reported by Fagbote and Olanipekun (2010b). Agbabu bitumen deposit area is presently characterized with seepages. The impact of bitumen seepages on the Nigerian physical environment may be enormous (Adewole, 2010). Seasonal and depth effects on physico-chemical parameters of the soils of farm settlements with bitumen deposit have been studied and it was observed that sources of the parameters varied from one location to another, except for Mn^{2+} which had a common source which was bitumen (Fagbote and Olanipekun, 2011).

The aim of the present study was to determine the levels of PAHs and PCBs in soils of the Agbabu bitumen field using GC-MS and GC-FID, respectively. Whenever commercial exploitation of the bitumen commences, it is expected that enormous quantities of both PAHs and PCBs will be introduced into the environment through anthropogenic activities. Knowledge of the pre-exploitation status of pollution in the area will thus provide baseline data which are essential in monitoring the extent of contamination by toxic substances.

Experimental

Collection of Samples

Samples were collected from five different points in Agbabu, Nigeria during the dry (March) and rainy (August) seasons. The sampling points were geo-located with GPS to ensure consistency. Composite soil samples were wrapped with aluminium foil, kept in dry ice and stored at -20°C.

Extraction

The samples were dried in an oven at 105°C, ground, sieved with 1mm sieve and extracted with dichloromethane using a Soxhlet extractor. The extracts were concentrated using Kuderna Danish (K-D) concentrator. The extracts were analyzed for PAHs and PCBs.

Methods of Analysis

A. PAHs in the extracts were quantified using Agilent 6890N gas chromatograph coupled with mass spectrometer (Lemoine and Hoberecht, 2000).

Extract peaks generated that were above scale were diluted with methylene chloride and re-analyzed.

Detection limits are <0.01ppm for Benzo(k)fluoranthene, <0.03ppm for Benzo(g,h,i)perylene and <0.02ppm for Naphthalene, 2-Methylnaphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benzo(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, Indeno(1,2,3-d)pyrene.

GC oven program for PAHs is as follows:

Column type – 30meters x 0.25mm ID x 0.25µm film thickness silicone-coated fused-silica capillary column (DB-5 or HP-5).

Oven - On

Set point - 65°C

Initial Temp - 65 °C hold for 1 minute
65°C to 140 °C @ 15 °C/minute for 4 minutes

Final Temp - 140 °C to 290 °C @ 10 °C/minute hold for 10 minutes

To validate the procedure the following quality controls were observed:

- A solvent blank was run every day prior to analysis. After every 20 samples, a sample was run as duplicate.
- The Relative Percent Difference (RPD%) was determined as follows:

$$\%RPD = [2(D1 - D2)/(D1 + D2)] \times 100$$

where D1 = Concentration of the analyte in the first duplicate sample

D2 = Concentration of the analyte in the second duplicate sample

- A mid-point calibration was run after every 20 samples. For each sample analyzed, the percentage recovery of each surrogate was calculated
- When recovery was not within 80 – 120%, it was checked to be sure that there were no errors in the calculation, otherwise the sample was re-extracted and re-analyzed.

B. PCBs in samples were analyzed using GC 610 connected to FID (Clescery et al., 1989).

Extract peaks generated that were above scale were diluted with dichloromethane and re-analyzed.

Detection limit for PCBs is <0.01 ppm.

GC oven program for PCB is as follows:

Column type – 30meters x 0.25mm ID x 0.25µm film thickness silicone-coated fused-silica capillary column (DB-5 or HP-5)

Oven - On

Set point - 125°C

Initial Temp - 125 °C hold for 3 minutes

Final Temp - 125 °C to 270 °C @ 12 °C/minute and held for 2 minutes

The procedure was validated as in (A) above.

C. Organic carbon in the samples was determined by the wet combustion method

(Schumacher, 2002)

Results and Discussion

Tables 1 and 2 show the sum of concentrations of PAHs in the soil samples in the dry and rainy seasons, respectively. In both seasons, the sum of concentrations of PAHs was highest at AGMILE2 (0.07 ± 0.036 ppm for dry) and (0.69 ± 0.19 ppm for rainy); no PAHs were detected at T2E in the dry season, and T1S and T2N in the rainy season.

