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Determination of Pahs in Smoke Generated from Different Woods: A Search for Greener Wood Fuel

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Abstract:
Most polycyclic aromatic hydrocarbons (PAHs) are carcinogenic to animals and humans and most of them are produced in the incomplete combustion of organic substances. However, smoke produced by some woods contain less PAHs than others. Different woods were used for this project in search of greener wood fuel. A simple, less expensive, easily constructed steam extraction of the PAHs was carried out. This was followed by liquid-liquid extraction and analysis by HPLC-FLD. The qualitative analysis was effected by comparing the retention times of PAHs in the standard mixture with those in the smoke samples and the results show that all the analytes under investigation were found in the samples except fluoranthrene and chrysene. Terminalia superb does not produce phenanthrene. The complete combustion of 1g of the soft wood samples (Ficuscapensis, Ceibapentadra, Garcinia kola, Anthocleistavegilii, Terminalia superb, Symphoniaglobuliferal) gave a concentration range of 4.31 – 3.10 µg of PAHs while the complete combustion of 1g of the hard wood samples (KlanedoxiaGabonensis, VapacaGuiniensis, MagiferaIndica, Alstoniaboonei, Alchorniacordifolia, Terminalia iverensis, Lophiraalata) gavea concentration range of 2.78 – 1.21 µg of PAHs. Statistical t-test on the data show that the levels of PAHs in the hard wood samples were significantly different from the levels in the soft wood samples; suggesting that hard woods are generally better wood fuels than soft ones in respect of environmental issues.

Keywords*: LC-FLD, PAHs, wood smoke, steam-extraction, liquid-liquid extraction*

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are included in the European Union and US Environmental Protection Agency priority pollutant lists because PAHs represent the largest group of compounds that are mutagenic, carcinogenic, and teratogenic (Sverdrup et al., 2002; Qiao et al., 2006; Adonis and Gill, 2000). Exposure to PAH occurs mainly by inhalation of air and by ingestion of food and drinking water (Barranco et al., 2003; Dissanayake and Galloway, 2004). Although food can be contaminated with PAHs from the environment (air, dust and soil), PAHs in food are mainly formed during industrial processing and food preparation, for example smoking, roasting, baking, drying, frying, or grilling (Adonis and Gill, 2000) .For this reason, their detection and monitoring has become an important problem and this has led to the development of new analytical methods with improved selectivity and sensitivity (Brouwer, 1994; Nirmaier et al., 1996; Kiss et al., 1996; Pino et al., 2002).

Most people living in the rural communities in the Niger Delta region (Nigeria) use wood fuel for cooking predominantly for economic reasons. Besides cooking at home, wood is also a source of fuel for bakeries, road-side roasting of fish, plantain, yam, etc. The aim of this work was to determine PAH concentrations in smoke generated from different woods in an attempt to search for greener wood fuel.

2. Materials and Methods

All reagents were analytical or HPLC grade. Acetonitrile, PAHs, toluene, and sodium sulphate were bought from Sigma-Aldrich (St Louis, MO, USA). The water used was from a milliQ system (Milford, Mass, USA). Mobile phase was filtered through a Whatman membrane filter (47 mm diameter and 2µm pore size. A G-1321A scanning fluorescence detector (all Agilent Technologies, Palo Alto, USA), Agilent Chemstation software for controlling LC and data analysis. Agilent 1200 series HPLC (Agilent Technologies, Santa Clara, CA, USA). Column: Agilent Pursuit PAH, 100 x 4.6 mm, 3µm.Soft wood samples (*Ficuscapensis, Ceibapentadra,*

Garcinia kola, Anthocleistavegilii, *Terminalia superb, Symphoniaglobuliferal*) and hard wood samples (*KlanedoxiaGabonensis, VapacaGuiniensis, MagiferaIndica, Alstoniaboonei, Alchorniacordifolia, Terminalia iverensis, Lophiraalata*).

2.1. Preparation of Standard Solutions of PAHs

Standard stock solutions (1 mg/mL) were prepared by dissolving 10 mg of the desired PAH in 10 mL acetonitrile and stored at 4^{o}C in the dark. All working solutions were prepared fresh daily by serial dilutions with acetonitrile.

2.2. Extraction and Pre-concentration

PAHs were steam-extracted from wood-smoke using the improvised laboratory set-up whose details were reported by Young and Inengite (2014). 1g of each wood sample was completely burnt and steam extraction of the PAHs from the smoke was carried out. The PAH-containing steam was cooled to PAH-containing liquid. The PAHs were extracted from the aqueous phase into an organic (toluene) phase. This sample was then pre-concentrated and stored for HPLC analysis of the PAHs.

2.3. HPLC Analysis

Analytical chromatography was performed with a mobile flow rate of 0.8 mL min^{-1} at 25°C. The injection volume was 20 µL. The column was stabilized at 25°C for 1 h before chromatography. The mobile phase was a gradient prepared from water (component A) and acetonitrile (component B). Details of the gradient are given in Table 1. Detector excitation and emission wavelengths were programmed as reported in Table 2.

Time (min)	% Water	% acetonitrile
0	60	40
7	0	100
15	0	100
20	60	40

Table 1: Mobile phase gradient for HPLC separation

Analyte (PAH)	Ex/Em wavelength (nm)
Naphthalen	270/385
Phenanthrene Fluoranthrene Pyrene	256/446
Chrysene Benzo[k]fluoranthene	274/507

Table 2: Wavelength changes for fluoresence detector

3. Results and Discussion

3.1. Qualitative Analysis

The HPLC analyses of the mixtures of PAH standards and the crude extracts of the wood samples were carried out and peak identification was effected by comparing retention times. The results are shown in Figures 1 – 14 for extracts generated respectively from *Ficuscapensis, Ceibapentadra, Garcinia kola, Anthocleistavegilii, Terminalia superb, Symphoniaglobuliferal, Klanedoxia Gabonensis, Vapaca Guiniensis, Macaranga Barteri, Magifera Indica, Alstoniaboonei, Alchorniacordifolia, Terminalia iverensis, Lophiraalata.* In all the figures, Chromatograms A, B, and C respectively represent PAH mixture, sample, and blank.

