



Contribution of Coal to the Bioavailability of PAHs in Environmental Samples

Itodo A. U.*

Department of Chemistry and Centre for Agrochemical Technology and Environmental Research (CATER), Federal University of Agriculture, PMB 2373 Makurdi, Nigeria
Email: itodoson2002@gmail.com

Eneji I. S.

Department of Chemistry and Centre for Agrochemical Technology and Environmental Research (CATER), Federal University of Agriculture, PMB 2373 Makurdi, Nigeria

Wuana R. A.

Department of Chemistry and Centre for Agrochemical Technology and Environmental Research (CATER), Federal University of Agriculture, PMB 2373 Makurdi, Nigeria

Edimeh P. O.

Department of Chemistry, Federal University of Agriculture, PMB 2373 Makurdi, Nigeria
Department of Medical Laboratory Technology, College of Health Science and Technology, PMB 1047, Idah Kogi State, Nigeria

Onuwa P.

Department of Chemistry, Federal University of Agriculture, PMB 2373 Makurdi, Nigeria

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Abstract

The contributory role of impure carbon in Okobo coal to the levels of polycyclic aromatic compounds (PAHs) in some environmental samples viz; water, soil and cassava samples was investigated. Bioavailability of the 16 USEPA priority PAHs was estimated, using GCMS after confirmation of high impure carbon load (> 80%) as unveiled by EDS analysis. The nearness in tPAHs of the coal (0.3781 ppm) and the values reported for their vicinity environmental samples including the harmonized cassava sample (0.2398 ppm) > soil sample (0.2331 ppm) > water sample (0.1151 ppm) are indications of direct impact from coal deposit. Water samples used for control experiment (> 10 km from the coal field) is totally void of PAH while the control cassava and soil samples gave 0.0398 and 0.0422 ppm respectively. Fascinating among the findings is the dominance of four membered ring PAHs (Chrysene) in all the samples and coal diagnosis revealed mixed contributory sources, majorly of petrogenic origin. Values are however within the threshold limit prescribed by existing legislation except for the possibilities of bioaccumulation.

Keywords: Carbon, polycyclic aromatic compounds; Carcinogenicity; Bioavailability; Coal.

1. Introduction

Coal mining is a common practice in Nigeria, the problem with mining activities here is the negligence of the miners on global best practices. The increasing use of coal as an energy source, the management of the resulting fly ash and the environmental issues and impacts of the trace elements released from coal combustion have become a great concern to life preservation and sustainability [1].

People that constitute these communities where coal mining activities take place, because of their low level education are ignorant of environmental obligations under the minerals and mining act, right to life, health, adequate standard of living, education, liberty and security [2, 3]. Coal combustion is usually accompanied with residual incombustible ash residue called fly ash and the coal properties impact the quality of coal combustion by-products (CCBs).

Major pollutants from coal mining and burning that negatively impacts the environment and health [4-6] include Destruction of groundwater regimes and rearranging the water tables, Impact of water use on flows of rivers and consequential impact on other land-uses, rendering land unfit for agricultural uses, emission of radionuclides including uranium, thorium, and other heavy metals presenting health hazards, Release of major conventional air pollutants during coal combustion process (particulate matter, NO_x, SO₂, Hg and other toxic substances, CO₂ and CH₄), Generation of acid rain, immense contribution to climate change. Coal associated heavy metals also pollute the environment [7, 8]. Coal mining adversely impact the environment, causing interference with groundwater and soil quality. Challenges linked with mining wastes disposal include the creation of geological hazards and visible and esthetical issues [7].

*Corresponding Author

2. Polycyclic Aromatic Hydrocarbons (PAHs)

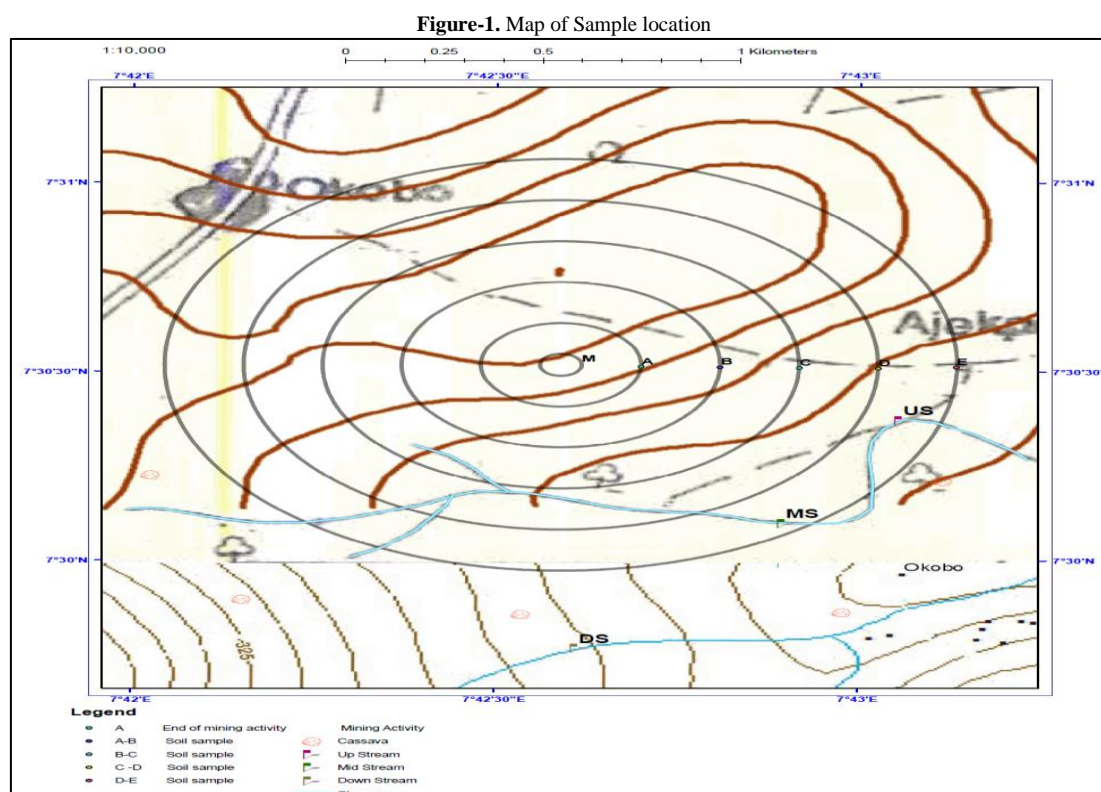
Polycyclic aromatic hydrocarbons (PAHs) are groups of organic compounds consisting of two or more fused aromatic rings. PAHs are a class of organic compounds produced by incomplete combustion or high-pressure processes. PAHs form when complex organic substances are exposed to high temperatures or pressures [9]. Light molecular weight PAHs (LMW PAHs) that have two or three aromatic rings are emitted in the gaseous phase, while high molecular weight PAHs (HMW PAHs), with five or more rings, are emitted in the particulate phase. In the atmosphere, PAHs can undergo photo-degradation and react with other pollutants including sulfur dioxide, nitrogen oxides, and ozone [10].

