

# Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Charcoal Production Areas in Nasarawa State

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## KeyWords

Charcoal, Soil, Polycyclic Aromatic Hydrocarbon (PAHS), Concentration, Gas chromatography/Mass Spectrometer (GC/MS)

## ABSTRACT

Wood charcoal is the most important means of human exposure to Polycyclic Aromatic Hydrocarbons (PAHs). The Polycyclic Aromatic Hydrocarbons (PAHs) were observed in soil sample and charcoal is the major source of human exposure to PAHs. In the present study, the PAHs concentrations were determined using gas Chromatograph/Mass Spectrometer (GC/MS), and the results showed that all the PAHs analyzed were below and above detection limits of the equipment; and these were considered to present little or high risk to the human health. Results of analytical validations revealed that the GC/MS sensitive to defect and analysed sample, suggesting that the method was accurate, sensitive, reliable and reproducible. The total PAHs concentration in charcoal sample ranged from  $0.31 \pm 0.05$  to  $1.63 \pm 0.015$  PPM while the PAHs concentration in soil sample ranged from  $12.68 \pm 0.02$  to  $16.93 \pm 0.01$  PPM. The dominant PAHs in soil sample were phenanthrene, naphthalene and anthracene. The concentration of lower-molecular weight PAHs compounds was found to be greater than higher molecular weight PAHs in soil samples. While in charcoal sample, the concentration of lower molecule weight PAHs and higher molecular weight PAHs are above the permissible level or limit of PAHs as compared to United States Environmental Protection Agency (2004) and Occupational Safety Health Administration (OSHA) Permissible Expose Level (PEL) 2008.

## 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals that are formed during incomplete burning of coal, oil and gas garbage, or other organic substances like burning of wood, tobacco or charbroiled meat, PAHs are usually found as mixture containing two or more of these compounds. They are a class of hazardous organic chemicals consisting of three or more fused benzene rings which can be linear, angular, and cluster arrangements, polycyclic aromatic hydrocarbons can be separated in two groups base on the number of the benzene rings in their molecule. Low molecular weight (LMN) PAHs has three or less aromatic rings, whole high molecular weight (HMW) PAHs has four or more rings.

The primary source of PAHs contamination is human activity, including fossil fuel combustion and industrial processing. polycyclicaromatic hydrocarbons enter the environment from the multiplicity of sources which include: direct aerial fallout, use disposal of petroleum products or from natural sources such as oil seeps, forest fires and burning of wood to made charcoal.

Although PAHs are not manufactured synthetically for industrial purposes, they have limited commercial applications as intermediates in pharmaceuticals, agricultural products, photographic materials, thermosculpting plastics, lubricating materials, and other chemical industries. The persistence of PAHs in the environment is primarily attributed to their low water solubility, which facilitates their rapid association with sediments that can biodegrade PAHs. This process ultimately leads to the decontamination of sediments

and surface soils. PAHs can be completely degraded or partially transformed through the actions of specific microorganisms or individual microorganisms. (Cerniglia 1992) and (maliszewska kordybach B; 1999).

Elevated levels of PAHs in charcoal and soil pose a significant risk to human health, with exposure to these compounds associated with cardiovascular diseases and adverse fetal development. The primary health concern linked to PAH exposure is cancer, including skin, bladder, liver, and stomach cancers. This research aimed to examine the presence of Anthracene, Pyrene, and Benzo[a]pyrene in wood charcoal and soil using gas chromatography-mass spectrometry in three settlements near Nasarawa State University in Keffi, Nasarawa State, Nigeria. The primary sources of Polycyclic Aromatic Hydrocarbons (PAHs) encompass the combustion of wood and fossil fuels, as well as vehicular exhaust. Furthermore, direct inputs from the spillage of petroleum products and drips of crankcase oil also contribute to the presence of PAHs. Research has demonstrated that PAHs can be effectively removed from sediment and water through the mechanisms of sunlight decomposition and microbial biodegradation (Ishizaki *et al.*, 2010). The incomplete combustion of wood and fuel is the primary source of many Polycyclic Aromatic Hydrocarbons (PAHs) in the air. PAHs are ubiquitous products of combustion, originating from common sources such as motor vehicles, gas-burning engines, wood-burning stoves and furnaces, cigarette smoke, industrial smoke or soot, and charcoal-boiled foods. Additionally, natural sources like volcanoes, forest fires, crude oil, and shale oil contribute to the presence of PAHs in the environment (Perwak *et al.*, 1982).

## 2. Materials and Methods

### 2.1 Sample Collection

Samples were obtained in Keffi in a small settlement called cross three (3) behind Nasarawa State University Keffi (NSUK). The charcoal was sampled directly from the source where the burning/charcoal formation was made statistically both on the surface and beneath the surface of the charcoal heap. The soil samples were taken from the North, South, East, and West direction from the charcoal heap source at a uniform distance of 6 meters at an interval of 1 meter each in all the directions within the circumference of the 6 meter diameter. The soil sample was obtained from the surface and sub surface at a distance of 3cm down the earth. These samples were mixed to obtain a representative sample ready for sample preparation.

### 2.2 Sample Preparation

The sample obtained were dried on the sun light for about 4-5 days. Then the samples were taken to the laboratory using mortar and to pulverized the samples into powdered form. The powdered samples were sieved using 20cm diameter micro sieve to obtain homogeneity of the samples and kept in air tight containers prior to extraction process.

### 2.3 Soxhlet Extraction

The pulverized sample (1kg) was carefully transferred into the extraction thimble and placed in the extraction chamber of the Soxhlet extraction unit. The unit consisted of a round bottom flask, condenser and extracted table, well seated in heating mantle with wide temperature range. Soxhlet extraction of the samples with hexane and dichloromethane (3:1v/v) at 50<sup>o</sup>C for 6 hours was adopted according to the EPA 3540 method. The extract was concentrated in a rotary evaporator (RE -520 Bibby instrument UK) at 60<sup>o</sup>C to 20ml. This was repeated for both charcoal and soil samples (Ikokoh, 2015).

### 2.4 Clean up of Extracts

The concentrated extract was dissolved in 50mL of n-hexane. The resulting solution was then adsorbed onto the surface of 5g of activated alumina, and the alumina extract slurry was dried under high vacuum. A glass column (10mm inner diameter x 40mm length) was filled with 70g of activated alumina absorbent, and the adsorbed extract was placed on top. Subsequently, a mixture of 50mL of n-hexane and dichloromethane (DCM) was used to elute the saturated and polycyclic aromatic hydrocarbons fractions from the absorbed extract, respectively. The collected saturated fraction did not undergo further analysis. The polycyclic aromatic fraction was concentrated in a rotary evaporator to approximately 10mL, transferred into a sample vial, and stored in a refrigerator until needed for analysis. This process was repeated for all the remaining samples (Burford, 1993).

