Chemistry Research Journal, **2017, 2(5):142-147**

Available online www.chemrj.org

ISSN: 2455-8990
CODEN(USA): CRJHA5

Research Article

Evaluation of Polycyclic Aromatic Hydrocarbons of Some Woods, Charcoals and Coal of Nasarawa State, Nigeria

E.M. Ndijiekwu, A.C. Etonihu*

Department of Chemistry, Nasarawa State University, P.M.B 1022, Keffi, Nasarawa State, Nigeria

Abstract Lafia-Obi coal, woods and charcoals from Keffi, Marke and Shamagay in Nasarawa State were evaluated for the presence of Polycyclic aromatic hydrocarbons (PAHs) using standard methods. Samples were saw-milled and pulverized to 200-mesh size and solvent extracted using *n-hexane* and dichloromethane at 80^{o}C and 30^{o}C for 48 h and fractionated in alumina column. Both fractions were characterized by gas chromatography-mass spectroscopy (GC-MS) that showed a total of 16 PAHs in the samples. Naphthalene was the highest in amount (0.583mg/kg) in the dichloromethane (DCM) extract of Lafia-Obi Coal while benzo(g,h,i)perylene was the least in amount (0.000mg/kg) in the *n-hexane* extracts. Benzo(a)pyrene was the highest in amount (0.326 mg/kg) and (0.300 mg/kg) for both DCM extracts for *P. erinaceus* wood (Shanjini) and *A. leocarpa* wood (Marke), while benzo(g,h,i)perylene was the least in amount with (0.000 mg/kg) for *n-hexane* extracts. In all the samples, the amounts of PAHs were far below their recommended toxic levels.

Keywords Polycyclic aromatic hydrocarbon, woods, coal, charcoal

Introduction

Nigeria is an agrarian country. About 80 % of its population are peasants and depend on firewood, charcoal and coal which contain PAHs as domestic sources of fuel [1]. Polycyclic aromatic hydrocarbons (PAHs) are a group of compounds that consist of two or more fused aromatic rings. These compounds are ubiquitous environmental pollutants generated primarily during the incomplete combustion of organic materials such as woods and fossil fuels [2]. The major route of exposure to PAHs in the general population is from breathing contaminated air, eating food containing PAHs, smoking cigarettes, or breathing smoke from open fire places [3]. Tobacco smoke contains a variety of PAHs such as benzo(a) pyrene and more than 40 known or suspected human carcinogens [4]. Charring meat or barbecuing food over charcoal, wood or other types of fire greatly increase the concentration of PAHs [3]. PAHs are known to be toxic environmental pollutants and can affect or threaten the health of humans as a result of their accumulation and persistence in the food chain through adsorption, absorption, cultivation, preparation, and repeated long-term exposures [5]. This may lead to cancer, decreased immune function, cataracts, kidney and liver damage (e.g. jaundice), breathing problems (asthma-like symptoms, and lung function abnormalities) [6].

Naphthalene can cause the breakdown of red blood cells if inhaled or ingested in large amounts [5]. PAHs bind to deoxyribonucleic acid (DNA) by a metabolic activation and conversion which causes genotoxicity and are carcinogenic to living organisms [7]. DNA and PAHs are made up of bunch of flat molecules stacked on top of each other which makes it easier for PAHs to intercalate between the base pairs in DNA. The metabolic activation of benzo(a) pyrene is shown in Figure 1. In this study, the presence of PAHs in Lafia-Obi coal, Shanjini (*Pterocarpus* *erinaceus*) and Marke (*Anogeissus leocarpa*) woods and charcoals from Nasarawa State were investigated and determined.