2.1. Sources and Emission of PAHs

PAHs are mainly derived from anthropogenic activities related to pyrolysis and incomplete combustion of organic matter. Emission sources; including domestic and industrial sources, mobile emissions, agriculture activities, and natural sources were reported [11].

2.2. Study Area

Okobo community, is a small town in Enjema district of Ankpa Local Government Area ($7^{\circ}22'14''\text{N}$ $7^{\circ}37'31''\text{E}$) in Kogi state with reserves of up to 380 million tonnes of coal. A GPS mapping of the study area or sample location is given in Figure 1.



Current study is on the quantitative determination of poly aromatic hydrocarbons (PAHs) in soil, water and biota (cassava plant) from the vicinity of Okobo coal field in Kogi state, Nigeria. It is hoped that this study will establish a background data or information on the priority organic pollutant in the Okobo environmental samples around the coal field.

3. Materials and Methods

3.1. Materials

Analytical grade reagents were used in this study. Instrument employed for analysis include GC-ECD, Hewlett Packard 7890A series II, and the scanning electron microscopy (Phenom ProX) used for surface morphology (SEM images, not presented) and the SEM-EDS for elemental analysis.

3.2. Sampling

The samples described in Table 1 were obtained as follows: water samples were collected at a depth of 2-10 cm at the water surface using a 1litre plastic container with a screw cap, with respect to the coal mining operation site. water samples were collected between 7 am and 10 am) in duplicates from 3 locations (50 cm upstream, midstream and downstream) with pre-cleaned glass bottles. The samples in 1-L amber bottles were adjusted to $\text{pH} < 2$ using 6 M of hydrochloric acid [12].

A documented sampling method for coal [13, 14] was carefully followed. A sample grid was established in which five samples of mass 20 g of coal was obtained from a split which was taken each 50 m away from the grid and then harmonized as one sample by means of a hand trowel and a hammer at the coal site. A gross sample of 60 g was obtained after homogenisation of the five samples. The gross coal samples were air-dried, milled and split carefully to obtain a representative 10 g sub-sample of particle size < 250 μm . The samples were labeled properly as Okobo harmonized coal sample (OHCS). Coal sample preparation involved crushing, screening and storage. In crushing of coal, samples were reduced to smaller sizes by mechanical means, followed by pulverising in a rotary mill. The powdered samples were passed through a 210 micron sieve to prepare a representative 50 g sub-sample for analysis [13]. The sample was tagged as Okobo coal (OC). Cassava samples were randomly collected as donations based on farm basket approach. Control samples for the duo (soil and cassava) were collected around Ogaji district of Ankpa LGA, following similar protocol. Control water sample is a commercial and registered potable water.

Table-1. Sampling Codes and Descriptions

S/N	Sample ID	Description
1	OC	Okobo coal
2	SS	Soil Sample
3	CSS	Control soil sample
4	WS	Water sample
5	CWS	Control water sample
6	CS	Cassava sample
7	CCS	Control cassava sample

3.3. PAH Analysis in Solid Samples

(i) Extraction and Clean-up of Samples: Extraction and clean-up were carried out according to QuEChERS method [15]. The milled sample was properly mixed and 2 g was weighed into a 50-mL centrifuge tubes. Anhydrous sodium sulphate (1 g) was added and mixed with the sample to absorb any moisture present. The sodium sulphate was previously heated at 650°C using oven (Lab. Hot air oven MRC LTD. 3566) for one hour and stored in a desiccator. The main extraction involved the addition of 20 mL of acetic acid–water–acetonitrile (1:5:94, v/v). The tube was closed and shaken vigorously by hand for 1 min. To induce phase separation and PAH partitioning, a buffer–salt mixture (consisting of 0.5 g sodium acetate and 3 g anhydrous MgSO_4) was added to the suspension. The tube was closed, shaken vigorously by hand for 1 min, and centrifuged for 5 min at 2500 rpm. The supernatant was carefully transferred into a flask. The residue was further extracted twice as described above. The solution was then transferred to a sample tube and reduced to about 1 ml under a gentle stream of nitrogen gas using a nitrogen evaporator at 36 °C.

The samples were cleaned up by using a column of about 15 cm (length) \times 1 cm (internal diameter) was packed first with glass wool and then with about 10 g activated silica gel prepared in a slurry form in acetonitrile. About 10 g of anhydrous sodium sulfate was placed at the top of the column to absorb any water in the sample or the solvent. Pre-elution was done with 30 mL of acetonitrile, without exposing the sodium sulfate layer to air, so as to prevent the drying up of the silica gel adsorbent. The reduced extract was run through the column and allowed to sink below the sodium sulfate layer. Elution was done with 3 \times 10 mL portions of the acetonitrile. The eluate was collected, dried with anhydrous sodium sulfate and evaporated to dryness under a stream of analytical grade nitrogen (99.99 %) for GC-ECD/MS analysis.

3.4. Standard Calibration

Stock solutions of the PAH were prepared and then serially diluted to produce different concentrations ranging from 0.5 to 10.0 $\mu\text{g/L}$. Stock standard solutions were stored in amber coloured bottles at 4°C in a refrigerator and working standard solutions were prepared fresh before use. Standard solutions of the PAH were run on GC-ECD/MS under the set chromatographic conditions and mean peak areas were plotted against concentrations to obtain calibration curves of the PAH.

