

Polycyclic Aromatic Hydrocarbons (PAHs) and Carcinogenic Polycyclic Aromatic Hydrocarbons (cPAHs); Implications for Groundwater and Stream qualities around Mamu Coal Exposure in Okaba-Odagbo Mining District, Ankpa, North-Central Nigeria

O. C. Adeigbe*, and A. A. Rahaman

Department of Geology, University of Ibadan, Nigeria

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Abstract

Some selected water and coal samples were picked from Mamu Formation, Anambra Basin at Okaba-Odagbo, Nigeria. This was with a view to carry out the lithologic description, geochemical characteristics of the coal and to determine the quality assessment of groundwater and stream samples as related to Polycyclic Aromatic Hydrocarbons (PAHs) and Carcinogenic Polycyclic Aromatic Hydrocarbons (cPAHs). The methodologies employed include field study relationship, proximate and ultimate analyses and Gas Chromatography-Mass Spectrometry (GC-MS) analysis.

Lithologic description shows that the coal is underlain by grey to black shale and overlaid by carbonaceous shales, sandy shales, silty shales, siltstone, mudstone in that order. The proximate and ultimate analyses indicate 3.60% moisture, 2.93% ash, 23.66% volatile matter, 69.82% fixed carbon, 90.09% organic carbon, 2.22% hydrogen, 2.77% oxygen, 0.42% nitrogen, 0.34% sulphur, 2.7 free swelling index and 7368kcal/kg heating value respectively. Thus showing the coal to be a non-coking, medium quality and sub-bituminous but suitable for electric power generation, domestic fuel and raw material for chemical and plastic industries but not suitable in steel industry and blast furnace for iron smelting. The total concentrations of the 15 PAHs detected around the mine site were in the range of 16.82-17.28µg/L, with total concentration of cPAHs ranged between 10.13-10.23µg/L which accounted for 59.20-60.70% of the total PAHs from the mine ponds; while the total amounts of the 15 detected PAHs from Omaji-oda stream was 16.93µg/l with cPAHs of 10.20µg/L which represented 60.25% of the total PAHs of the sample. Concentrations of PAHs in water samples are higher than WHO (2.00µg/L) standard, Standard Organization of Nigeria (SON) standard (7.00µg/L) and European Union (0.10µg/L) for PAHs in water. The higher concentrations values of high molecular weight (HMW) PAHs compare to low molecular weight (LMW) PAHs makes degradation of PAH difficult. This is because of their affinity for particulate matter due to decreasing bioavailability and higher hydrophobicity/toxicity plus longer environmental persistence. Using diagnostic ratios HMW/LMW, the source of PAHs into the surface water is believed to be pyrogenic and could be attributed to the coal mining activity in the community. Also, possible continuous erosion and drains from the coal mine field (acid mine drainage) into the stream could possibly heighten the level of PAHs/cPAHs concentration in the stream.

Keywords: Longer environmental persistence; Bioavailability; High molecular weight- PAHs and Low molecular weight- PAHs, Okaba-Odagbo.

1. Introduction

Coal is a fossil fuel extracted from ground by mining. From mining to coal cleaning, from transportation to electricity generation to disposal, coal releases numerous toxic pollutants into the environment which possibly endanger animals, plants and affects human health. Some cause cancer, others damage the nervous and immune systems, and some impede reproduction and development [1]. Environmental and health impacts arise from blowing coal dust, acid mine drainage into potable water. Over the past few decades, the world has become wary of coal mining and combustion because of concern about pollutants released into the environment. Polycyclic aromatic hydrocarbons (PAHs) refers to a large class of organic compounds composed of carbon and hydrogen atoms arranged in form of two or more fused aromatic

rings in various arrangements [2-3]. PAHs are ubiquitous pollutants frequently found in a variety of environments such as food, water, air, soil, sediments; they have been documented to cause several health problems [4] and are detrimental to the environment when they exceed the threshold limit [5]. They are introduced into the environment by natural and anthropogenic sources [6]. PAHs along with other toxic pollutants can be leached from coal into water supplies (e.g. groundwater or stream) due to erosion thereby reducing the quality of water by rendering water unsafe and non-potable, as many PAHs are known carcinogens, mutagens and teratogens [7].