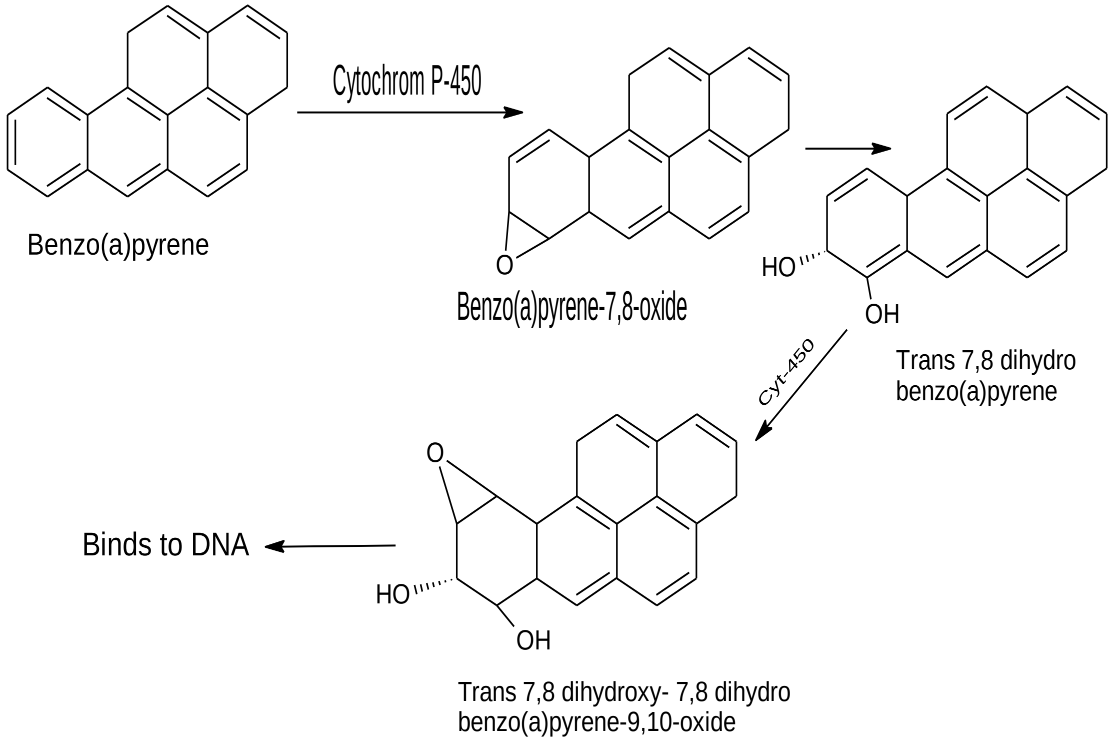

Figure 1: Activated PAH binds to DNA [6]

Materials and Methods

Collection of Samples

Coal samples

The coal sample was collected as outcrop from Lafia-Obi in Lafia LGA area of Nasarawa State, Nigeria.

Charcoal Samples

The charcoal samples were collected from Marke in Kokona LGA and Shamagay in Nasarawa LGA of Nasarawa State.

Wood Samples

Shanjini (*Pterocarpus erinaceus*) and Marke (*Anogeissus leocarpa*) woods were collected respectively, from Keffi and Marke in Kokona LGA area of Nasarawa State. The samples were authenticated at the Department of Plant Science and Biotechnology of Nasarawa State University, Keffi.

Treatment of Samples

Coal Sample

The coal outcrop sample was reduced by quartering to a laboratory sample, air-dried and crushed, ground and sieved with a 200 mesh [8].

Charcoal Samples

The charcoal samples were reduced by pounding with mortar and pestle, air-dried and sieved with a 200 mesh.

Wood Samples

The wood samples were reduced by means of a Wiley mill to sawdust, air-dried and sieved with 200 mesh according to American Society for Testing Materials D1105-96 [9].

Solvent extraction and fractionation of extracts

Each of the prepared samples was extracted in a Soxhlet extractor using *n-hexane* and dichloromethane, respectively at 80°C for 48 h. The extract was concentrated using a rotary evaporator, and fractionated by column chromatography with alumina as adsorbent and was activated in an oven at 120°C for 1 h. Slurry of alumina with the two solvents (*n-hexane* and dichloromethane) was packed respectively with care in a glass column of 10 cm and 1.5 internal diameter (id). The extract (2 g) was dissolved in 2 cm^3 of *n-hexane* and dichloromethane respectively, poured on the top of the column and allowed to drain. The extract was fractionated successively using *n-hexane* and dichloromethane. Fractions from the respective solvents were concentrated by removing the solvent using rotary evaporator, and dried at room temperature.