3.5. Qualitative Identification and Quantitative Evaluation of the PAHs

The eluate was reconstituted with 1 mL 2, 2,4–trimethylpentane (isooctane). With the aid of a micro syringe, 1 μL of the 1.0 mL purified extract was injected into the injection port of a gas chromatograph coupled with a ^{63}Ni electron capture detector (GC-ECD, Hewlett Packard 7890A series II). The column consisted of a DB-17 fused silica capillary column (30 m \times 0.32 mm i.d. \times 0.25 μm film thickness). The temperatures of the injector and detector were 300 °C and 350 °C (held for 5 min), respectively. Oven temperature programme started from 80 °C (1 min) and continued at 25 °C/min to 180 °C and at 5 °C/minute to 280 °C held for 4 min injected sample volume was 1 μL . The injection was carried out on a splitless injector at 200 °C and the purge activation time was 30 s. The carrier gas was N_2 at 30 mL/min; and the splitless flow rate was 20.0 mL/min. The run time was 40 min. The individual PAHs were identified by comparing the elution time of standard PAH with those in the samples, while each PAH was quantified by comparing the peak areas of the PAHs in samples with those in standard.

$$E = (A_c/A_i) \times (Rf) \times C_i \quad (1)$$

where E = concentration of the selected compound in the sample extract, in Microgram per liter A_c = area of peak of the c quantitation ion for the selected compound; A_i = area of peak of the quantitation ion for the internal standard; RF = response factor calculated in equation. C_i = concentration of the internal standard in microgram per

liter. Concentrations in ug/g for solid sample can be obtained by using the expression; $C = (E \times 200 \mu L) / \text{sample weight}$.

3.6. Quality Control

Several quality control methods was employed include spiking of samples, use of internal and external standards, standard reference materials, control samples, sample blank.

4. Results and Discussion

4.1. Physical Inspection of Sites and Samples

The sampling sites for coal samples, cassava, soil and water samples were thoroughly surveyed. The physical outlay of cassava farm land from Okobo coal-mining areas physically shows varieties of stunted growth. Outburst of water from the coal mining regions in both downstream and upstream water samples from Okobo vicinity were well observed during sampling.

4.2. Elemental Composition of Coal

EDS analysis was carried out to determine the elemental composition of coal sample. Figures 2 3 4 are typical of EDS spectra of coal samples, coal vicinity soil sample and control soil samples respectively. Worthy of note is the pronounced peak representing carbon in the coal sample; Expectedly is that of silicon in soil samples (Figures 2 and 3)

Table 2 represents the elemental composition deduced from the Figures 2 3 4. Coal sample shows > 84% weight concentration of carbon. This is an indication that organic pollutants, including PAHs estimated within coal vicinity environmental samples could point to partial de-coalification via fragmentation, weathering and transport of constituents from coal deposit to the neighbouring environment. Availability of other element shown in Table 2 (Al, Si, Fe, Cr,S, P,K N, Na) further proved the impure nature of the coal samples.

Figure-2. EDX SEM Spectrum of Coal Sample from Okobo Coal Mine (Oxygen Disabled; focus is on carbon dominance)

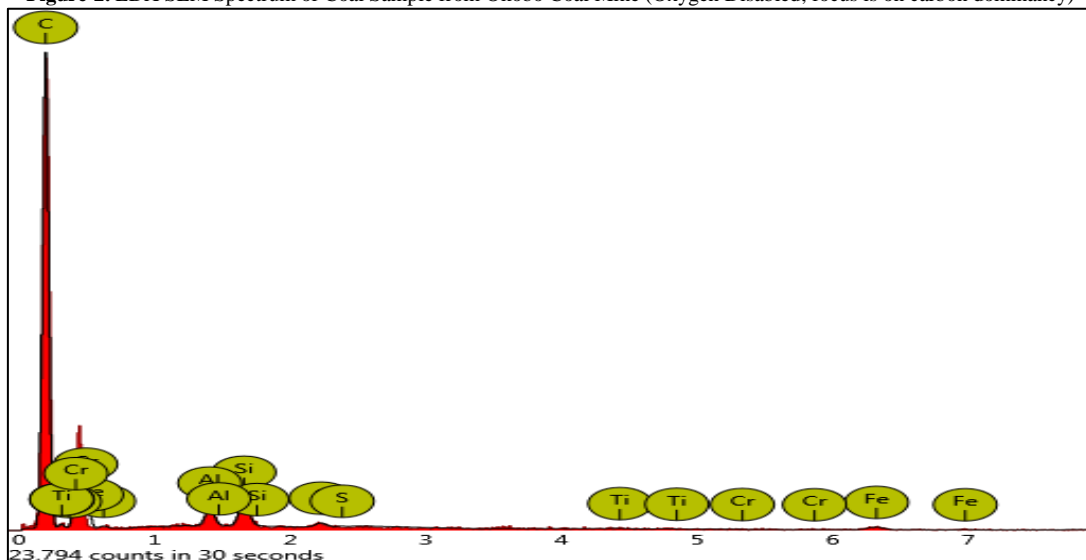


Figure-3. EDX SEM Spectrum of Homogenized Soil Sample within Okobo Coal Mine (Oxygen Disabled; Si dominates)

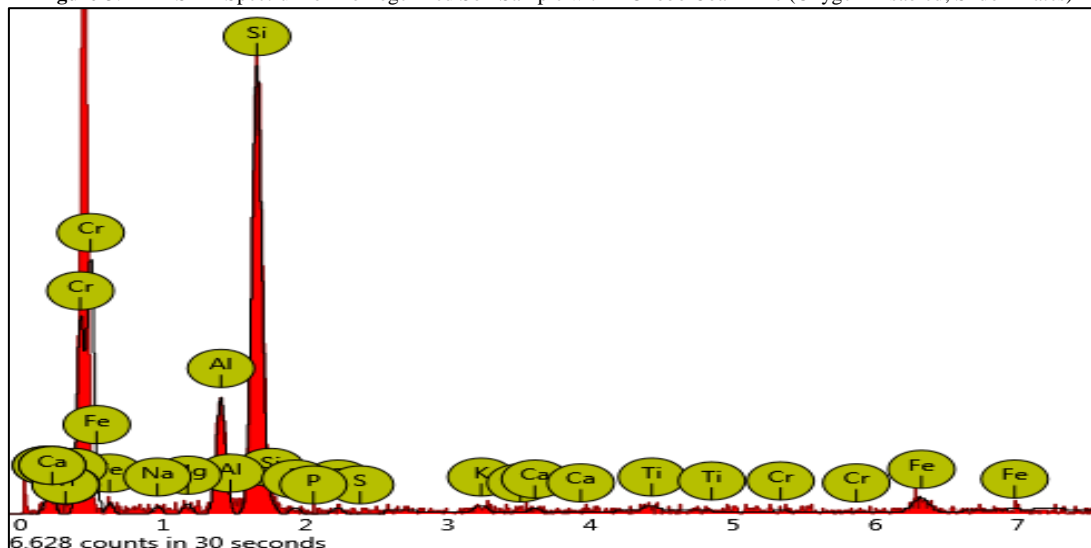


Figure-4. EDX SEM Spectrum of Soil Sample from Control Site (Oxygen Disabled; Si and V are pronounced)