Several agencies including the United States Environmental Protection Agency [3,8], World Health Organisation (WHO) and California Environmental Protection Agency [9] classified sixteen PAHs as priority pollutants and monitor them due to health concerns: naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, fluoranthene, pyrene, benzo[*g,h,i*]-perylene, chrysene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*cd*]pyrene and dibenz[*a,h*]anthracene. These 16 PAHs are unsubstituted, very small subset of a much larger suite of unsubstituted and substituted PAHs. PAHs known for their carcinogenic properties based on the available evidence are: benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene and indeno(1,2,3-*cd*)pyrene [8,10] PAHs are classified into Low Molecular Weight (LMW) with two or three fused rings and High Molecular Weight (HMW) with four or more fused rings [11]. LMW-PAHs are more susceptible to degradation and volatilisation compared to the HMW- PAHs [5]. As molecular weight increases, hydrophobicity/lipophilicity increases, water solubility decreases, vapour pressure decreases [12-13]. Studies have also shown that the strong adsorption capacity that PAHs have for particulate matter contributes largely to the recalcitrance of PAHs, which in turn significantly reduces their bioavailability for degradation [14]. Human exposure to PAHs includes ingestion, inhalation and dermal contact in both occupational and non-occupational settings, the lipophilic nature of PAHs makes it easier to penetrate biological membranes and accumulate in organisms. The study area, Okaba district is a rural community in central region of Nigeria, is located between latitudes 7°23'31.1"N - 7°30'01"N and longitudes 7°42'05"E - 7°44'65"E, on the outskirts of Okaba (Figs 1 and 2) in North-Central region of Nigeria where coal mining had been a central socio-economic concern for over forty years, Odagbo is the host community to the coal mine [16].

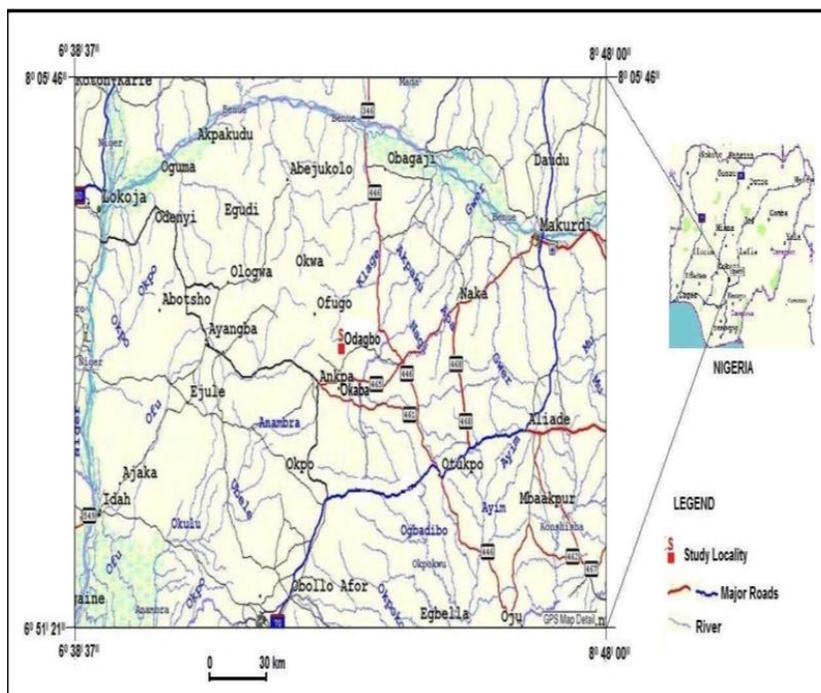


Figure 1. Location map of Odagbo coal mine [15]