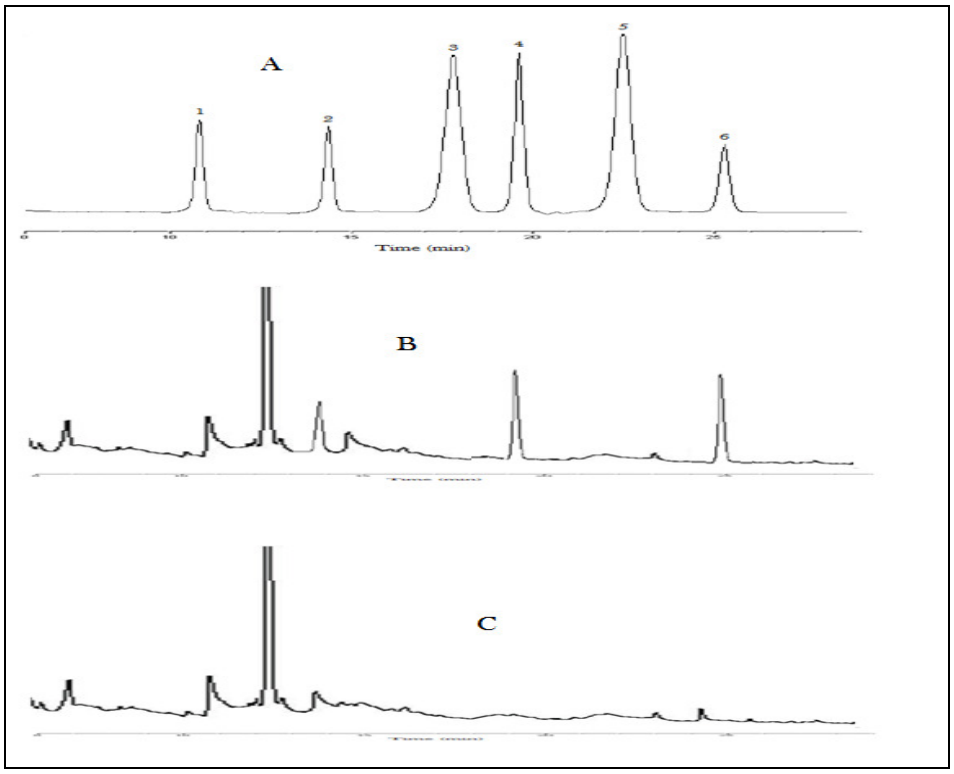

Figure 1: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Ficuscapensis wood sample. Chromatogram C: blank

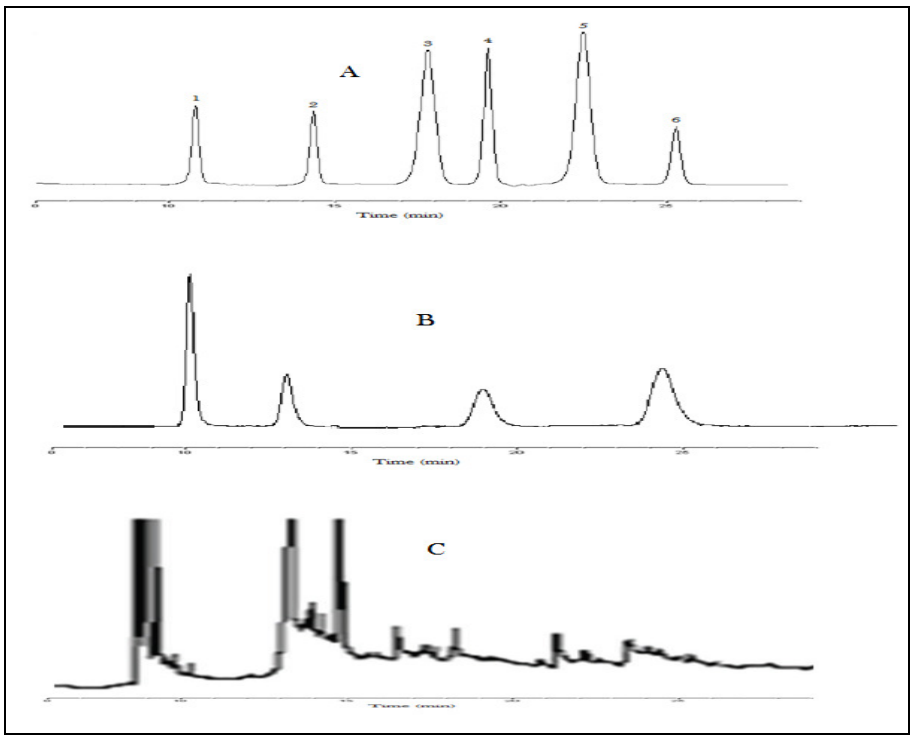

Figure 2: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Ceibapentadra wood sample. Chromatogram C: blank