Determination of Polycyclic Aromatic Hydrocarbons (PAHs)

The samples were subjected to GC-MS analysis using the instrument Trace GC Ultra Thermo Scientific DSQII, equipped with TR-5ms fused silica capillary column of 30 m length, 0.25 mm diameter and 0.25 µm film thickness. Electron ionization system with ionization energy of 70eV was used for GC-MS detection. Nitrogen gas (99.99 %) was used as a carrier gas at a constant flow rate of 1.5 ml/min. The sample injector temperature was maintained at 250 °C, using split less mode and volume injected was 2 cm^3.The column temperature was programmed as follows; hold at 68 °C for 2 min; 68-260 °C at 12 °C/min; 250-320 °C at 15 °C/min and maintained at 320 °C for 8 minutes [10]. At the end of run-time, integrated chromatogram results were displayed on a computer and printed.

Results and Discussion

A total of 16 PAHs was present in some woods, charcoals and coal samples evaluated in Nasarawa State as shown in Tables 1-3. Amongst the PAHs, naphthalene was the highest in amount (0.583 mg/kg) in dichloromethane (DCM) of the Lafia-Obi Coals, while Benzo(g,h,i)Perylene was the least in amount (0.001 mg/kg) for both *n-hexane* and DCM extracts in Table 1. This could be as a result of high temperatures in sedimentary environment resulting from igneous activity [11]. The presence of the PAHs analyzed in the Lafia-Obi Coal will have no much effect on human except when exposed to it for long period of time which is in agreement with findings of previous works [8].

Table 1: PAHs in Samples of Coal from Lafia – Obi, Nasarawa State (mg/kg)

S/N	**PAH**	**Coal Sample**	
		***n-hexane* extract**	**DCM extract**
1	Naphthalene	0.552	0.583
2	Acenaphthylene	0.077	0.084
3	Acenaphthene	0.104	0.115
4	Fluorene	0.033	0.035
5	Phenanthrene	0.023	0.029
6	Anthracene	0.023	0.024
7	Floranthene	0.032	0.034
8	Pyrene	0.023	0.024
9	Benzo(a)anthracene	0.016	0.016
10	Chrysene	0.056	0.057
11	Benzo(b) Fluoranthene	0.037	0.038
12	Benzo(k) Fluoranthene	0.042	0.043
13	Benzo(a) Pyrene	0.535	0.543
14	Indeno(1,2,3-cd) Pyrene	0.006	0.006
15	Dibenzo(a,h) anthracene	0.004	0.004
16	Benzo (g,h,i) Perylene	0.001	0.001
	Total	**1.564**	**1.636**
	Mean	**0.098**	**0.102**

Table 2 showed that benzo(a)pyrene was highest in amount (0.337 mg/kg) and (0.410 mg/kg) of PAHs in charcoals sourced from *Shamagey* and *Marke* for *n-hexane* and DCM extracts, while (0.000 mg/kg) benzo(g,h,i)perylene was approximately the least in amount of PAHs for both *n-hexane* extracts of the charcoal samples. The reason for high concentration of the PAHs in charcoal sourced from Shamagey when compared with charcoal sourced from Marke, could depend on the wood type and temperature as reported [12].

Table 2: PAHs in samples of Charcoals from Shamagay and Marke, Nasarawa State (mg/kg)

S/N	**PAH**	**Charcoal from Shamagay**		**Charcoal from Marke**	
		***n-hexane* extract**	**DCM extract**	***n-hexane* extract**	**DCM extract**
1	Naphthalene	0.163	0.001	0.376	0.341
2	Acenaphthylene	0.016	0.001	0.016	0.022
3	Acenaphthene	0.031	0.030	0.057	0.063
4	Fluorene	0.007	0.007	0.018	0.021
5	Phenanthrene	0.015	0.014	0.017	0.018
6	Anthracene	0.011	0.009	0.013	0.015
7	Floranthene	0.011	0.010	0.019	0.015
8	Pyrene	0.010	0.009	0.012	0.014
9	Benzo(a)anthracene	0.007	0.006	0.008	0.010
10	Chrysene	0.022	0.020	0.025	0.027
11	Benzo(b) Fluoranthene	0.014	0.014	0.016	0.023
12	Benzo(k) Fluoranthene	0.015	0.015	0.016	0.019
13	Benzo(a) Pyrene	0.337	0.301	0.387	0.410
14	Indeno(1,2,3-cd) Pyrene	0.002	0.002	0.002	0.003
15	Dibenzo(a,h) anthracene	0.000	0.000	0.001	0.001
16	Benzo (g,h,i) Perylene	0.000	0.000	0.000	0.000
	Total	**0.661**	**0.439**	**0.983**	**1.002**
	Mean	**0.041**	**0.027**	**0.061**	**0.063**