THICKNESS (Meters)	Lithology			Description	Depositional Environment
	Fine	Medium	coarse		
2.0	[Hatched pattern]			Overburden	Fluvial or fluvio-deltaic
4.1	[Dotted pattern]			Reddish ironstone capping	
	[Dotted pattern]			Ferruginised thinly laminated white sandstone with channel flow presence	
14.1	[Dotted pattern]			Mudstone intercalated with sandstone	Fluvial/Upper deltaic
15.4	[Dotted pattern]			Massively bedded fine grained sandstone	
17.9	[Dotted pattern]			Yellowish brown massively bedded siltstone	
21.5	[Dotted pattern]			Parallel laminated dark grey shale with an erosional surface	Lagoonal/Marshly marine
23.9	[Dotted pattern]			Wavy laminated light grey silty shale (heterolithic)	
25.1	[Dotted pattern]			Sandy shale	
25.5	[Dotted pattern]			Shale with presence of organic matter	Raised bog/Swamp
26.0	[Solid black]			Coal	
28.1	[Dotted pattern]			Shale	Marine
28.7	[Dotted pattern]				

Fig 2. Litho-log of the Okaba-Odagbo coal field section

It extends north-westward into the Niger Valley, directly overlies the Basement Complex and interfingers with the Bida Basin; northward to the Jos massif and north-eastward into Lafia [22].

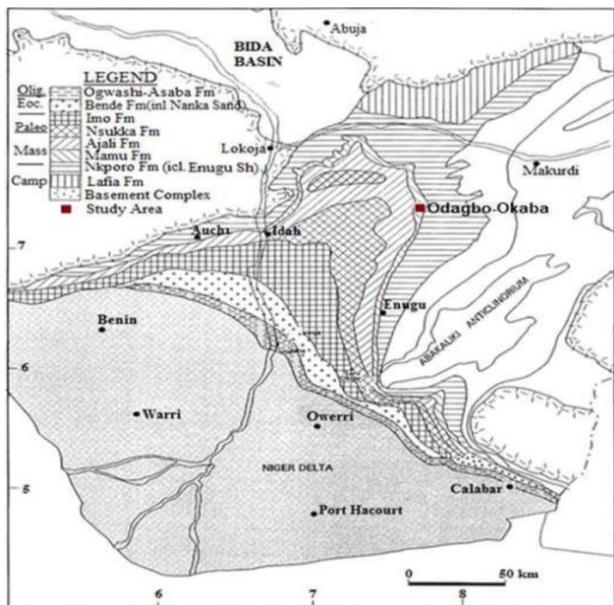


Fig. 3. Geological map of Anambra Basin showing the study area [17]

The area falls within the Anambra Basin (Figure 3) which is a structural (synclinal) depression and one of the intracratonic basins in Nigeria whose genesis has been linked with the development of the Niger Delta Miogeosyncline and the opening of the Benue Trough, [18]. It is a nearly triangular shaped embayment covering about 3000sqKm with a total sedimentary thickness of approximately 9 km [19-20]. Anambra basin is an Upper Cretaceous sedimentary basin situated west of the Lower Benue Trough and often considered newest formation from the Benue Trough [21]. The basin is bounded to the south by the Niger Delta Basin hinge line and southwesterly direction by the

Anambra Basin is generally considered a sedimentary succession that directly overlies the facies of the Southern Benue Trough and consists of post-deformational Campanian-Maastrichtian to Eocene lithofacies. It is characterized by enormous lithologic homogeneity in both lateral and vertical extensions derived from a range of paleoenvironmental settings, [23]. Sedimentation in the Anambra Basin commenced during the Campanian, with marine and paralic shales of the Enugu and Nkporo Formations and the fluvio-deltaic Owelli Sandstone which are regarded as the Nkporo Group. The Campanian was a period of short marine transgression and regression, the shallow-sea later became shallower due to subsidence, thereby resulting in a regressive phase during the Maastrichtian which deposited the flood