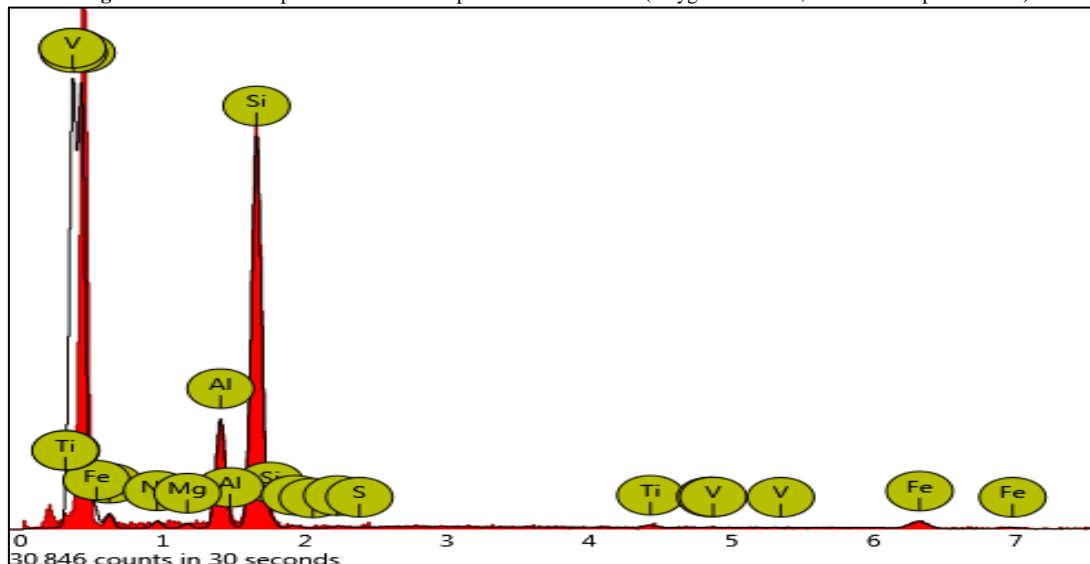


Table-2. Elemental Composition of Coal and Soil Samples Obtained from EDX Analysis

Elementa	Control soil ,		Soil within coal Mine		Coal sample	
	Atomic Conc.	Weight Conc.	Atomic Conc.	Weight Conc.	Atomic Conc.	Weight Conc.
Carbon	-	-	-	-	88.87	84.41
Nitrogen	-	-	-	-	9.01	9.98
Sodium	1.54	1.21	1.48	1.1	-	-
Magnesium	0.84	0.69	1.49	1.17	-	-
Aluminium	17.64	16.18	15.81	13.8	0.64	1.36
Silicon	72.6	69.31	66.04	60.03	0.91	2.03
Phosphorus	0.9	0.94	1.29	1.29	-	-
Sulphur	0.5	0.55	1.23	1.27	0.14	0.35
Potassium	-	-	1.38	1.75	-	-
Calcium	-	-	0.74	0.97	-	-
Titanium	0.82	1.33	1.25	1.93	0.04	0.15
Chromium	-	-	0.85	-	-	-
Iron	5.16	9.8	8.44	15.26	0.39	1.74

4.3. Polycyclic Aromatic Hydrocarbons (PAH) Analytical Samples

Figures 5 6 7 8 9 10 11 are typical of chromatograms of PAHs in the samples. More evident is the presence of both low and high molecular weight PAHs across the 2,3,4, and 5 membered ring PAHs in the coal sample. The six-member ring PAHs were not detected. The prevalence of PAHs as indicated by the prominent peaks were less for all the control samples and totally absent for control water sample. This points at the contributory role of Okobo coal to the bioavailability of PAHs in neighbouring environmental samples.

Tables 3 4 5 6 7 8 9 shows the quantitative representation of PAHs in the coal, soil, cassava (plant) and water samples with those of their respective control samples. For the coal sample, all (except the six-member ring) PAHs were within the limits of identification (LOI), detection (LOD) and quantification (LOQ). PAH value for anthracene (0.0213 ppm) is less than the USEPA Reference Dose (RfD) of 0.3 mg/kg/day [16]. Results were obtained at varying concentrations (in ppm) with the four-member ring chrysene (47.0%), leading the distribution. The general trend of the PAH load follows the order of tPAHs of coal (0.3781 ppm) > cassava (0.2398 ppm) > soil (0.2331) > water sample (0.1151 ppm) > control soil sample (0.0422 ppm) > control cassava sample (0.00398 ppm). PAHs were not detected in the potable and registered water sample used for control experiment.

4.4. Health Implication

The most significant endpoint of PAH toxicity is cancer. PAHs generally have a low degree of acute toxicity to humans. PAHs are carcinogens in existence, causing tumours in some organisms exposed to it even at microgram quantities [16]. The chrysene level in coal, was estimated at 0.0653 ppm (17.3%). This value poses no health threat since chrysene has been tagged as non-carcinogenic to human [9]. There is no production of chrysene as a pure product. Chrysene, like most other polycyclic aromatic hydrocarbons (PAHs), is however present in fossil fuels and derived products; human use of these products is one of the main source of chrysene in the environment [17]. The authors concluded that chrysene is a suspected carcinogen and has derived a human toxicological limit of 0.050 mg.kgbw/day. This value is based on a cancer risk of 10-4 per lifetime for non-threshold toxicity [18]. For inhalation toxicity, no individual TCA (Tolerable Concentration in Air) is available for chrysene while the relative carcinogenic potency of chrysene is set at 0.01 [18]. Next to chrysene is the four-member ring pyrene (0.0446 ppm) covering 11.8% abundancy. Most available five-member ring high molecular weight PAH include Benzo(k)

fluoranthrene (0.0421 ppm; 11.1%) and Benzo(b) fluoranthene (0.0324 ppm; 8.6%). These carcinogenic compounds were detected in Okobo soil at concentrations of 0.0277 and 0.025 ppm respectively. Their respective concentrations in Okobo cassava is 0.0297 and 0.0244 ppm. Benzo(k) fluoranthrene and Benzo(b) fluoranthene were not detected in Okobo water sample with reasons linked to instrumental detection limit, exposure of the shallow water and possible volatility. Benzo(b)fluoranthene is a known animal carcinogen while benzo(k)fluoranthene is possibly a human carcinogen [9].