### 2.5 Analysis

The samples were analyzed using GC-MS, specifically the Instrument Trace GC ultra thermo scientific DSQ, MA, USA, equipped with a TR-5MS fused silica capillary column measuring 30m in length, 0.25mm in diameter, and 0.25mm in film thickness. For GC-MS detec-

tion, an electron ionization system with an ionization energy of 70eV was employed. Helium gas (99.99%) was used as the carrier gas at a constant flow rate of 1.5mL/min. The sample injector temperature was maintained at 300°C, using the splitless mode, and the injection volume was 2mL. The column temperature was programmed as follows: held at 68°C for 2min; 68-260°C at 12°C/min; 260-320°C at 15°C/min and maintained at 320°C for 8 minutes, following the procedure by Olabamiwo et al. (2011). Peak verification was carried out based on retention times and compared with those of the sample PAHs. Procedural blanks and solvent blanks were analyzed and quantified, but no PAHs were found in these blanks, as expected. The detection limits of the GC/MS equipment were 0.001ng/kg (Ikokoh, 2015).

### 3. Result and Discussion

TABLE 1

SOME CHEMICAL PARAMETERS OF SAMPLE CHARCOAL: CROSS THREE (3) BEHIND NASARAWA STATE UNIVERSITY

Sample charcoal PAHs	Naphthalene (ppm)	Acenaphthylene (ppm)	Acenaphthene (ppm)	Fluorene (ppm)	Phenanthrene (ppm)	Anthracene (ppm)	Fluoranthene (PPM)
Cross three (3) behind Nasarawa State University, Keffi	0.17 ± 0.022	0.2	0.94 ± 0.0071	0.2	0.31 ± 0.005	0.2	ND
PEL	200	200	200	200	200	2008	200

ND NOT DETECTED

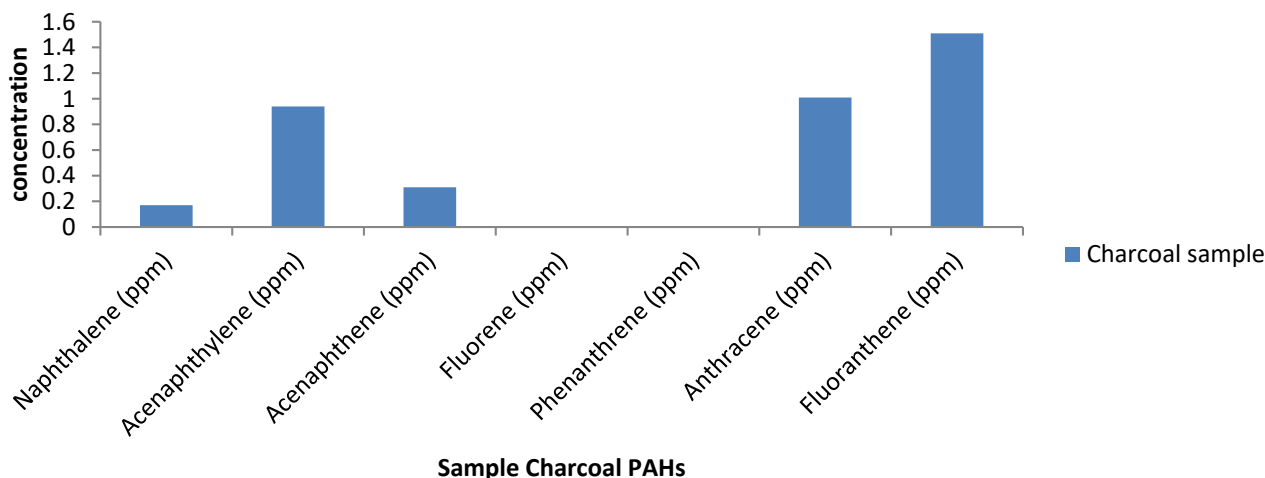


Figure 1. The graph of charcoal sample concentration against PAHs

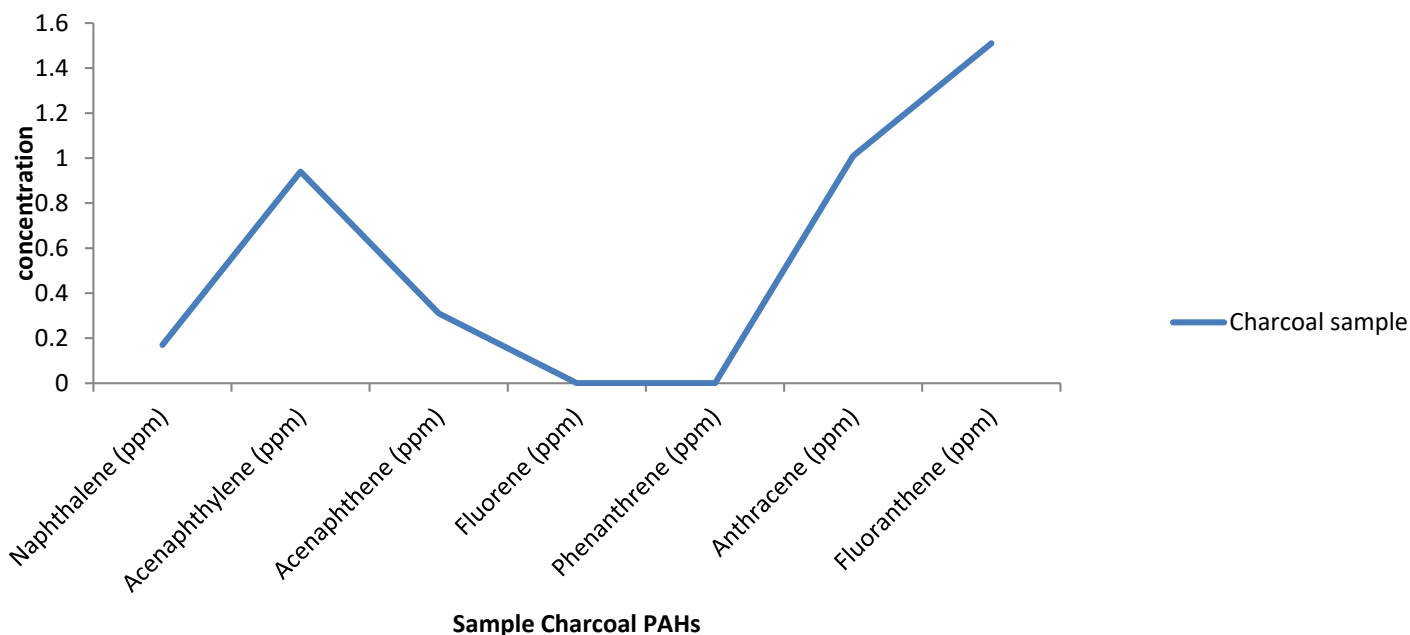


Figure 2. The graph of charcoal sample concentration against PAHs

TABLE 2

SOME CHEMICAL PARAMETERS OF SAMPLE CHARCOAL: CROSS THREE (3) BEHIND NASARAWA STATE UNIVERSITY

Sample charcoal PAHs	Pyrene (ppm)	Benzo [c] phenanthrene (ppm)	Benz (a) anthracene (ppm)	Chrys-ene (ppm)	Benzo [k] Fluoranthene (ppm)	Benzo [bti] Fluoranthene (ppm)	3-Methylchol-anthrene (PPM)
Cross three (3) behind Nasarawa State University, Keffi	1.00 ± 0.2	0.09 ± 0.001	1.45 ± 0.01	ND	0.11 ± 0.015	0.07 ± 0.325	0.71 ± 0.02
PEL	2008	2008	2008		2008	2008	2008