plain sediments and deltaic foresets of Mamu Formation that was regarded as the Lower Coal Measures. Mamu Formation is overlain by the fluvio-deltaic Ajali Sandstone, marine shales of Nsukka and Imo Formations were deposited in the Paleocene and overlain by the tidal Nanka Sand of the Ameki Group of the Eocene in that order. The regulatory framework to mitigate mining impacts including pollution had been weakly defined coupled with ineffective enforcements by the Ministry of Solid Minerals and Inspectors of Mines, especially at the rural settlement level. Coal mining activities which includes extracting, loading and transportation might have interfered with traditional livelihood activities (mainly farming) and causing environmental degradation. At present, no known data is available on the occurrence and sources of polycyclic aromatic hydrocarbons (PAHs) in Odagbo coal environment. Hence, the purpose of this study, to determine the concentration of PAHs in the groundwater (coal mine ponds) and

water of the Omaji-oda/Aji-Achokpa stream; compare to the standard maximum permissible level from different agencies, and to determine the source(s) of PAHs in the stream. Also included is the insitu determination of the physicochemical properties of water samples obtained from the sampling points and examine geochemical parameters of Okaba-Odagbo coal deposit in order to elucidate on its best application for use.

2. Materials and methods

The field work afforded the collection two sets of samples; water and sediment (coal). Water samples were collected at random from groundwater (mine ponds) and Omaji-Oda stream, close to the mine field in Okaba-Odagbo community (Figure 4) with geographical coordinates of all locations taken using Global Positioning System (GPS) (Figure 5).

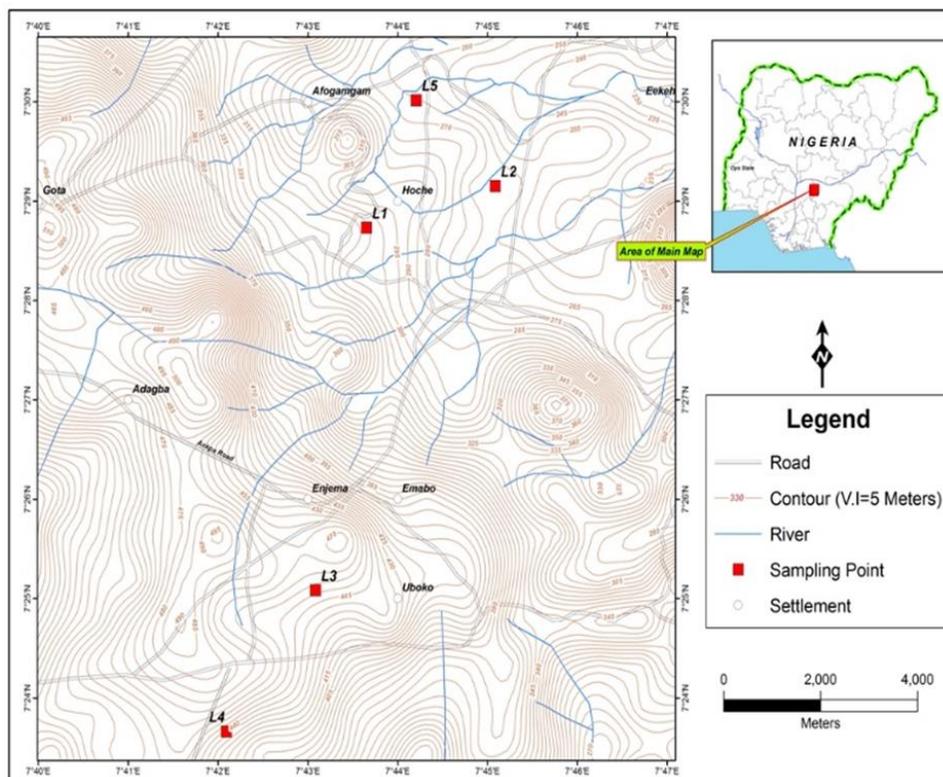


Fig. 4. Map of the study area showing the sampling points

The water samples were collected below the water surface in tinted 1litre amber glass bottles to protect samples from light (in order to minimize photolytic decomposition), fitted with a screw cap lined with Teflon to prevent leaking. Physiochemical parameters measurements were carried out in the field, the samples were measured on-site by probe method to determine temperature (using thermometer), pH, total dissolved solids (TDS) and conductivity (EC) were measured using a standard Milwaukee pH/EC/TDS combo mini-bench metre. Each bottle was carefully placed in a cooler filled with dry ice so as to preserve it before taking to the Geo-Environmental Research Centre (GRC) Laboratory (Basel Convention Coordinating Centre), University of Ibadan for further analyses. Six coal samples were taken following standard procedures around the coal mine from the coal seams (in-situ), run-off-mine and mine pond, the samples were carefully labeled and bagged in airtight polythene bags prior to various geochemical analyses.