Generally, sum of concentrations of PAHs in soil samples analysed were higher in the rainy season than in the dry season; this observation is in agreement with what was reported by Teaf (2008). Some of the Σ PAH concentrations determined were within the limit of values expected for a rural environment as given in Table 4. However, sum of concentrations of PAHs obtained in the rainy season: 0.20 ± 0.04 ppm for Benzo(b)flouranthene, 0.23 ± 0.06 for Benzo(k)flouranthene, 0.21 ± 0.05 ppm for Benzo(g, h, i)perylene, and 0.32 ± 0.04 ppm for Indenol (1, 2, 3 - cd) pyrene; exceeded the recommended limits. Σ PAH concentrations in the soil samples ranged between 0.02 ± 0.015 ppm and 0.07 ± 0.036 ppm in the dry season, and 0.22 ± 0.053 ppm and 0.69 ± 0.019 ppm in the rainy season. These values are higher than Σ PAH concentrations of 1 - 10 μ g/kg, indicating that the PAHs were likely to come from anthropogenic sources (Olajire and Brack, 2005).

A significant factor that controls the concentration of PAHs in soil is total organic carbon (Opune et al., 2007). The organic carbon of soils determines the sorption of organic molecules. The linear regression analyses between the mean concentrations and percentage soil organic carbons are shown in Figures 2 and 3 for dry and rainy seasons, respectively; while the correlation coefficients for Figures 2 and 3 are given in Tables 5 and 6, respectively. The linear regression analysis showed no significant correlation ($r^2=0.002$) between mean concentrations and percentage soil organic carbon in the dry season samples. This suggests that the sites were contaminated to different levels probably due to easy degradation of PAHs. However, there was a significant correlation ($r^2=0.57$) between mean concentrations and percentage soil organic carbon in the rainy season samples. This implies that during the rainy season, degradation of PAHs was apparently slowed down and there was a significant influence of percentage organic carbon on the distribution of PAHs in the soil samples.

Table 1: Sum of concentrations and ratios of PAHs in soil (Dry season)

S/No	Name		T0 (SOIL) ppm	T2E (SOIL) ppm	T1S (SOIL) ppm	T2N (SOIL) ppm	AGMILE2 (SOIL) ppm
1	Benzo(b)flouranthene (BbF)	5 rings	0.02 \pm 0.01	ND	ND	ND	0.02 \pm 0.006
2	Benzo(k)flouranthene (BkF)		0.02 \pm 0.005	ND	ND	ND	0.02 \pm 0.01
3	Benzo(a)pyrene (PaP)		ND	ND	0.02 \pm 0.008	0.03 \pm 0.01	0.03 \pm 0.02
	Sum		0.04 \pm 0.015	0	0.02 \pm 0.008	0.03 \pm 0.01	0.07 \pm 0.036
	SumPAHs		0.02 \pm0.015	ND	0.02 \pm0.008	0.03 \pm0.01	0.07 \pm0.036
	% Org. Carbon		1.2 \pm 0.01	2.28 \pm 0.02	2.27 \pm 0.07	2.21 \pm 0.07	2.03 \pm 0.02
	RATIOS OF PAHs						
	BbF/BkF		1.00	ND	ND	ND	1.00
	BkF/BaP		ND	ND	ND	ND	0.67
	BbF/BaP		ND	ND	ND	ND	0.67

ND = Not Detectable

Table 2: Sum of concentrations and ratios of PAHs in soil (Rainy season)

S/No	Name		T0 (SOIL) ppm	T2E (SOIL) ppm	T1S (SOIL) ppm	T2N (SOIL) ppm	AGMILE2 (SOIL) ppm
1	Naphthalene (NAPH)	2-3 rings	0.01 \pm 0.003	ND	ND	ND	0.02 \pm 0.01
2	Acenaphthylene		ND	0.04 \pm 0.02	ND	ND	ND
3	Anthracene (ANT)		ND	ND	ND	ND	0.06 \pm 0.02
4	Phenanthrene (PHEN)		ND	ND	ND	ND	0.07 \pm 0.03
	Sum		0.01 \pm 0.003	0.04 \pm 0.02	0	0	0.15 \pm 0.06
5	Benzo(b)flouranthene	5	ND	ND	ND	ND	0.2 \pm 0.04

	(BbF)	rings								
6	Benzo(k)flouranthene (BkF)		ND		ND		ND		ND	0.23 ±0.06
7	Benzo(a)pyrene (PaP)		ND		ND		ND		ND	0.11 ±0.03
8	Benzo(g,h,i)perylene (BPE)		0.21 ±0.05		ND		ND		ND	ND
		Sum	0.21 ±0.05		0		0		0	0.54 ±0.13
9	Indeno (1,2,3-cd)pyrene (INPY)	6 rings	ND		0.32 ±0.04		ND		ND	ND
SumPAHs			0.22 ±0.05		0.36 ±0.06		ND		ND	0.69 ±0.19
% Org. Carbon			2.40 ±0.08		2.38 ±0.03		2.7 ±0.14		2.95 ±0.27	2.40 ±0.02
RATIOS OF PAHs										
NAPH/ANT					ND		ND		ND	0.33
NAPH/PHEN					ND		ND		ND	0.29
ANT/PHEN					ND		ND		ND	0.86
BbF/BkF					ND		ND		ND	0.87
BkF/BaP					ND		ND		ND	2.09
BbF/BaP					ND		ND		ND	1.82