ND NOT DETECTED

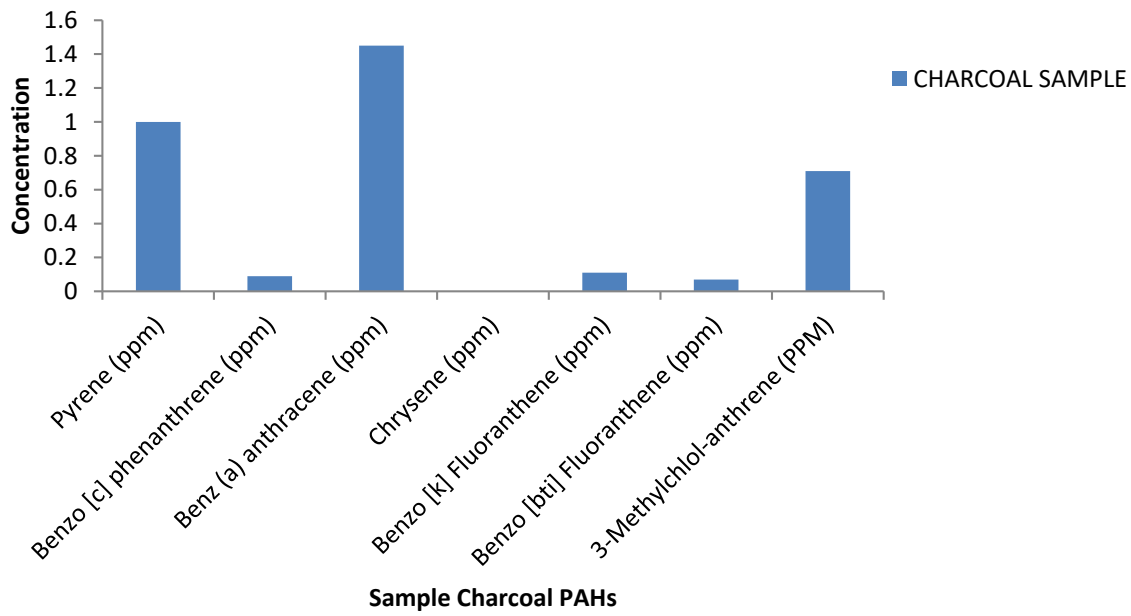


Figure 3. The graph of charcoal sample concentration against PAHs

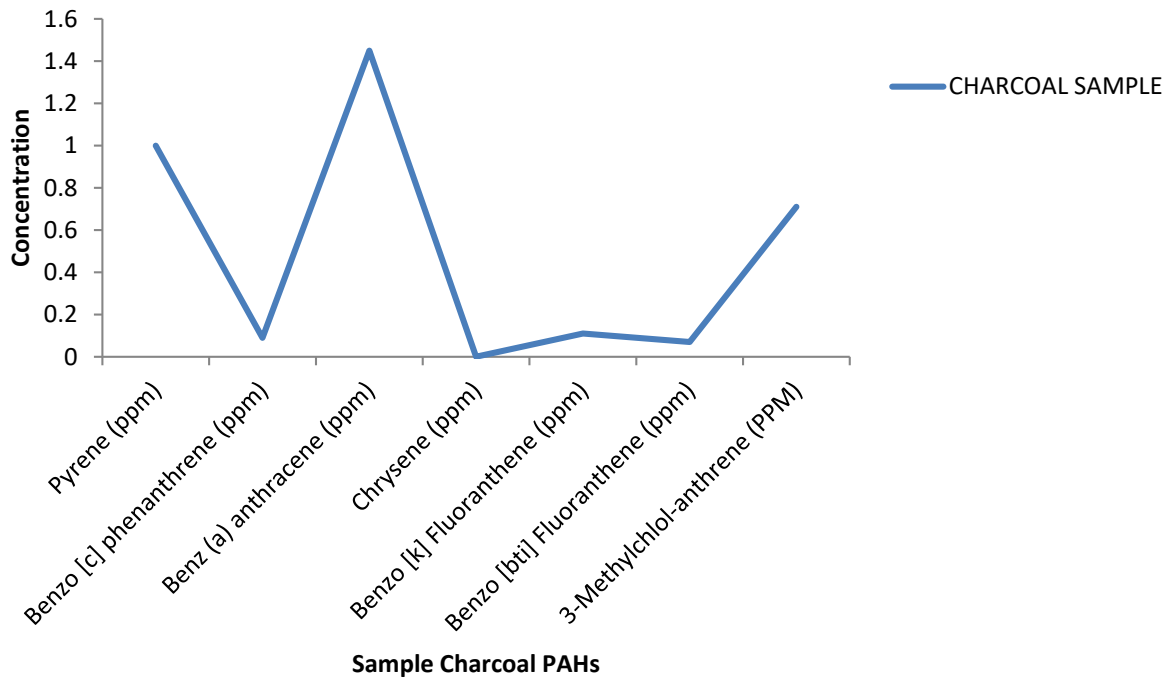
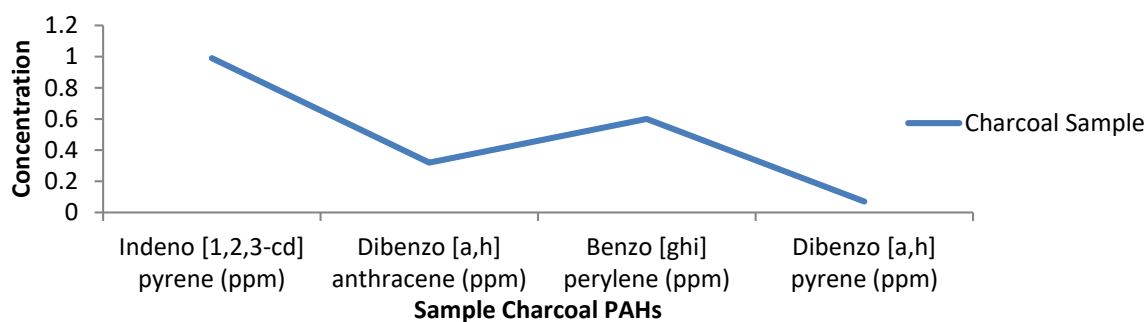
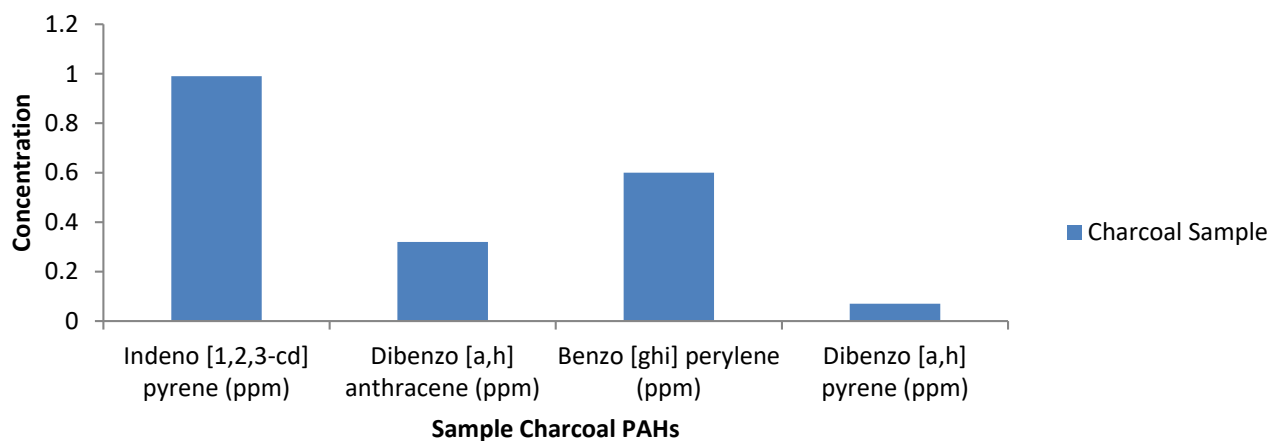