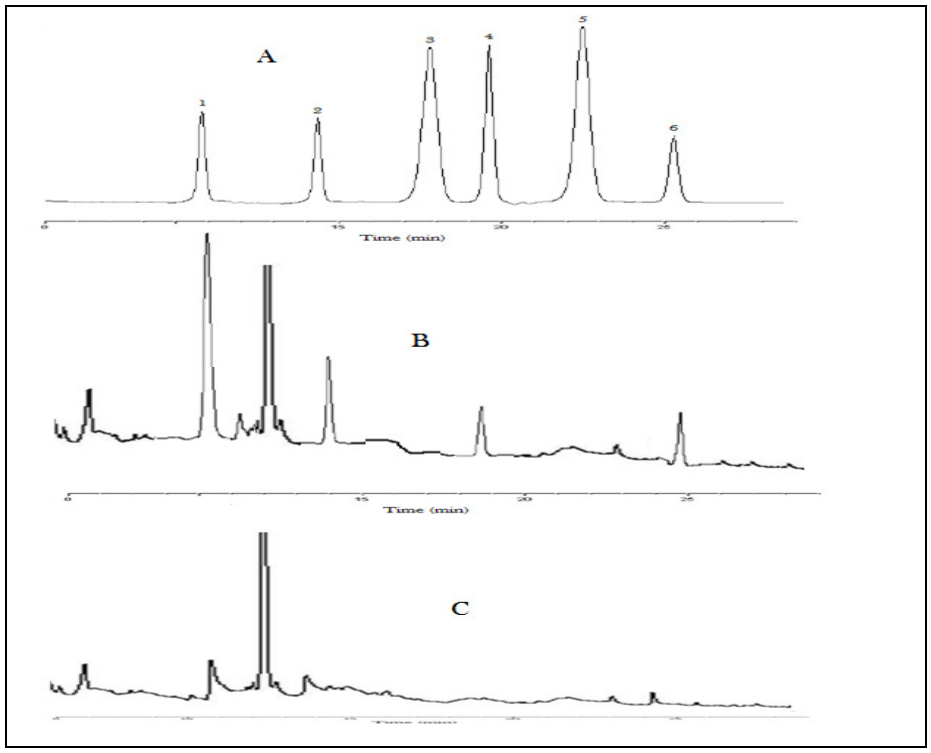

Figure 3: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Garcinia kola wood sample. Chromatogram C: blank

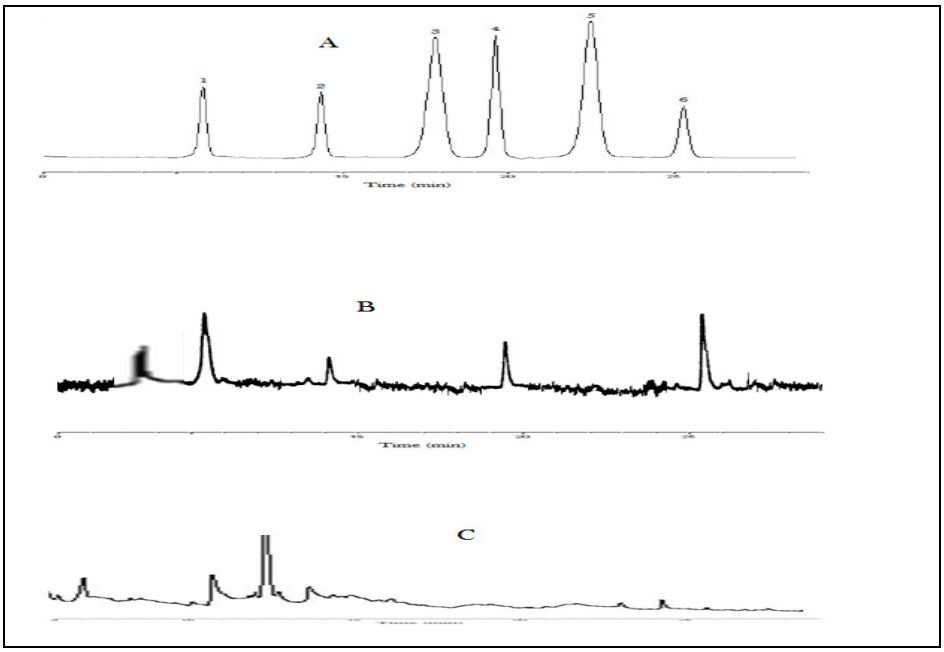

Figure 4: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Anthocleistavegilii wood sample. Chromatogram C: blank

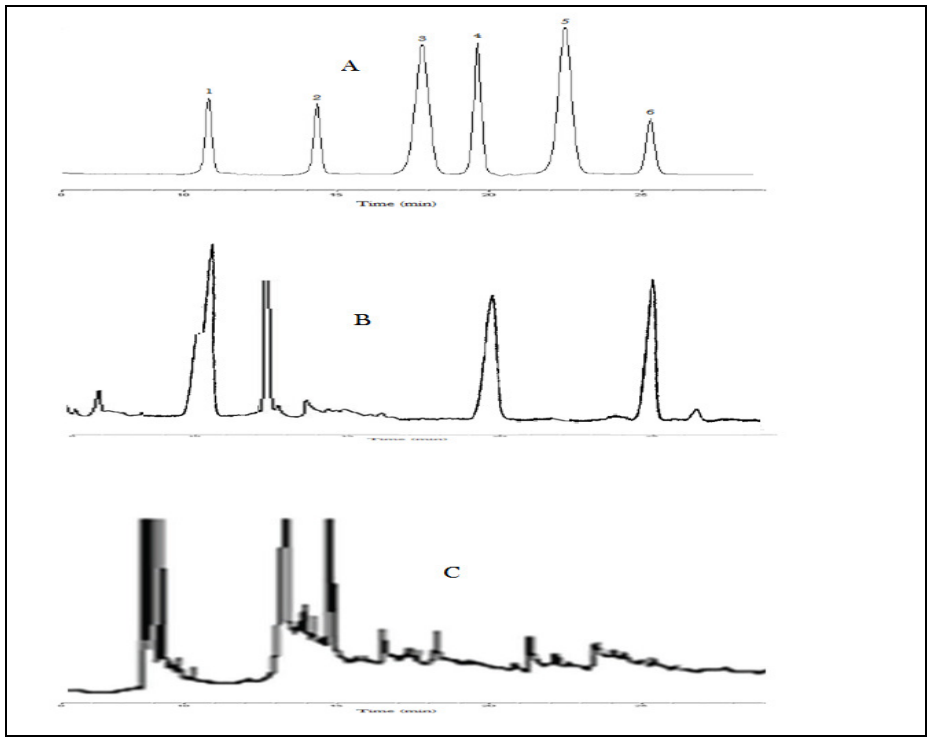

Figure 5: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Terminalia superb wood sample. Chromatogram C: blank