From Table 3, benzo(a)pyrene was the highest in amount (0.326 mg/kg) and (0.300 mg/kg) for both DCM extracts for *P. erinaceus* wood (Shanjini) and *A. leocarpa* wood (Marke), while benzo(g,h,i)perylene was the least in amount with (0.000 mg/kg) for *n-hexane*. The reasons for higher concentration in amount of PAHs in *P. erinaceus* (Shanjini) wood could be as a result of the type of wood. The high intensity of the color from the wood extract is characteristic of the presence of more phenolic compounds. Comparing the PAHs extract of *n-hexane* and DCM in Tables 1, 2 and 3 showed that DCM was a better extracting solvent than *n-hexane*. This could be due to difference in polarity. Dichloromethane is a more polar solvent than *n-hexane*. Coal was found to contain more of the PAHs than the woods and charcoal samples. This is expected due to the compact mass of the coal as a result of high temperature, pressure and the less oxygen available beneath the earth crust for its formation [13]. PAHs are produced by incomplete combustion of organic matter such as wood, coal or oil. As a general rule, the lower the temperature of the fire and the less oxygen available, the more incomplete do these materials burn and higher probability of PAHs formation. From the results it could be inferred that there are higher concentrations of these polycyclic aromatic hydrocarbons in coal than woods and charcoals. This could be due to the reflex input from combustion of organic matter and fossil fuels. Suitably high temperatures for the formation of the PAHs can occasionally arise in sedimentary environment as a result of igneous activity (Murchinson & Raymond, 1989).

[8] reported the detection of pyrolytic PAHs in oil seeps in the Guyamas Basin of California (USA) as a result of PAH generation by igneous activity. PAH formation was attributed to the *in situ* pyrolysis of contemporary organic matter (with significant terrestrial component) at temperatures in excess of 300^{o}C and the heat was supplied hydrothermally by activity associated with spreading center in the basin.

Table 3: PAHs in *Pterocarpus erinaceus* and *Anogeissus leocarpa* woods, Nasarawa State (mg/kg)

S/N	**PAH**	**Wood from Shanjini (*P. erinaceus*)**		**Wood from Marke (*A. leocarpa*)**	
		***n-hexane* extract**	**DCM extract**	***n-hexane* extract**	**DCM extract**
1	Naphthalene	0.158	0.164	0.126	0.156
2	Acenaphthylene	0.010	0.012	0.010	0.010
3	Acenaphthene	0.026	0.029	0.024	0.025
4	Fluorene	0.004	0.005	0.004	0.004
5	Phenanthrene	0.013	0.017	0.009	0.011
6	Anthracene	0.009	0.011	0.005	0.006
7	Floranthene	0.009	0.012	0.009	0.009
8	Pyrene	0.003	0.009	0.008	0.008
9	Benzo(a)anthracene	0.006	0.007	0.005	0.006
10	Chrysene	0.019	0.019	0.016	0.017
11	Benzo(b) Fluoranthene	0.013	0.014	0.013	0.010
12	Benzo(k) Fluoranthene	0.014	0.014	0.013	0.014
13	Benzo(a) Pyrene	0.306	0.326	0.278	0.300
14	Indeno(1,2,3-cd) Pyrene	0.002	0.002	0.001	0.001
15	Dibenzo(a,h) anthracene	0.001	0.001	0.000	0.000
16	Benzo (g,h,i) Perylene	0.000	0.000	0.000	0.000
	Total	**0.593**	**0.642**	**0.521**	**0.577**
	Mean	**0.037**	**0.040**	**0.033**	**0.036**

Tables 1–3 have shown that PAHs were detected but in a miniscule amounts in relation to Environmental Protection Agency (EPA) of US who suggested that taking into the body each day the following amounts of individual PAHs is not likely to cause any harmful health effects: 0.3 mg of anthracene, 0.06 mg of acenaphthene, 0.04 mg of fluoranthene, 0.04 mg of fluorene, and 0.03 mg of pyrene per kg of body weight.