Fig. 5. The exposed section of the Okaba-Odagbo coal seam (illegal miners)

The laboratory analytical work was carried out at the Agronomy Laboratory, University of Ibadan, Oyo state; the analytical determinations were done according to American Standard Testing Method [24-25] and the Kjeldahl method (nitrogen). The variables analyzed included

the organic carbon, hydrogen, nitrogen, and oxygen contents as well as heating value, all of which constitute the ultimate analysis. The proximate analysis included moisture content, ash content and the volatile matter.

2.1. Water sample extraction and cleanup

Liquid-liquid extraction was used to extract liquid samples. 200 mL of liquid sample was first filtered through filters paper to remove suspended particles and was transferred into a separating funnel. 20 mL of 1:1 hexane and dichloromethane was added and shaken for 20 minutes. The phases on the water samples were separated. The extraction was done twice and extract was pooled together into a beaker. Packed silica gel column was used for the clean-up. The extract was loaded on the silica gel and eluted with 10 mL n-hexane and then concentrated. The cleaned extract was injected into the GC-MS for the determination of PAHs.

2.2. Instrument condition for PAHs

Gas Chromatography Mass Spectrometry analyses (GC-MS) were carried out on an Agilent Technologies 7890 A equipped with 5975 MSD. Separations were achieved using a HP-5ms Capillary column (30 m by 0.32 mm internal diameter, 0.25 μm film thickness). The oven temperature was programmed at 60°C for 1 minute, ramped to 200°C at a rate of 5°C per minute and held at this temperature for 1 minute. Then ramped to 250°C at a rate of 2°C per minute and held at this temperature for 1 minute. Then ramped to 280°C at a rate of 10°C per minute and held at this temperature for 5 minutes. Then ramped to 290°C at a rate of 10°C per minute and held at this temperature for 5 minutes. The samples were injected in splitless mode, injection volume of 1.0 μL with an injection temperature of 290°C. Helium gas (at a flow rate of 1.2 mL/min) was used as a carrier gas. Data acquisition was in electron impact and the MS mode used was selected ion monitoring (SIM) mode with a MSD Transfer line temperature of 300°C. Characteristic ions were selected for each compound, which together with their retention times, allowed for their identification in SIM mode. Before analysis, relevant standards (reference mixture of PAHs) were run to check column performance, peak height and resolution. With each set of samples to be analyzed, a solvent blank and a standard mixture were run in sequence to check for contamination, peak identification and quantification. Results are expressed in $\mu\text{g/L}$.

2.3. Coal sample preparation and analysis

Two methods of analytical approach were used. These are the Proximate and Ultimate analyses. The Ultimate analysis allows for the determination of all coal component elements, solid or gaseous while the proximate analysis determines only the fixed carbon, volatile matters, moisture and ash percentages. The ultimate analysis is determined in a properly equipped laboratory by a skilled chemist, while proximate analysis can be determined with simple apparatus. However, both the proximate and ultimate analyses must follow the standard procedure of this analysis; for this study, the American Society for Testing and Materials (ASTM D3174-76) standards were used [24-25]. The percentage Nitrogen was analysed chemically using Kjeldahl technique using the official method of analysis described by the Association of Official Analytical Chemist (AOAC) [26]. The approach consists of three techniques namely digestion, distillation and titration [26].