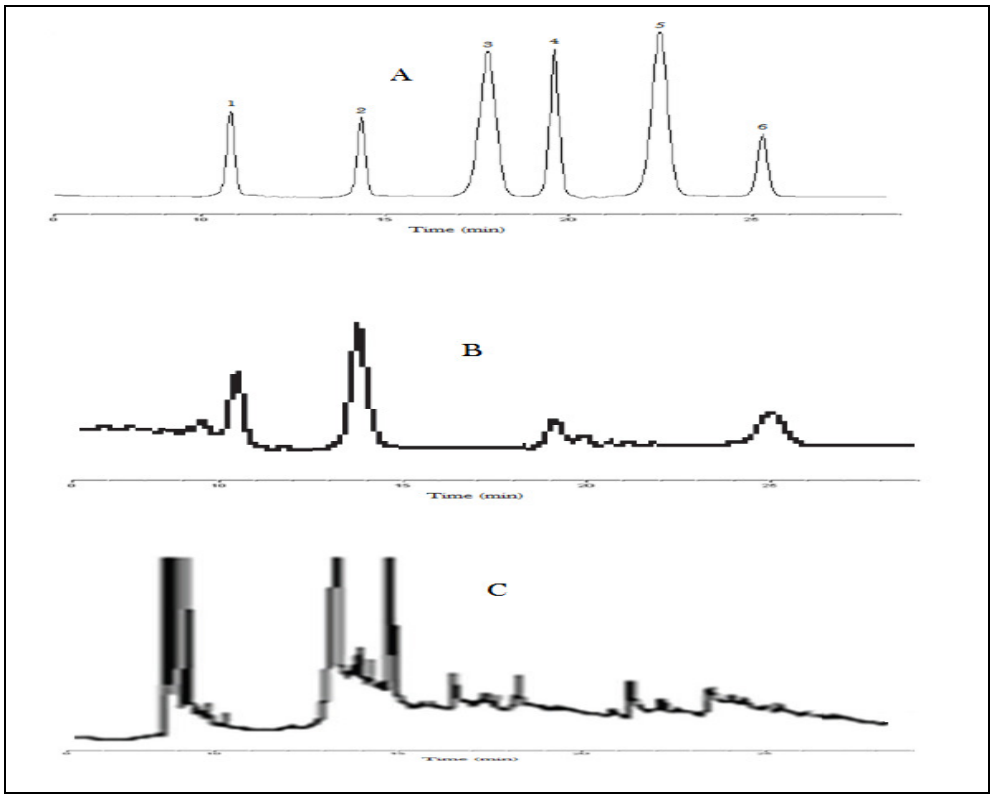

Figure 6: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Symphoniaglobuliferal wood sample. Chromatogram C: blank

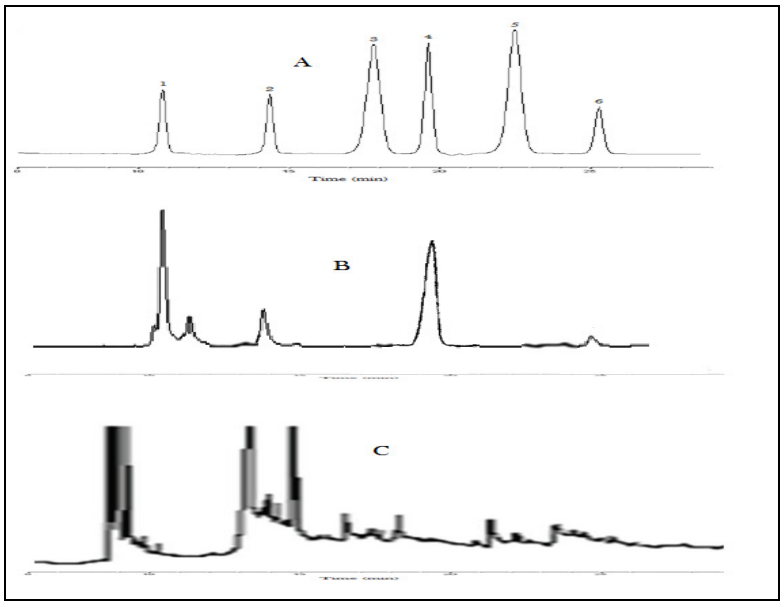

Figure 7: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Klanedoxia Gabonensis wood sample. Chromatogram C: blank

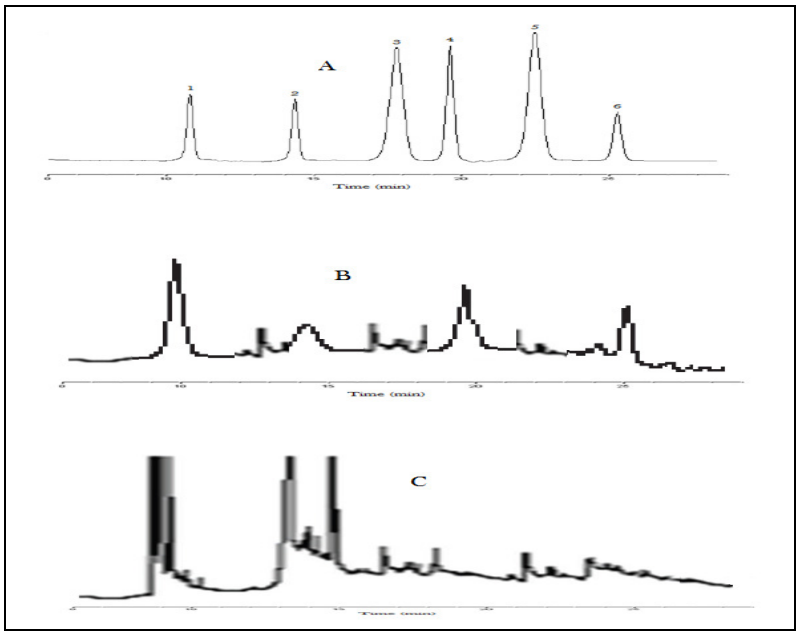

Figure 8: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of VapacaGuiniensis wood sample. Chromatogram C: blank