Figure 4. The graph of charcoal sample concentration against PAHs

**TABLE 3.**  
**SOME CHEMICAL PARAMETERS OF SAMPLE CHARCOAL: CROSS THREE (3) BEHIND NASARAWA STATE UNIVERSITY**

Sample charcoal PAHs	Indeno [1,2,3-cd] pyrene (ppm)	Dibenzo [a,h] anthracene (ppm)	Benzo [ghi] perylene (ppm)	Dibenzo [a,h] pyrene (ppm)				
Cross three (3) behind Nasarawa State University, Keffi (OSHA) PEL	0.99 ± 0.005	0.2	0.32 ± 0.0015	0.2	0.60 ± 0.01	0.2	0.07±0.003	0.2
		2008		2008		2008		2008

**ND NOT DETECTED**



**Figure 5. The graph of charcoal sample concentration against PAHs**

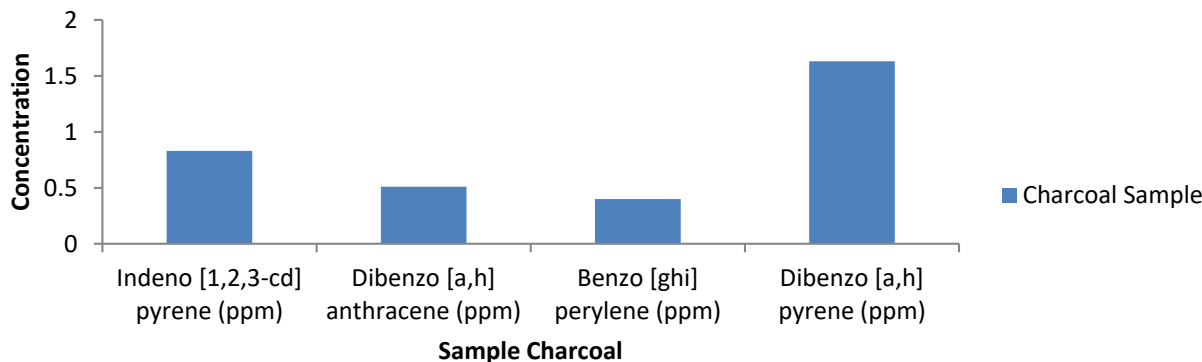
**TABLE 4**  
**SOME CHEMICAL PARAMETERS OF SAMPLE CHARCOAL: CROSS THREE (3) BEHIND NASARAWA STATE UNIVERSITY**

Sample charcoal	Indeno [1,2,3-cd]	Dibenzo [a,h] an-	Benzo [ghi]	Dibenzo [a,h] py-
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PAHs	pyrene (ppm)	thracene (ppm)	perylene (ppm)	rene (ppm)
Cross three (3) behind Nasarawa State University, Keffi (OSHA) PEL	0.83± 0.15	0.2	0.51 ± 0.02	0.2
		2008	2008	2008

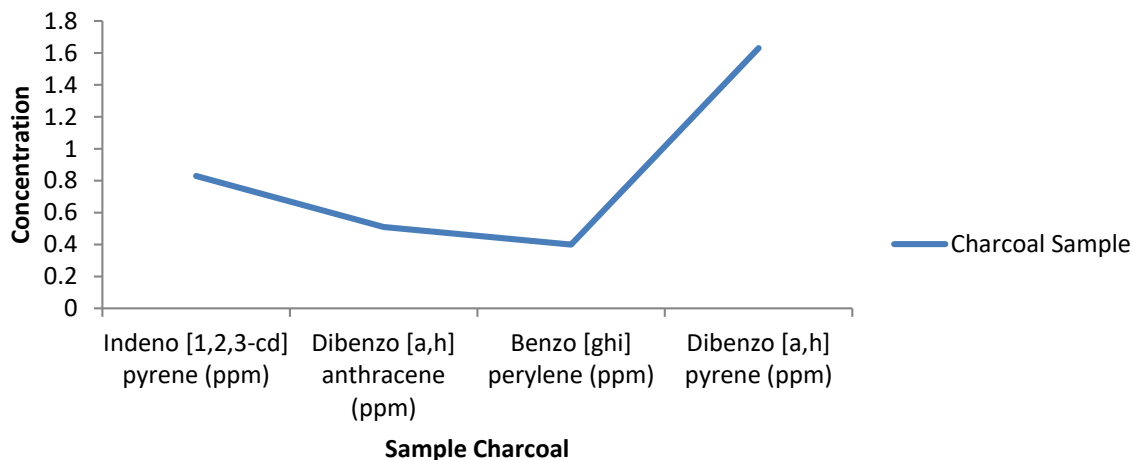
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### Charcoal Sample



**Figure 6. The graph of charcoal sample concentration against PAHs**

### Charcoal Sample



**Figure 7. The graph of charcoal sample concentration against PAHs**

**TABLE 5**

**SOME CHEMICAL PARAMETERS OF SOIL SAMPLE: CROSS THREE (3) BEHIND NASARAWA STATE UNIVERSITY, KEFFI.**

Soil sample	Naphthalene (PPM)	Acenaphthylene (PPM)	Acenaphthene (PPM)	Fluorene (PPM)	Phenanthrene (PPM)					
Cross three (3) behind Nasarawa State University, Keffi	13.54±0.01	0-5.0	2.06 ±0.005	0-5.0	0.81 ±0.02	0-5.0	1.68 ± 0.0047	0-5.0	12.68±0.002	0-5.0
USEPA		2004		2004		2004		2004		2004