Figure-5. GC-MS Chromatogram of PAHs in Okobo Harmonized Coal Sample

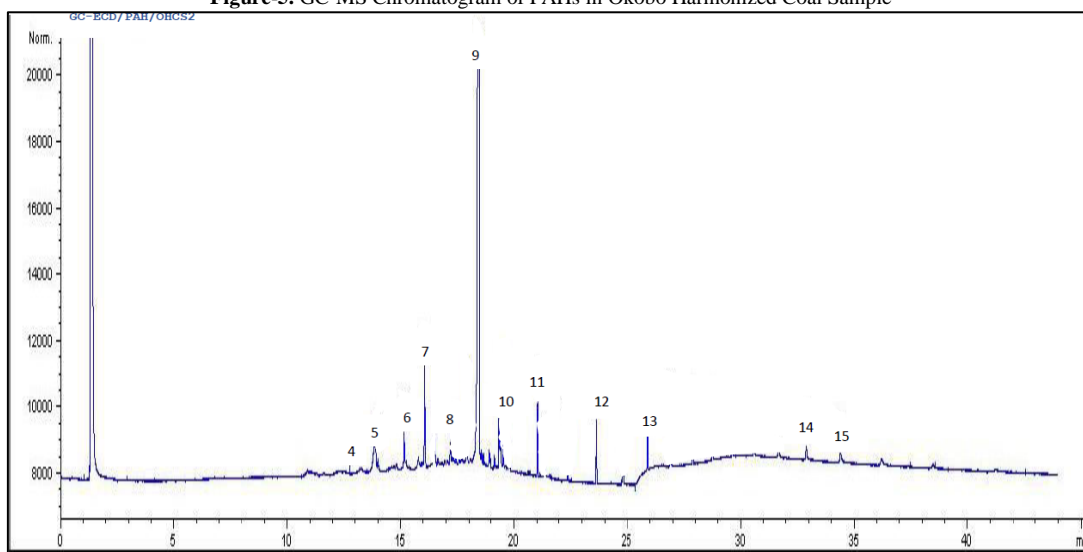


Figure-6. GC-MS Chromatogram of PAHs in Okobo Harmonised Soil Sample (OHSS)

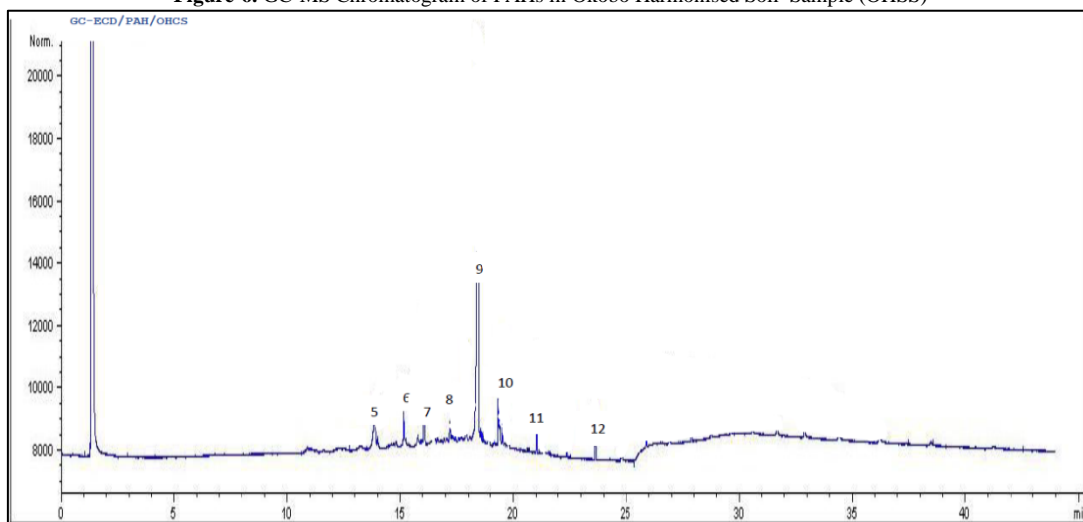


Figure-7. GC-MS Chromatogram of PAHs in Control Soil Sample

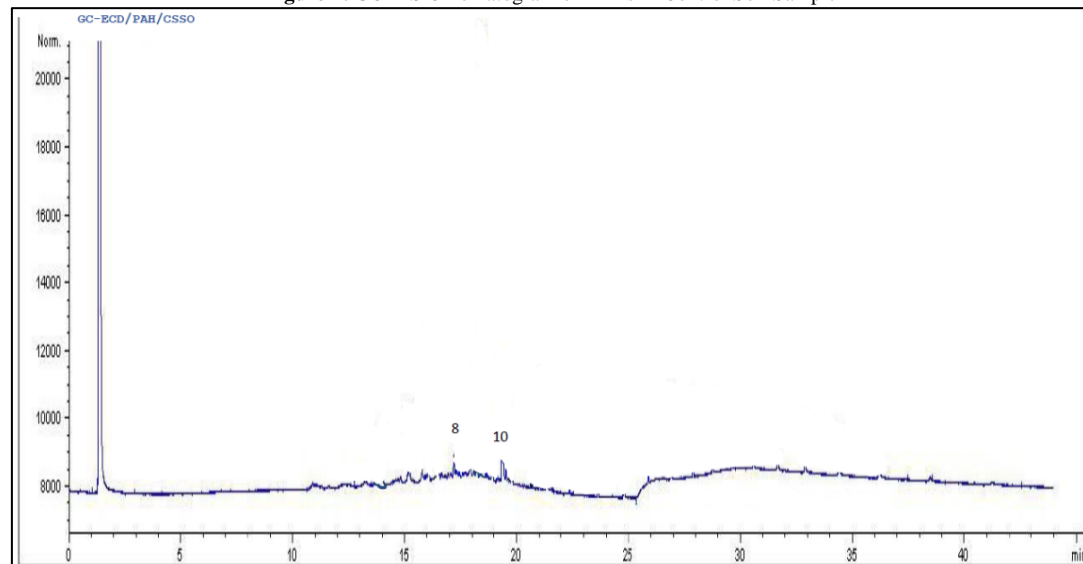


Figure-8. GC-ECD Chromatogram of PAHs in Okobo Harmonised Water Sample (OHWS)