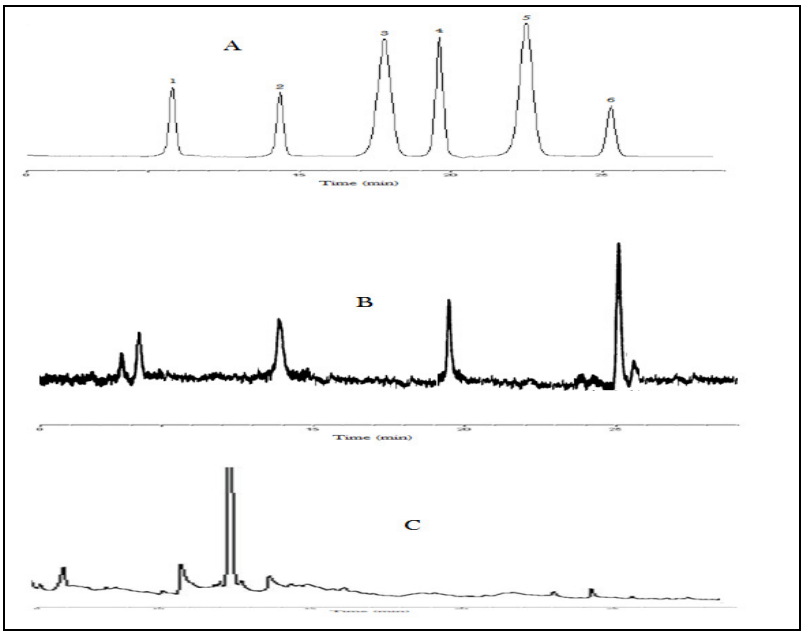

Figure 9: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of MacarangaBarteri wood sample. Chromatogram C: blank

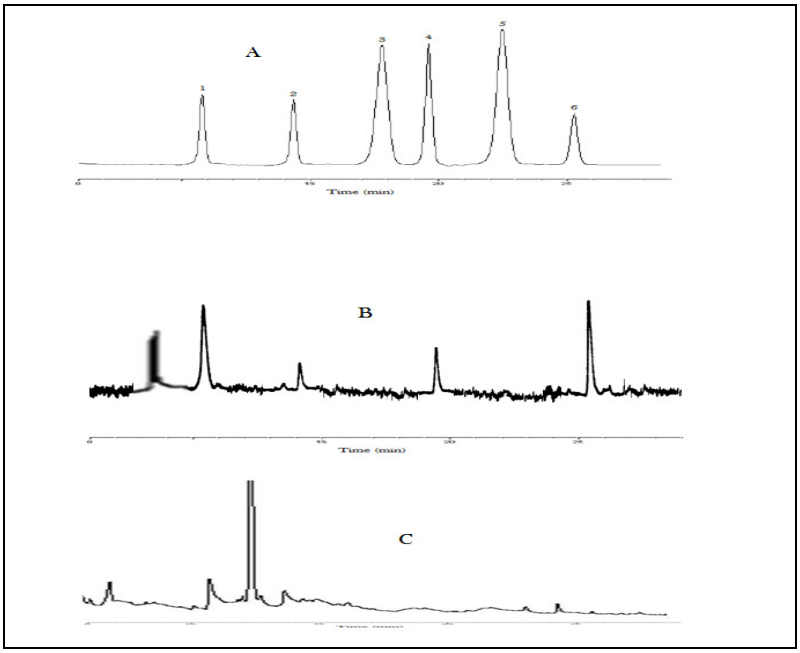

Figure 10: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of MagiferaIndica wood sample. Chromatogram C: blank

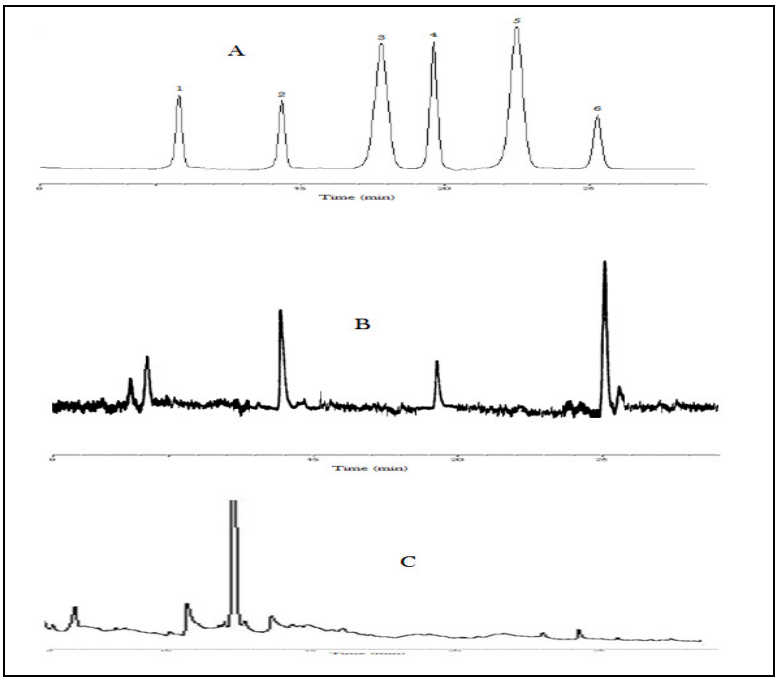

Figure 11: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Alstoniaboonei wood sample. Chromatogram C: blank