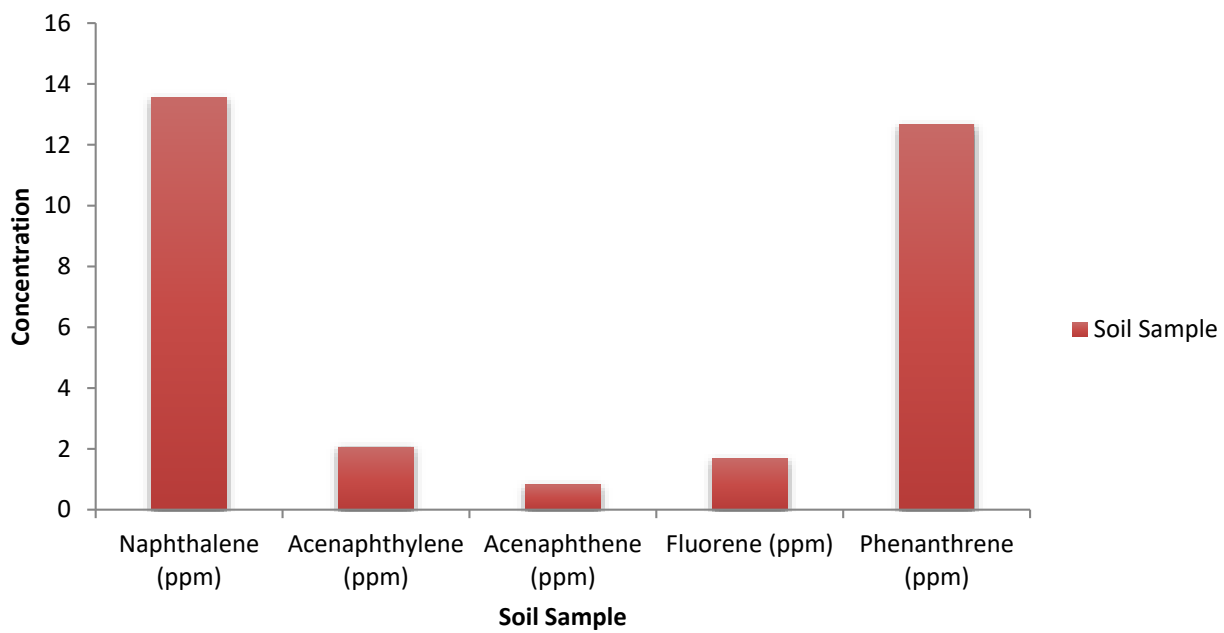


Figure 8. The graph of Soil sample concentration against PAHs



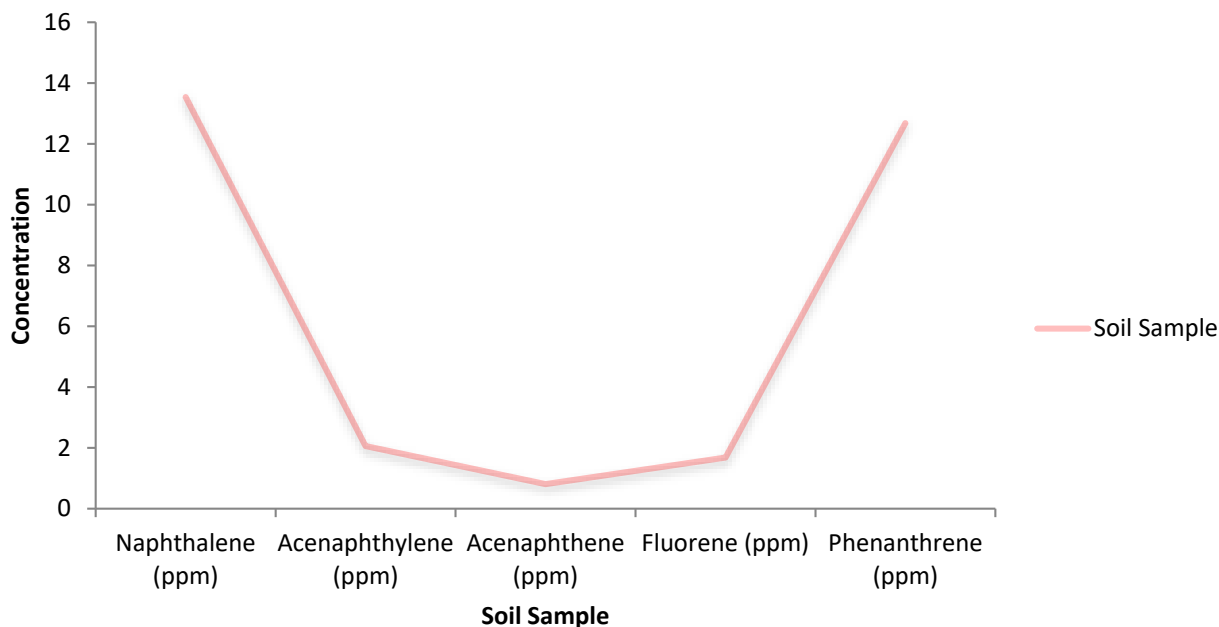
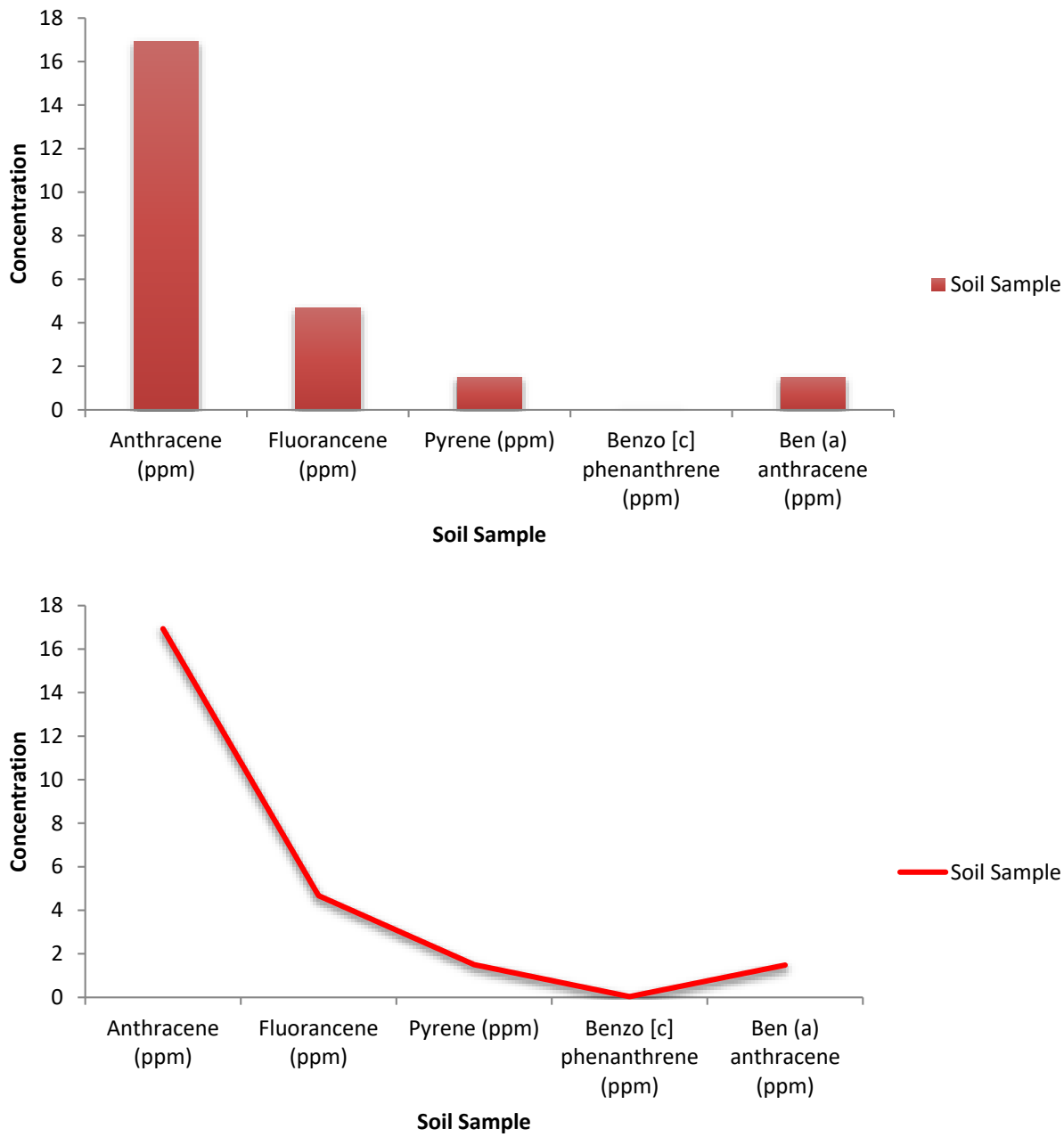