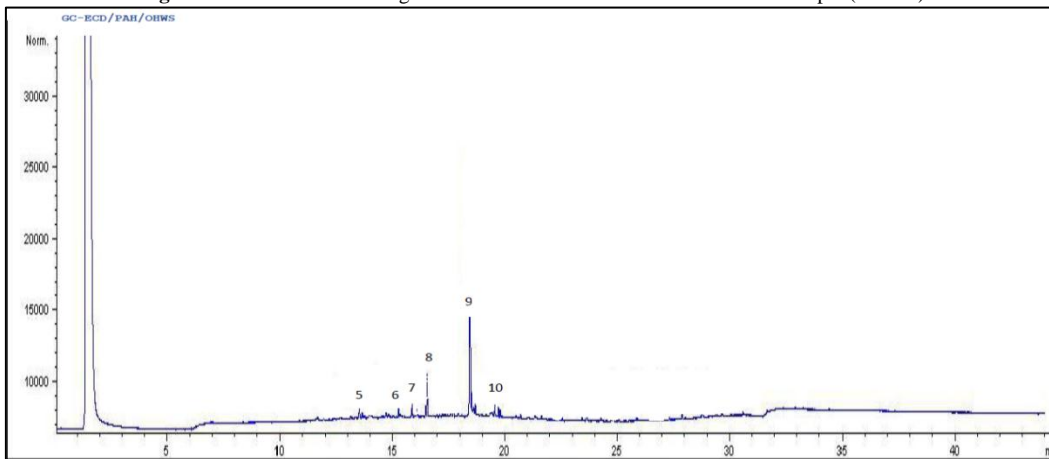


Figure-9. GC-ECD Chromatogram of PAHs in Control Water Sample

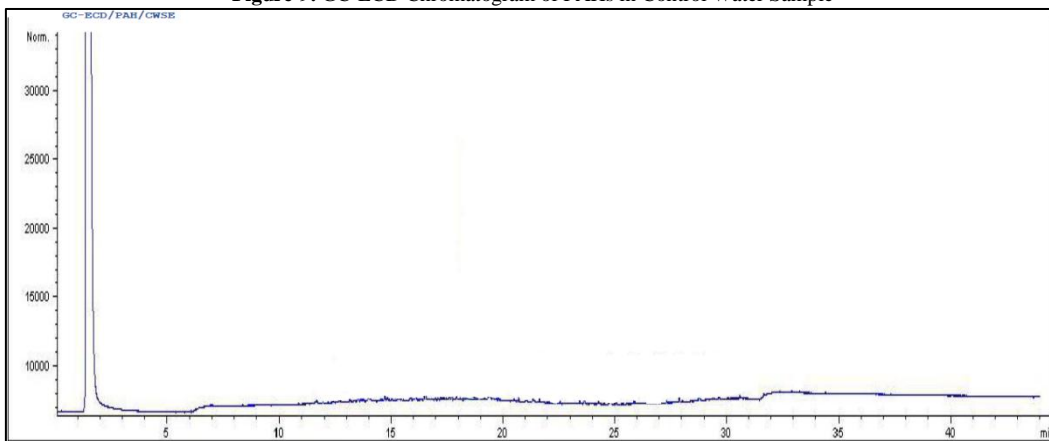


Figure-10. Typical GC-MS Chromatogram of Okobo Cassava Sample

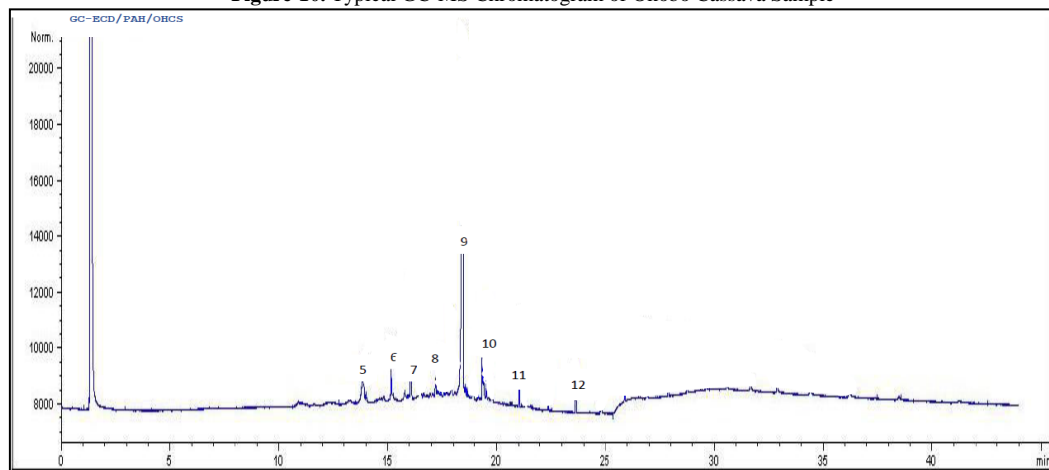


Figure-11. GC-MS Chromatogram of PAHs in Control Cassava Sample

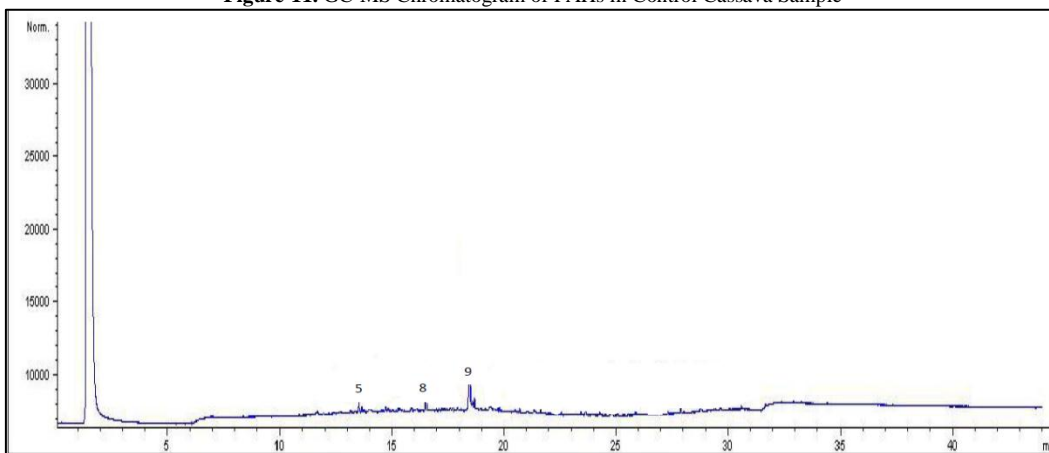


Table-3. Concentration of PAH (ppm) in Okobo Harmonised Coal Sample (OHCS)