Conclusion

Evaluation of PAHs in Lafia-Obi coals, woods and charcoals from Keffi and Marke in Nasarawa State showed higher concentrations of these polycyclic aromatic hydrocarbons in coal than woods and charcoals. Benzo(a)pyrene was the highest in amount (0.326 mg/kg) and (0.300 mg/kg) for both DCM extracts for *P. erinaceus* wood (Shanjini) and *A. leocarpa* wood (Marke), while benzo(g,h,i)perylene was the least in amount with (0.000 mg/kg) for *n-hexane* extracts. Furthermore, the PAHs concentrations were far below their recommended toxic levels.

References

1. Edwards, N.T. (1983). Polycyclic Hydrocarbons In The Terrestrial Environment (Review). J. Environ. Quality 12, 427-441.
2. Tomoaki O., Kazuki, O., Shigeru, T., Zhenxing S., Yuemei H., & Zongquan H. (2010). Measurement And Source Identification of Polycyclic Aromatic Hydrocarbons (PAHs in the Aerosol In Xi'an, ihina, by using Automated Column Chromatography and Applying Positive Matrix Factorization (PMF). *Science of the Total Environment. 408 (8),* 1909-1914.
3. Public Health England (PHE, 2008). Polycyclic aromatic hydrocarbons (Benzo [a] pyrene), *Toxicology. 1,* 1-22.
4. Aleksandra, B. (2010). Petroleum and Individual polycyclic aromatic hydrocarbons. Handbook of Toxicology. 342-351.
5. Shulte, F. (1993). Polycyclic aromatic hydrocarbons and their molecular diagnostic ratios in urban atmospheric respirable particulate matter. *Atmospheric Research, 75(6),* 267-281.

6. Kisselev, P., Schwarz, D. & Platt, K.L. (2002). Epoxidation Of Benzo[A]Pyrene-7,8-Dihydrodiol by Human CYP1A1 In Reconstituted Membranes. Effects of Charge and Nonbilayer Phase Propensity of The Membrane. *Eur J Biochem, PubMed.*
7. Staffan, L. (2003). Analysis of PAHs And Their Transformation Product In Contaminated Soil and Remediation Process Retrieved from https://www.researchgate.net/publication/265100739_Analysis_of_PAHs_and_their_ transformation_ products_in_cont aminated_soil_and_remedial_processes
8. Etonihu, A.C. (2010). Pristane, Phytane and Polycyclic Aromatic Hydrocarbon Distributions in Nigerian Coals. *Int. J. Chem. Sci. 3(2*), 142-150.
9. American Society for Testing Materials (ASTM, 2012). *Standard Test Method for Preparation of Extractive-Free Wood D1105-96. ASTM International,* West Conshocken, 147-148.
10. Olabemiwo, O.M., Alade, A.O., Tella, A.C. & Adediran, G.O. (2011). Assessment of Polycyclic Aromatic Hydrocarbons Content in Smoked *C. gariepinnus* and *T. guineensis* fish species available in Western Nigeria. *International Journal of Basic & Applied Science* 11(2), 135.
11. Murchinson, D. & Raymond, A. (1989). Igneous Activity and Organic Maturation in the Midland Valley of Scotland. *Int. Jour. Coal Geo.*14**:** 47-82.
12. Lui, W.W., Liang, J. & Donovan, E.F. (2010). Electrostatic Field and ion Temperature Drop in Thin Current Sheets. Journal of Geophysical Research.115 (A3), 1-15.
13. Kolok, A.S. (2016) Combustion. In: Modern Poisons. Earth and Environmental Science pp. 76-78.