Figure 9. The graph of Soil sample concentration against PAHs

**TABLE 6**  
**SOME CHEMICAL PARAMETERS OF SOIL SAMPLE: CROSS THREE (3) BEHIND NASARAWA STATE UNIVERSITY, KEFFI.**

Soil Sample PAHs	Benzo [e] pynene		Benzo [a] pynene	
	(ppm)		(ppm)	
Cross three (3) behind Nasarawa State University, Keffi	0.43 ± 0.005	0-5.0	1.60 ± 0.01	0-5.0
USEPA		2004		2004



*Figure 10. The graph of Soil sample concentration against PAHs*

**TABLE 7**

**SOME CHEMICAL PARAMETERS OF SOIL SAMPLE: CROSS THREE (3) BEHIND NASARAWA STATE UNIVERSITY, KEFFI.**

Soil sample	Chrysene (ppm)	Ben [k] fluo- ranthene (ppm)	Benzo [b,t,j] Fluoranthene (ppm)	3 – methylchloro- threne (ppm)	Indeno [1,2,3 cd] Pyrene (ppm)
Cross three (3) behind Nasarawa State Univer- sity, Keffi	ND	0.03 ±0.005	0.68 ±0.50	1.19 ± 0.005	0.99±0.001
USEPA	0-5.0	0-5.0	0-5.0	0-5.0	0-5.0
2004	2004	2004	2004	2004	2004