ND = Not Detectable

Table 3: Ratios of PAHs from literature

PAHs	RATIO OF PAH	INFERENCE
PHEN/ANT	3	Motor vehicle exhaust
PHEN/ANT	>50	From mineral oil
FLT/PYR	1	Paralytic process
FLT/PYR	>1	Pathogenic process
BaP/PaP	1	Motor vehicle exhaust
BaP/PBE	0.2 – 05	Motor vehicle exhaust
BaP/PBE	>1	Coal combustion
IND/BPE	0.37	PAH arising from traffic exhaust
PYR/BaP	<1 to 50	Diesel fuel-powered truck exhaust
NAPH/PHEN	>1	Pathogenic sources
BbF/BkF	0.8-1.1	Wood combustion
	1.1-1.5	Gasoline exhaust
	2.5-2.9	Smelters
	3.5-3.9	Coal/coke

(Olajire and Brack, 2005).

Table 4: Background concentrations of PAHs in rural soils

PAH	Conc. (x10 ⁻³ mg/kg)
Acenaphthene	1.7
Acenaphthylene	NE
Anthracene	NE
Benzo(a)anthracene	5-20
Benzo(a)pyrene	2-1,300
Benzo(b)flouranthene	20-30
Benzo(e)perylene	NE
Benzo(g,h,i)perylene	10-70
Benzo(k)flouranthene	10-110
Chrysene	38.3
Flouranthene	0.3-40
Flourene	NE
Indeno(1,2,3-c,d) pyrene	10-15
Phenanthrene	30.0
Pyrene	1-19.7

NE = Not Established.

(Jones et al., 1987; Eviassogie et al., 2006).

Table 5: Correlation coefficient table for Figure 2 (PAH versus % Org carbon in soil – Dry season)

	T0 (Soil)	T2E	T1S	T2N	AGM2	total
Sum(PAHs) (x)	0.02	0	0	0.03	0.07	0.14
% Org. Carbon (y)	1.2	2.28	2.3	2.21	2.03	9.99
x ²	0.0004	0	0	9E-04	0.005	0.01
y ²	1.44	5.1984	5.2	4.884	4.121	20.8
Xy	0.024	0	0	0.066	0.142	0.28

-0.040556267 Corr. Coeff
0.001644811 R2

Table 6: Correlation coefficients for Figure 3 (PAH versus % Org carbon in soil – Rainy season)

	T0 (Soil)	T2E	T1S	T2N	AGM2	Total
Sum(PAHs) (x)	0.22	0.36	0	0	0.67	1.25
% Org. Carbon (y)	2.4	2.38	2.7	2.95	2.4	12.83
x ²	0.0484	0.1296	0	0	0.449	0.627
y ²	5.76	5.6644	7.29	8.703	5.76	33.18
Xy	0.528	0.8568	0	0	1.608	2.993

-0.758086081 Corr. Coeff
0.574694506 R2

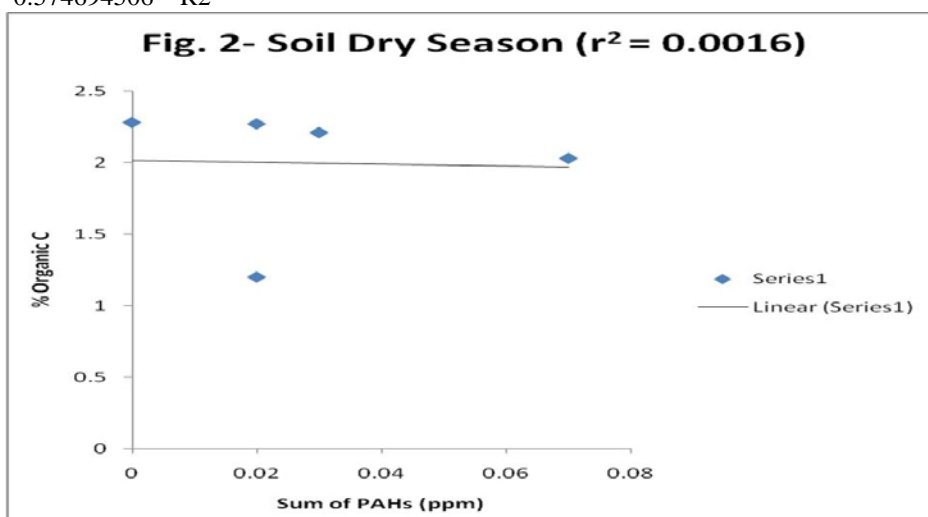


Figure 2: Mean concentration versus percentage organic carbon (Dry season)