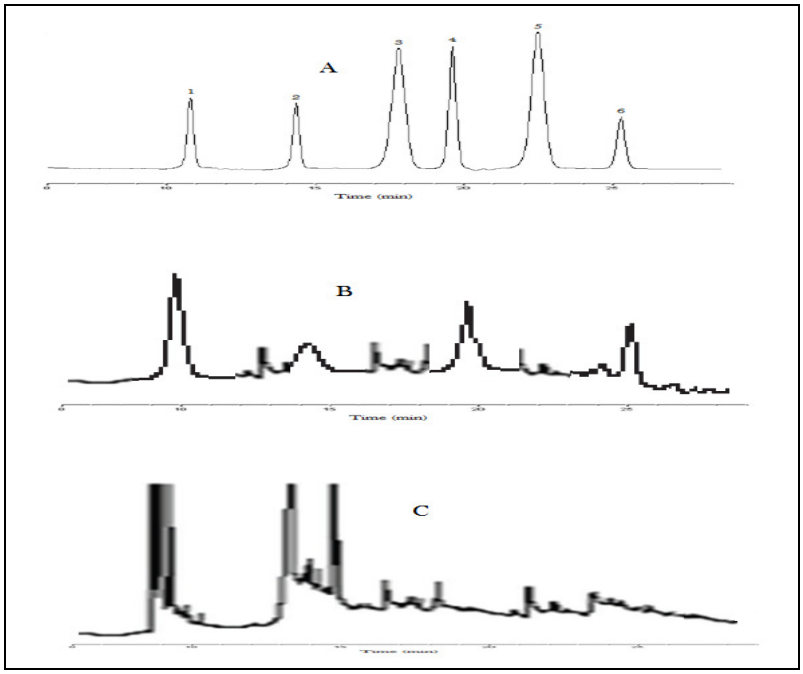

Figure 12: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Alchorniacordifolia wood sample. Chromatogram C: blank

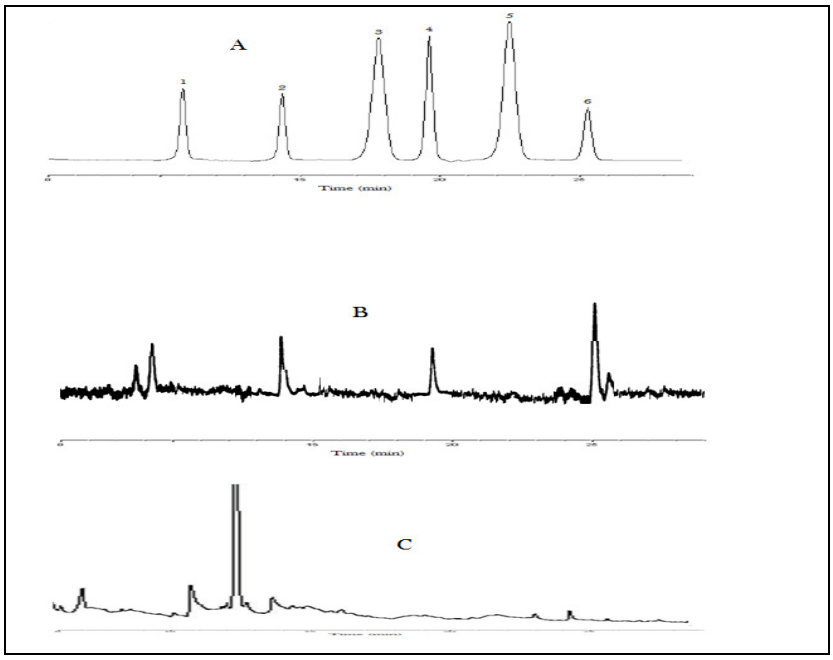

Figure 13: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Terminalia iverensis wood sample. Chromatogram C: blank

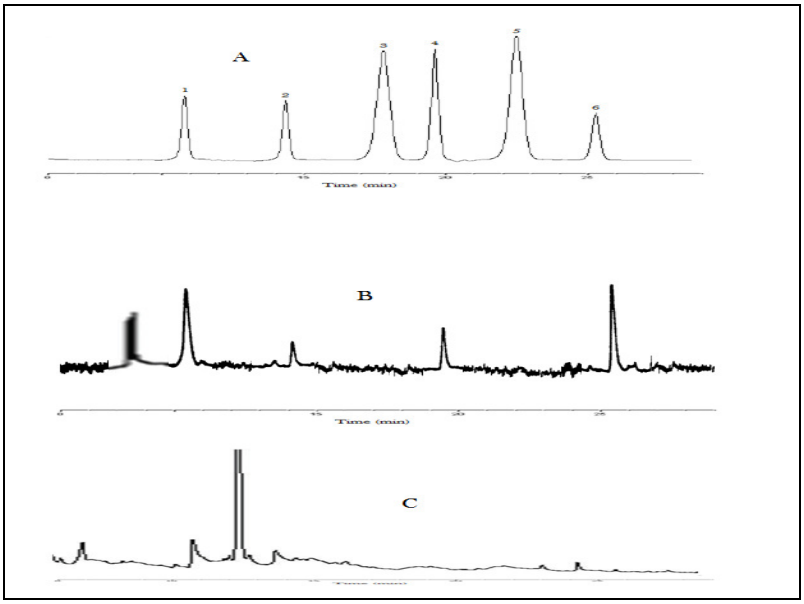

Figure 14: LC-FLD chromatograms: Chromatogram A: Standard mixture of 6 PAHs (20 ng/mL each). Peak identification: 1 = naphthalene, 2 = phenanthrene, 3 = fluoranthrene, 4 = pyrene, 5 = chrysene, 6 = benzo[k]fluoranthene. Chromatogram B: PAH extract of Lophiraalata wood sample. Chromatogram C: blank