**ND NOT DETECTED**

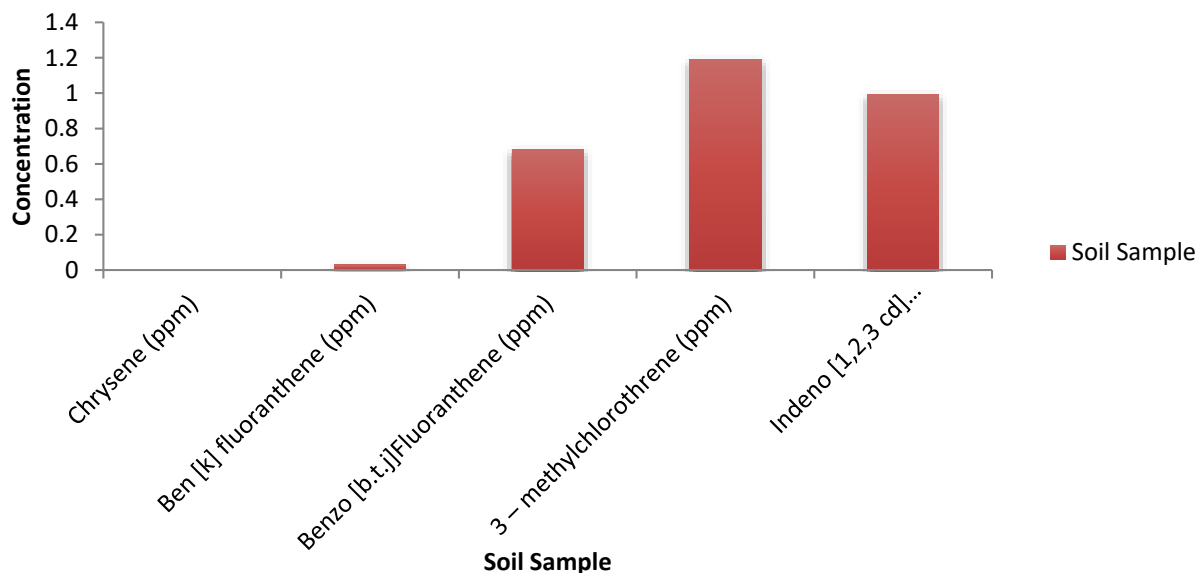


Figure 11. The graph of Soil sample concentration against PAHs

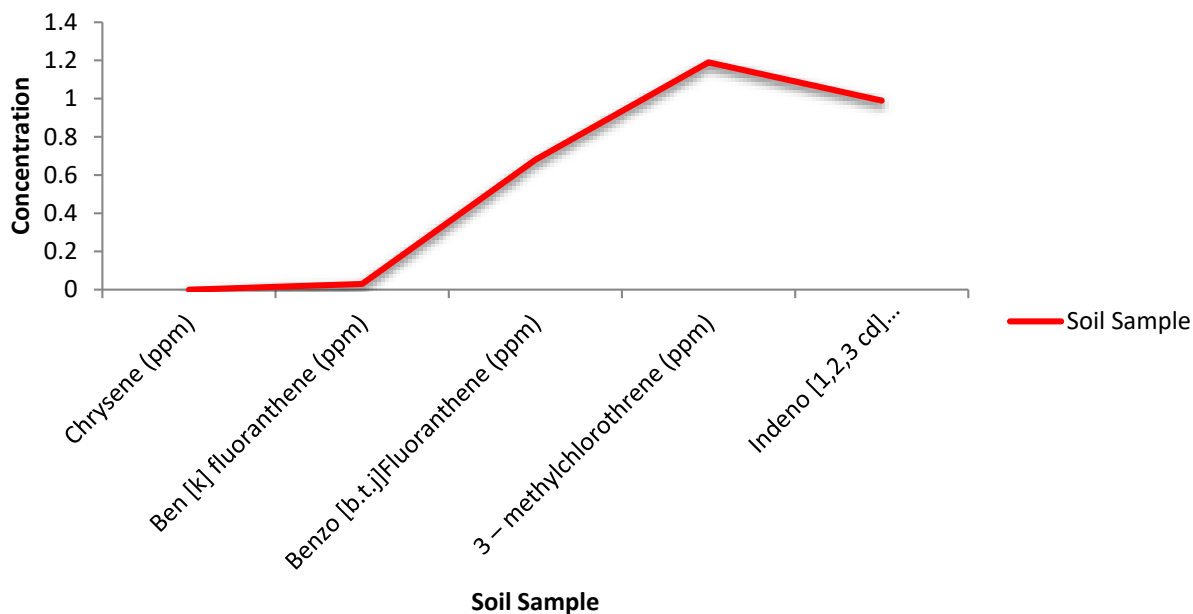


Figure 12. The graph of Soil sample concentration against PAHs

**TABLE 8.**  
**SOME CHEMICAL PARAMETERS OF SOIL SAMPLE: CROSS THREE (3) BEHIND NASARA-  
WA STATE UNIVERSITY, KEFFI.**

Soil sample	Dibenzo [a,h] anthracene	Benzo [ghi] Perylene(ppm)	Dibenzo [a,h] Pyrene(ppm)	Dibenzo [a,i] Pyrene (ppm)	Dibenzo [a,l] Pyrene (ppm)
Cross three (3)	4.25±0.02	0.33 ±0.01	0.27 ±0.015	0.89 ± 0.055	0.43±0.002
USEPA	0-5.0	0-5.0	0-5.0	0-5.0	0-5.0

behind Na-  
sarawa State  
University,  
Keffi

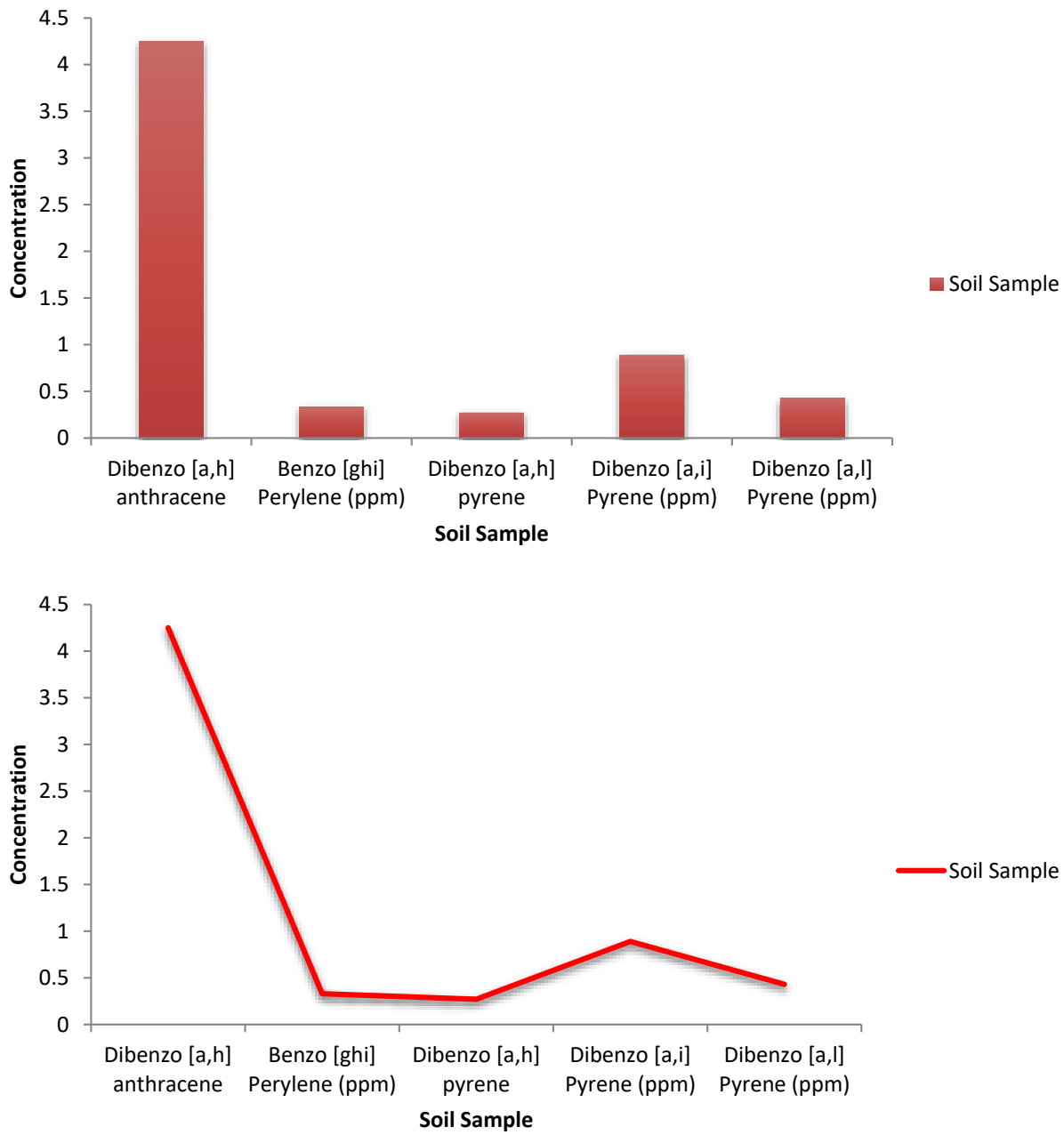


Figure 13. The graph of Soil sample concentration against PAHs

TABLE 9.

**SOME CHEMICAL PARAMETERS OF SOIL SAMPLE: CROSS THREE (3) BEHIND NASARAWA STATE UNIVERSITY, KEFFI.**

Soil Sample PAHs	Benzo [e] pynene		Benzo [a] pynene	
	(ppm)		(ppm)	
Cross three (3) behind Nasarawa State University, Keffi	0.43 ± 0.005	0-5.0	1.60 ± 0.01	0-5.0
USEPA	2004		2004	