3. Results and discussion

3.1. Physiochemical parameters of the water samples collected

The results of the in-situ measurements of the physiochemical parameters of the water samples collected from the mine ponds in the Okaba-Odagbo coal field and Omaji-oda stream of Ankpa L.G.A in the North Central Nigeria are presented below (Tab. 1). The sampling sites including that of L₅ (Omaji-oda stream) had pH level fall slightly below the WHO and SON) recommended range value of 6.5 – 8.5 [3,27] (Table 1), this is included in the category of weak acid. The value of the pH in stream water falling below the recommended value could be

attributed to acid rain or erosion of acid mine water into the stream from the coal mine. Conductivity value for samples, L₁, L₂, L₃ and L₄ collected from the mine ponds are above WHO maximum contaminant level of 1000 μscm^{-1} [27] (Table 1); that of the stream, L₅ was way below the maximum contaminant level. However, the high conductivity level in the mine pond mentioned could obviously be linked to the coal mining activity. Total Dissolved Solids (TDS) was also analyzed and it shows TDS values way above WHO, USEPA, SON and EU maximum allowable concentration of 500ppm while that of the stream was much below the maximum allowable concentration (Table 1). Based on taste, TDS>500ppm results in excessive scaling in water pipes, water heaters, boilers and appliances such as kettles and steam irons; while water with extremely low concentrations of TDS may also be unacceptable to consumers because of its flat, insipid taste; it is also often corrosive to water-supply systems [29]. Although conductivity and TDS level was way below maximum contaminant set by WHO in the stream, continuous acid mine drainage with no neutralization along its flow path could introduce the high TDS-Conductivity infused water of the mine ponds into the groundwater and surface water, this in turn could affect the drinking water from nearby streams, rivers or wells in the community.

Table 1. Physiochemical parameters of the water samples collected

Samples	Temperature (°C)	pH	Conductivity ($\mu\text{S/cm}$)	Total dissolved solids (ppm)
L ₁ (Mine pond)	30.00	6.2	1310	660
L ₂ (Mine pond)	33.00	6.1	1550	1050
L ₃ (Mine pond)	35.00	6.2	1950	1310
L ₄ (Mine pond)	36.10	6.2	2120	1460
Mean+S.D	33.53±2.68	6.18±0.05	1732.5±369.36	1120±350.33
L ₅ (Omaji-oda stream)	31.50	6.2	40	0020
WHO	-	6.5-8.5	1000	500
SON	-	6.5-8.5	-	500

WHO-World Health Organization standards [2]; SON- Standard Organization of Nigeria standards [28]

3.2. Polycyclic aromatic hydrocarbons (PAHs) concentrations

Fluoranthene and benzo(g,h,i)perylene were below detection limit; acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, benz(a)anthracene, benzo(b)fluoranthene, chrysene, benzo(k)fluoranthene, benzo(a)pyrene, indeno(1,2,3-cd) pyrene, dibenz(a,h)anthracene (13 of 16 unsubstituted priority PAHs), and 1-methylnaphthalene and 2-methylnaphthalene (2 of naphthalene-related compounds/alkyl PAHs) were detected at various concentrations (Table 2). Surface water pollution is unequivocally one of the major environmental problems confronting both urban and rural communities in Nigeria [32]. In the Okaba-Odagbo community, this situation is further accentuated by inputs from the coal mine within the region. The present study looked at the risks in terms of the levels of PAHs in the mine ponds and that of the surface water (Omaji-oda stream). The total concentration of PAHs from each is substantially higher than the PAH permissible guideline value for WHO, SON and EU (Table 3). The high levels of PAHs recorded in surface water in Okaba-Odagbo community poses a threat to the health risks for the people in this community. According to WHO [2], exposure to water containing PAHs could predispose the population to symptoms such as nausea, vomiting, and convulsions after one to several days, and often followed by diarrhoea. Lengthy and concentrated exposure to water containing high amount of PAHs may cause negative health effects which include decreased immune function, cataracts, kidney and liver damage (e.g., jaundice), breathing problems, asthma-like symptoms, lung function abnormalities. Meanwhile, repeated contact with skin may induce redness and skin inflammation [33]. It is observed that HMW-PAH compounds (4-6 rings) were found in concentrations almost twice higher than LMW-PAHs (2-3 rings).