S/No	PAH	Conc. (ppm)	Abundance (%)	No of Rings	∑PAHs in ppm (%)
	Two Membered Ring PAHs				
1	Naphthalene	0.0183	4.8	2	0.0183 (4.8)
	Three Membered Ring PAHs				
2	Fluorene	ND	0	3	
3	Phenanthrene	0.0432	11.4	3	
4	Acenaphthene	ND	0	3	
5	Acenaphthylene	ND	0	3	
6	Anthracene	0.0213	5.6	3	0.0645(17.1)
	Four Membered Ring PAHs				
7	Fluoranthene	0.0356	9.4	4	
8	Pyrene	0.0446	11.8	4	
9	Chrysene	0.0653	17.3	4	
10	Benzo(a)anthracene	0.0321	8.5	4	
				4	0.1776 (47.0)
	Five Membered Ring PAHs				
11	Benzo (k) fluoranthene	0.0421	11.1	5	
12	Benzo(b) fluoranthene	0.0324	8.6	5	
13	Benzo (a) pyrene	0.0216	5.7	5	
14	Dibenzo (a h) anthracene	0.0108	2.9	5	
15	Dibenzo(bc) fluoranthene	0.0108	2.9	5	0.1177 (31.1)
	Six Membered Ring PAHs				
16	Benzo(ghi) pyrene	ND	-	6	-
	tPAHs	0.3781			0.3781

Foot note: ND = Not Detected, OHCS2 = Okobo Harmonised Coal Sample

Table-4. Concentration of PAH (ppm) in Okobo Harmonised Soil Sample (OHSS)

S/No	PAH	Conc. (ppm)	Abundance (%)	No of Rings	∑PAHs in ppm (%)
	Two Membered Ring PAHs				
1	Naphthalene	ND	0	2	0 (0)
	Three Membered Ring PAHs				
2	Fluorene	ND	0	3	
3	Phenanthrene	0.0126	5.4	3	
4	Acenaphthene	ND	0	3	
5	Acenaphthylene	ND	0	3	
6	Anthracene	0.0132	5.7	3	0.0258 (11.1)
	Four Membered Ring PAHs				
7	Fluoranthene	0.0295	12.7	4	
8	Pyrene	0.0286	12.3	4	
9	Chrysene	0.0488	20.9	4	
10	Benzo(a)anthracene	0.0266	11.4	4	0.1335(57.3)
	Five Membered Ring PAHs				
11	Benzo (k) fluoranthene	0.0270	11.6	5	
12	Benzo(b) fluoranthene	0.0252	10.8	5	
13	Benzo (a) pyrene	0.0216	9.3	5	
14	Dibenzo (a h) anthracene	ND	0	5	
15	Dibenzo(bc) fluoranthene	ND	0	5	0.0738 (31.7)
	Six Membered Ring PAHs				
16	Benzo(ghi) pyrene	ND	-	6	-
	tPAHs	0.2331			0.2331

Foot note: ND = Not Detected, OHSS = Okobo, Harmonised Soil Sample

Table-5. Concentration of PAH (ppm) in Control Soil Sample Ogaji (CSSO)

S/No	PAH	Conc. (ppm)	Abundance (%)	No of Rings	∑PAHs in ppm (%)
	Two Membered Ring PAHs				
1	Naphthalene	ND	0	2	0 (0)
	Three Membered Ring PAHs				
2	Fluorene	ND	0	3	
3	Phenanthrene	ND	0	3	
4	Acenaphthene	ND	0	3	

5	Acenaphthylene	ND	0	3	
6	Anthracene	ND	0	3	0 (0)
	Four Membered Ring PAHs				
7	Fluoranthene	0.0196	46.4	4	
8	Pyrene	0.0226	53.6	4	
9	Chrysene	ND	0	4	
10	Benzo(a)anthracene	ND	0	4	0.422(100)
	Five Membered Ring PAHs				
11	Benzo (k) fluoranthene	ND	0	5	0 (0)
12	Benzo(b) fluoranthene	ND	0	5	0 (0)
13	Benzo (a) pyrene	ND	0	5	0 (0)
14	Dibenzo (a h) anthracene	ND	0	5	0 (0)
15	Dibenzo(bc) fluoranthene	ND	0	5	0 (0)
	Six Membered Ring PAHs				
16	Benzo(ghi) pyrene	ND	-	6	-
	tPAHs	0.0422			0.0422

Foot note: ND = Not Detected, CSSO = Control Soil Sample, Ogaji

Table-6. Concentration of PAH (ppm) in Okobo Harmonised Water Sample (OHWS)

S/No	PAH	Conc. (ppm)	Abundance (%)	No of Rings	∑PAHs in ppm (%)
	Two Membered Ring PAHs				
1	Naphthalene	ND	0	2	0 (0)
	Three Membered Ring PAHs				
2	Fluorene	ND	0	3	
3	Phenanthrene	0.0137	11.9	3	
4	Acenaphthene	ND	0	3	
5	Acenaphthylene	ND	0	3	
6	Anthracene	0.0120	10.4	3	0.0257 (22.3)
	Four Membered Ring PAHs			4	
7	Fluoranthene	0.0205	17.8	4	
8	Pyrene	0.0211	18.3	4	
9	Chrysene	0.0311	27.0	4	
10	Benzo(a)anthracene	0.0167	14.5	4	0.0894(77.7)
	Five Membered Ring PAHs				
11	Benzo (k) fluoranthene	ND	0	5	
12	Benzo(b) fluoranthene	ND	0	5	
13	Benzo (a) pyrene	ND	0	5	
14	Dibenzo (a h) anthracene	ND	0	5	
15	Dibenzo(bc) fluoranthene	ND	0	5	0 (0)
	Six Membered Ring PAHs				
16	Benzo(ghi) pyrene	ND	-	6	-
	tPAHs	0.1151			0.1151

Foot note: ND = Not Detected, OHWS = Okobo Harmonised Water Sample

Table-7. Concentration of PAH (ppm) in Control Water Sample, Eva Water (CWSE)

S/No	PAH	Conc. (ppm)	Abundance (%)	No of Rings	∑PAHs in ppm (%)
	Two Membered Ring PAHs				
1	Naphthalene	ND	-	2	0 (0)
	Three Membered Ring PAHs				
2	Fluorene	ND	-	3	
3	Phenanthrene	ND	-	3	
4	Acenaphthene	ND	-	3	
5	Acenaphthylene	ND	-	3	
6	Anthracene	ND	-	3	0 (0)
	Four Membered Ring PAHs				
7	Fluoranthene	ND	-	4	
8	Pyrene	ND	-	4	
9	Chrysene	ND	-	4	
10	Benzo(a)anthracene	ND	-	4	0 (0)
	Five Membered Ring PAHs				
11	Benzo (k) fluoranthene	ND	-	5	
12	Benzo(b) fluoranthene	ND	-	5	