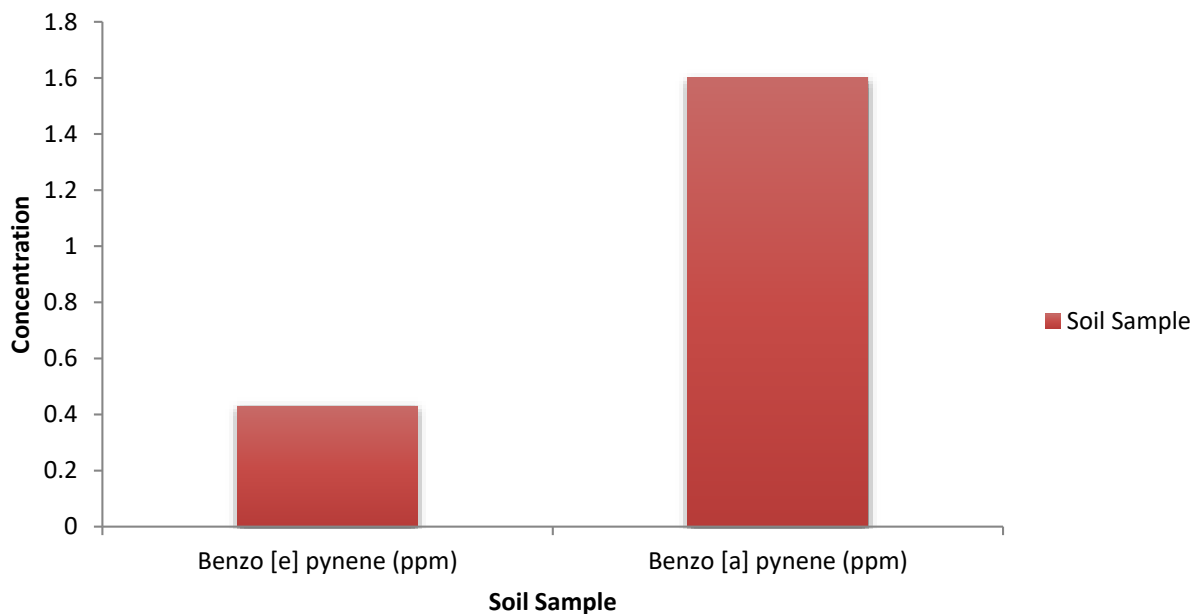
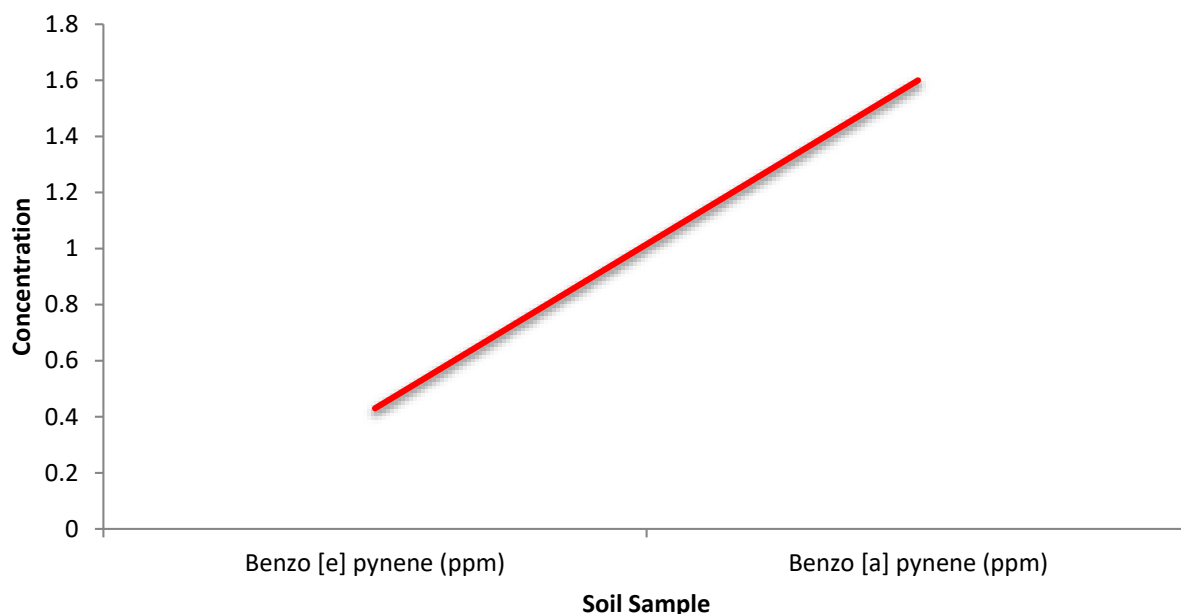


Figure 14. The graph of Soil sample concentration against PAHs



**Figure 15.** The graph of Soil sample concentration against PAHs

### 3.1 Some Chemical Parameters of Charcoal Sample

The result obtained for the presence of PAHs in charcoal such as Naphthalene, Acenaphthylene, are present in the charcoal sample while Fluorene, Phenanthrene and Chrysene was absent. The Anthracene, Fluoranthene, Pyrene, Benzo [c] phenanthrene, Ben (a) anthracene, Benzo [ghi] perylene, Dibenzo [a,h] pyrene, dibenzo [a,i] pyrene, dibenzo [a, l] pyrene, benzo [e] pyrene and benzo [a] pyrene are all present in the charcoal sample. This observation indicates that the instrument detected the amount on injected PAHs into test samples and thereby validated the analytical method adopted in this work (Table Fig 1 4.0) above. This showed that the concentration of PAHs in charcoal sample were below the detected limit of the instrument or completely absent or not detected.

### 3.2 Some Chemical Parameters of Soil Sample

The presence of chrysene was not detected in soil sample analysed from the table Fig 2. Its absence showed that the concentration level was so trace that it could not be within the limits of detection of the GC/MS. While the presence of Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, anthracene, fluorancene, pyrene, Benzo [c] phenanthrene, Ben (a) anthracene Ben [k] fluoranthene, Benzo [b, t, j] fluoranthene, 3 – methylcholanthrene, indenol [1,2,3 – cd] pyrene, dibenzo [a,h] anthracene, Benzo [ghi] perylene, Dibenzo [a,h] pyrene, Dibenzo [a,i] pyrene, Dibenzo [a,l] pyrene, Benzo [e] pyrene and Benzo [a] pyrene showed the presence of PAHs in Soil sample in cross three (3) behind Nasarawa State University, Keffi, Nasarawa State, Nigeria.

### 4.0 Conclusion

The concentration of PAHs in the charcoal samples is more than the moderate level contamination concentration (0.2ppm) which is given, by the Occupational Safety Health Administration (OSHA) Permissible Expose Level (PEL) 2008 of some chemical parameters of PAHs in charcoal sample was found to be  $0.31 \pm 0.005$  to  $1.63 \pm 0.015$ ppm. While for soil sample, which is given by United States Environmental Protection Agency (2004) of some chemical parameters of PAHS in soil sample is more than the moderate level contamination concentration (0-5.0ppm) ranged from  $12.68 \pm 0.02$  to  $16.93 \pm 0.01$ ppm.

In soil sample, the accumulation of lower molecular weight compounds of PAHs such as phenanthrene  $12.68 \pm 0.02$ , Naphthalene  $13.54 \pm 0.01$  and Anthracene with the highest value  $16.93 \pm 0.01$ ppm. While in charcoal sample, the accumulation are both in lower molecular weight and higher molecular weight ranged from  $0.31 \pm 0.005$  to  $1.63 \pm 0.015$ ppm.

Charcoal sample are more contaminated with the higher concentration of PAHs as compared to soil sample only phenanthrene, naphthalene and anthracene which are above USEPA (2004) standard. While the other chemical parameters are within USEPA (2004) standard value ranged from 0-5.0ppm.

The charcoal producers and people living or working near the studied area, Cross Three behind Nasarawa State University, Keffi in Nasarawa State, Nigeria, face potential health risks due to the presence of certain chemical parameters, specifically PAHs, detected in both charcoal and soil samples analyzed by GC-MS.

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