3.2. Quantitative Analysis

The complete combustion of the samples gave the following results. All reported concentration values are referenced to 1g of wood sample. *Ficuscapensis* of wood gave 4.21 µg ofnaphthalene, 4.01 µg of phenanthrene, 3.68 µg of pyrene, and 3.81 µg of benzo [k] fluoranthrene. *Ceibapentadra* of wood gave3.56 µg ofnaphthalene, 4.15 µg of phenanthrene, 4.41 µg of pyrene, and 3.87 µg of benzo [k] fluoranthrene. *Garcinia kola* of wood gave 3.55 µg ofnaphthalene, 4.11 µg of phenanthrene, 3.81 µg of pyrene, and 4.31 µg of benzo [k] fluoranthrene. wood gave 3.98 µg ofnaphthalene, 3.99 µg of phenanthrene, 4.21 µg of pyrene, and 3.10 µg of benzo [k] fluoranthrene. *Terminalia superb* wood gave 3.81 µg ofnaphthalene, phenanthrene was not detected, 4.01 µg of pyrene, and 3.95 µg of benzo [k] fluoranthrene. *Symphoniaglobuliferal* wood gave 4.02 µg ofnaphthalene, 3.90 µg of phenanthrene, 4.21 µg of pyrene, and 3.85 µg of benzo [k] fluoranthrene. *KlanedoxiaGabonensis* wood gave 1.86 µg ofnaphthalene, 1.98 µg of phenanthrene, 2.01 µg of pyrene, and 2.54 µg of benzo [k] fluoranthrene. *VapacaGuiniensis* wood gave 2.01 µg ofnaphthalene, 2.45 µg of phenanthrene, 2.22 µg of pyrene, and 2.15 µg of benzo [k] fluoranthrene. *MacarangaBarteri* wood gave 1.98 µg ofnaphthalene, 1.75 µg of phenanthrene,

1.22 µg of pyrene, and 1.67 µg of benzo [k] fluoranthrene. *MagiferaIndica* wood gave 1.77 µg ofnaphthalene, 1.65 µg of phenanthrene, 1.46 µg of pyrene, and 1.99 µg of benzo [k] fluoranthrene. *Alstoniaboonei* wood gave 2.35 µg ofnaphthalene, 2.27 µg of phenanthrene, 2.38 µg of pyrene, and 2.78 µg of benzo [k] fluoranthrene. *Alchorniacordifolia* wood gave 1.29 µg ofnaphthalene, 1.21 µg of phenanthrene, 1.36 µg of pyrene, and 1.45 µg of benzo [k] fluoranthrene. *Lophiraalata* wood gave 2.57 µg of naphthalene, 2.28 µg of phenanthrene, 2.36 µg of pyrene, and 2.30 µg of benzo [k] fluoranthrene. However, phenanthrene and chrysene were not detected in any of the wood samples. Quantitative analyses results are presented in Tables 3, 4; Figures 15 - 18). Figures 15 – 18 show that the concentration of PAHs in the soft woods are higher than the concentrations in the hard woods; this trend is also shown in the results of the statistical t-test (Table 4); t-test result show that the concentrations of PAHs in the hard wood are significantly lower than those of the softwoods.

Wood sample	Naphthalene	Phenanthrene	Fluoranthrene	Pyrene	Chrysene	Benzo[k]fluoranthene
Ficuscapensis	4.21	4.01	ND*	3.68	ND*	3.81
Ceibapentadra	3.56	4.15	ND*	4.41	ND*	3.87
Garcinia kola	3.55	4.11	ND*	3.81	ND*	4.31
Anthocleistavegilii	3.98	3.99	ND*	4.21	ND*	3.10
Terminalia superb	3.81	ND*	ND*	4.01	ND*	3.95
Symphoniaglobuliferal	4.02	3.90	ND*	4.21	ND*	3.85
KlanedoxiaGabonensis	1.86	1.98	ND*	2.01	ND*	2.54
VapacaGuiniensis	2.10	2.45	ND*	2.22	ND*	2.15
MacarangaBarteri	1.98	1.75	ND*	1.22	ND*	1.67
MagiferaIndica	1.77	1.65	ND*	1.46	ND*	1.99
Alstoniaboonei	2.35	2.27	ND*	2.38	ND*	2.78
Alchorniacordifolia	1.29	1.21	ND*	1.36	ND*	1.45
Terminalia iverensis	2.54	2.47	ND*	2.48	ND*	2.40
Lophiraalata	2.57	2.28	**ND***	2.36	**ND***	2.30

Table 3: Average concentration of PAHs in wood samples.
ND - not detected in sample*

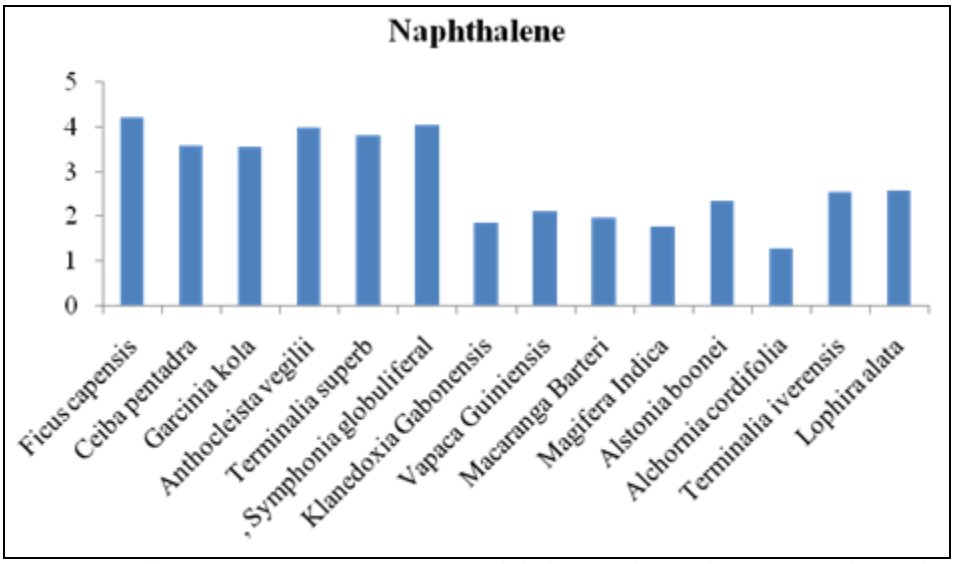

Figure 15: The average concentration of Naphthalene in the smoke of 14 wood samples