13	Benzo (a) pyrene	ND	-	5	
14	Dibenzo (a h) anthracene	ND	-	5	
15	Dibenzo(bc) fluoranthene	ND	-	5	0 (0)
	Six Membered Ring PAHs				
16	Benzo(ghi) pyrene	ND	-	6	-
	tPAHs	Nil	0		0

Foot note: ND = Not Detected, CWSE = Control Water Sample (Eva Water)

Table-8. Concentration of PAH (ppm) in Okobo Harmonised Cassava Sample (OHCS1)

S/No	PAH	Conc. (ppm)	Abundance (%)	No of Rings	∑PAHs in ppm (%)
	Two Membered Ring PAHs				
1	Naphthalene	ND	0	2	0 (0)
	Three Membered Ring PAHs				
2	Fluorene	ND	0	3	
3	Phenanthrene	0.0314	13.1	3	
4	Acenaphthene	ND	0	3	
5	Acenaphthylene	ND	0	3	
6	Anthracene	0.0184	7.7	3	0.0498 (20.8)
	Four Membered Ring PAHs				
7	Fluoranthene	0.0297	12.4	4	
8	Pyrene	0.0334	13.9	4	
9	Chrysene	0.0444	18.5	4	
10	Benzo(a)anthracene	0.0284	11.8	4	0.1359 (56.7)
	Five Membered Ring PAHs				
11	Benzo (k) fluoranthene	0.0297	12.4	5	
12	Benzo(b) fluoranthene	0.0244	10.2	5	
13	Benzo (a) pyrene	ND	0	5	
14	Dibenzo (a h) anthracene	ND	0	5	
15	Dibenzo(bc) fluoranthene	ND	0	5	0.0541(22.6)
	Six Membered Ring PAHs				-
16	Benzo(ghi) pyrene	ND	-	6	
	tPAHs	0.2398			0.2398

Foot note: ND = Not Detected, OHCS1 = Okobo Harmonised Cassava Sample

Table-9. Concentration of PAH (ppm) in Control Cassava Sample, Ogaji (CCSO)

S/No	PAH	Conc. (ppm)	Abundance (%)	No of Rings	∑PAHs in ppm (%)
	Two Membered Ring PAHs				
1	Naphthalene	ND	0	2	0 (0)
	Three Membered Ring PAHs				
2	Fluorene	ND	0	3	0 (0)
3	Phenanthrene	ND	0	3	0 (0)
4	Acenaphthene	ND	0	3	0 (0)
5	Acenaphthylene	ND	0	3	0 (0)
6	Anthracene	0.0041	10.3	3	0.0041 (10.3)
	Four Membered Ring PAHs				
7	Fluoranthene	0.0115	28.9	4	
8	Pyrene	ND	0	4	
9	Chrysene	0.0242	60.8	4	
10	Benzo(a)anthracene	ND	0	4	0.0357 (89.7)
	Five Membered Ring PAHs				
11	Benzo (k) fluoranthene	ND	0	5	
12	Benzo(b) fluoranthene	ND	0	5	
13	Benzo (a) pyrene	ND	0	5	
14	Dibenzo (a h) anthracene	ND	0	5	
15	Dibenzo(bc) fluoranthene	ND	0	5	0 (0)
	Six Membered Ring PAHs				
16	Benzo(ghi) pyrene	ND	-	6	-
	tPAHs	0.0398			0.0398

Foot note: ND = Not Detected, CCSO = Control Cassava Sample, Ogaji

4.5. Ring Size Diagnostic Ratio and PAH Source Identification

Ring size distribution followed a decreasing order $4 > 5 > 3 > 2 > 6$ in the coal samples (Table 3). This shows that 4 rings PAHs were the most abundant whereas member 6 rings PAHs were not detected. Distribution of high molecular weight PAHs (HPAHs) and low molecular weight PAHs (LPAHs) were calculated by ratio to identify the possible sources of PAHs pollution in the estuary. The ratio $\Sigma\text{LMW}/\Sigma\text{HMW} > 1$ in coal sample (Table 10), implied that the concentration of the more toxic HPAHs was generally lower in the environment than the less toxic LPAHs, suggesting a dominant petrogenic input rather than the pyrolytic sources [12]. This was further verified.

Itodo, *et al.* [19], reported that the probable sources of environmental PAHs could be evaluated using diagnostic ratio reported [20] and presented in Table 10. Lower-molecular-weight (LPAHs) is characterized by the predominance of 2- 4 membered ring PAH. They are known with high volatility, with higher risk of mobility than HPAHs with less volatility, owing to the heavier weight. Okobo coal is majorly diagnosed as majorly petrogenic. Petrogenic contamination is characterized by the predominance of the lower-molecular-weight (LPAHs) PAHs as evident in Table 3 and verified in Table 10. On the other hand, pyrolytic contribution generated mainly through incomplete combustion of organic matter at carbonation temperatures (within 400 degrees) characterized by high-molecular-weight PAHs 5-6 benzenoid ring is low in the study area.

Table-10. Diagnostic ratio of PAHs [22,23]

PAHs Ratio	scale	Origin (source)	PAH source for coal (current study)
PHen/ANth	<10	Pyrogenic	Pyrogenic
LPAH/HPAH	>1	Petrogenic	Petrogenic
Pyr<Flth	-	Pyrogenic	Petrogenic
FLth>PYr	-	Pyrogenic	Petrogenic
PYR/FLth	>1	Petrogenic	petrogenic
BaA/(BaA +CHR)	<0.2	Petrogenic	pyrogenic
ΣLPAH	abundant	Petrogenic	Petrogenic

Generally, the main source of the PAHs in the coal is petroleum derived. Values obtained in the vicinity environmental samples (soil, water and plants) could be linked to a drift of these PAHs from the coal deposits.

5. Conclusions

Highlights from this study informed that Okobo coal has a verified role in the bioavailability of Polycyclic Aromatic Hydrocarbons in soil, water and cassava samples. The high level of PAHs in cassava sample has a link with its adsorbent nature as common to soft tissues. Results revealed mixed contributory sources with petrogenic dominancy by the four membered ring Chrysene. Overall results indicated values that are within the acceptable legislative thresholds.

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