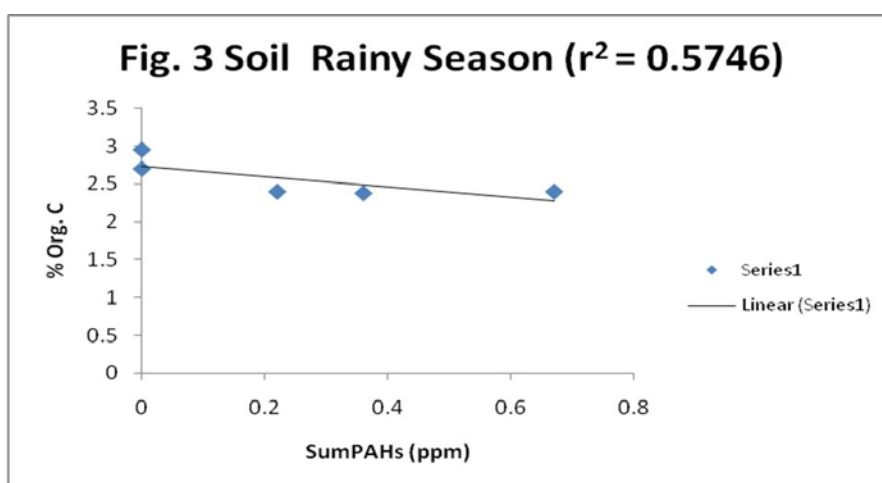


Figure 3: Mean concentration versus percentage organic carbon (Rainy season)

Sources of PAHs and PCBs

AGMILE2 (Station 5) was the most polluted with PAHs, probably because of its proximity to the road. PAHs in bitumen are not available when they are in the pure form, but when in contact with some solvents, they become mobile and can contaminate the environment. In the rainy season, naphthalene (0.02 ± 0.01 ppm), anthracene (0.06 ± 0.02 ppm) and phenanthrene (0.07 ± 0.03 ppm) were detected at AGMILE2. These PAHs with 2-3 rings were probably coming from petrogenic sources. PAHs of 2 – 3 rings were not detectable at this sampling point in the dry season, but those with 4-6 rings were determined in both seasons at this location, which showed that this group of PAHs was more predominant. On the whole, the most predominant PAHs in the Agbabu soils were those with 4-6 rings (Tables 1 and 2), indicating that they were probably formed by pyrolysis (Olajire and Brack, 2005). Several PAHs containing 4-6 aromatic rings in their structure are known to be mutagenic, carcinogenic and inducers of tumours in mammals (Nagpal, 1994).

The most significant sources of PAHs in an environment can be identified from the ratios between pairs of concentrations of individual PAHs, and the literature values, presented in Table 3, were used to characterize the PAHs in this study. The ratios of the concentrations of PAHs calculated from Tables 1 and 2 for BENZO(b) FLOURANTHENE/BENZO (k) FLOURANTHENE (BbF/BkF) were 1.0 at T0 and AGMILE2 in the dry season, and 0.87 for AGMILE2 in the rainy season. These values suggest that the PAHs were apparently from wood combustion sources. The ratio of PHENANTRENE/ANTHRACENE (PHEN/ANT) was 0.86 at AGMILE2 in the rainy season, suggesting that the PAHs were probably not from motor vehicle exhaust and mineral oil; the ratio of NAPHTHALENE/PHENANTRENE (NAPH/PHEN) was 0.29 at AGMILE2, which is indicative that the PAHs were apparently not derived from pathogenic sources. Sum of PAH concentrations above $1-10 \mu\text{g}/\text{kg}$ show that the PAHs may likely come from anthropogenic sources and not from plant synthesis and natural fires (Edward, 1987).

Conclusion

The concentrations of most of the PAHs in the soils at the study area were lower than the recommended limits and the PAHs were probably from anthropogenic sources, including pyrolysis. Higher concentrations were obtained in the rainy season, apparently due to dilution and lower rates of degradation of the PAHs. The predominance of PAHs containing 4 – 6 rings in the investigated samples suggests that they could be mutagenic and carcinogenic.

As at the time of this study, PCBs were not detectable in any of the soil samples investigated; but despite this, it was still necessary to know the pre-exploitation status of PCBs in the area. Finally, monitoring of the levels toxic substances in Agbabu and its vicinity should be conducted periodically.

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