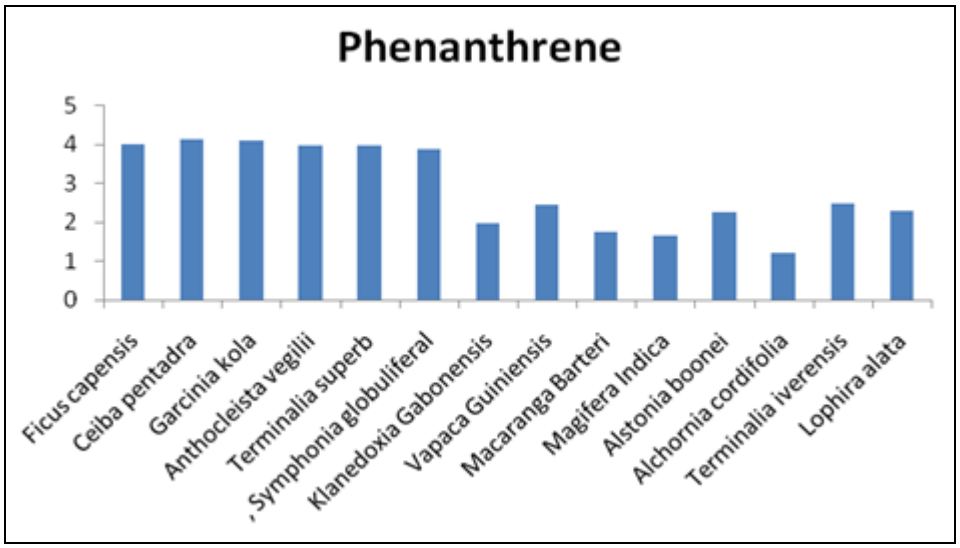

Figure 16: The average concentration of Phenanthrene in the smoke of 14 wood samples

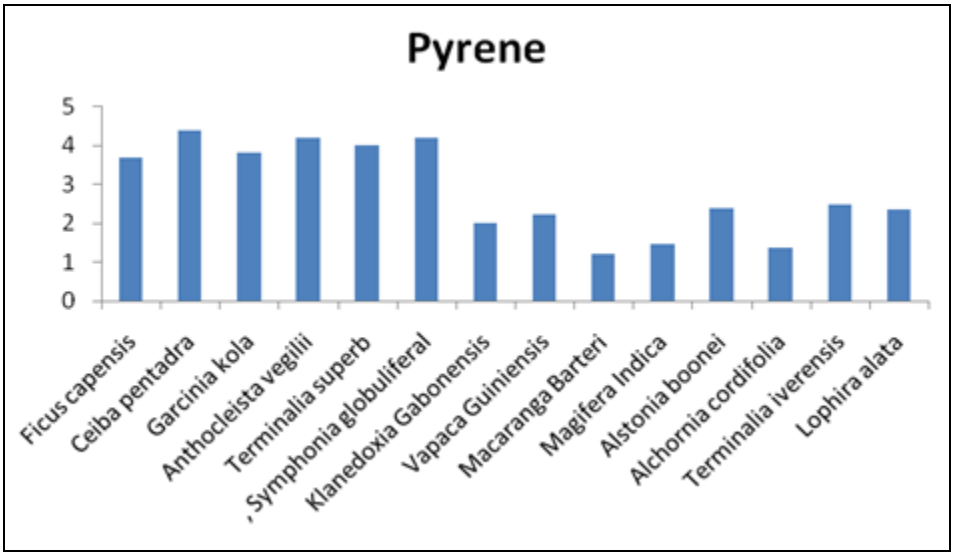

Figure 17: The average concentration of Pyrene in the smoke of 14 wood samples

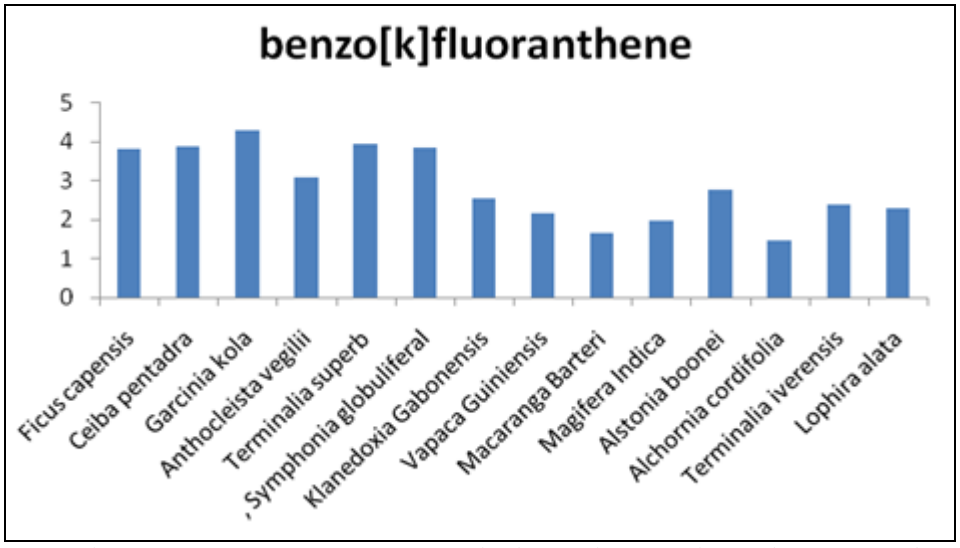

Figure 18: The average concentration of Benzo [k] fluoranthrene in the smoke of 14 wood samples

	N	Mean	SD	df	t-value calculated
Naphthalene	6	3.855	0.265	12	8.974
	8	2.038	0.43		
Phenanthrene	5	4.032	0.100	11	9.872
	8	2.008	0.445		
Pyrene	6	4.055	0.275	12	9.149
	8	1.936	0.511		
Benzo [k] fluoranthrene	6	3.815	0.395	12	7.226
	8	2.160	0.444		

Table 4: Statistical evaluation of the concentration of the PAHs in the smoke of the 14 wood samples

All the t-calculated values are higher than the critical table values.

4. Conclusion

In this project, PAHs were determined from different woods used as fuel for various purposes in the Niger Delta region in Nigeria. The results showed that soft woods generate significantly higher levels of PAHs than hard woods when burnt. Therefore, hard woods as fuels are greener wood fuels.

5. References

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