Table 2. Concentrations of PAHs ($\mu\text{g/L}$) in water from Okaba-Odagbo coal mine pond and Omaji-oda stream

PAHs	L ₁ (Mine pond)	L ₂ (Mine pond)	L ₃ (Mine pond)	L ₄ (Mine pond)	L ₅ (Omaji-oda stream)
1-Methylnaphthalene	0.95	0.93	0.92	1.32	1.05
2-Methylnaphthalene	0.47	0.45	0.51	0.72	0.65
Acenaphthylene	0.53	0.53	0.53	0.53	0.53
Acenaphthene	0.45	0.46	0.45	0.46	0.45
Fluorene	0.74	0.75	0.76	0.71	0.71
Phenanthrene	1.29	1.24	1.29	1.12	1.14
Anthracene	1.27	1.23	1.26	1.16	1.17
Fluoranthene	BDL	BDL	BDL	BDL	BDL
Pyrene	1.05	1.02	1.04	1.03	1.03
Benz(a)anthracene	1.42	1.42	1.42	1.42	1.42
Chrysene	1.30	1.30	1.30	1.30	1.30
Benzo(b)fluoranthene	1.40	1.40	1.40	1.41	1.40
Benzo(a)pyrene	1.42	1.42	1.34	1.42	1.42
Benzo(k)fluoranthene	1.37	1.37	1.37	1.37	1.37
Indeno(1,2,3-cd)pyrene	1.52	1.52	1.52	1.52	1.51
Dibenz(a,h)anthracene	1.78	1.78	1.78	1.79	1.78
Benzo(g,h,i) perylene	BDL	BDL	BDL	BDL	BDL
Σ PAHs	16.96	16.82	16.89	17.28	16.93
Σ LMW PAHs	5.70	5.59	5.72	6.02	5.70
Σ HMW PAHs	11.26	11.23	11.17	11.26	11.23
Σ Carcinogenic PAHs* (cPAHs)	10.21	10.21	10.13	10.23	10.20
% Carcinogenic PAHs (cPAHs)	60.20	60.70	59.98	59.20	60.25

- Carcinogenic PAHs*: Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Chrysene, indeno[1,2,3-cd] pyrene, Dibenz[a,h]anthracene
- BDL- Below Detection Limit
- LMW PAHs: 1-Methylnaphthalene, 2-Methylnaphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene
- HMW PAHs: Fluoranthene, Pyrene, Benz(a)anthracene, Chrysene, Benzo(b)fluoranthene, Benzo(a)pyrene, Benzo(k)fluoranthene, Indeno(1,2,3-cd)pyrene, Dibenz(a,h)anthracene, Benzo(g,h,i) perylene

Table 3. Showing the total concentrations of 15 PAHs with some known standards

Samples	$\mu\text{g/L}$					% cPAHs
	Σ PAHs	SON	WHO	EU	Σ cPAHs	
L ₁ , L ₂ , L ₃ , L ₄ (Mine ponds)	16.82-17.28				10.13-10.23	59.20-60.70
L ₅ (Omaji-oda stream)	16.93	7.00*	2.00*	0.10*	10.20	60.25

SON-Standard Organization of Nigeria [28]; WHO-World Health Organization [30]; EU-European Union [31]; *-Standard values for PAHs in water

Generally, the higher the molecular weight of a PAH molecule, the higher the hydrophobicity and toxicity, and the longer the environmental persistence of such a molecule [34-35]. Hence, the high concentration of HMW-PAHs makes it difficult for degradation to take place due to their affinity for particulate matter which decreases their bioavailability. All the cPAHs namely: benzo(a)pyrene, benz(a)anthracene, benzo(b)fluoranthene, chrysene, benzo(k)fluoranthene, dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene were detected at various concentrations. The total concentration of cPAHs and their percentages for both the mine ponds and Omaji-oda stream are shown in Tables 2 and 3. USEPA, as a regulatory agency, sets a maximum contaminant level (MCL) for carcinogenic PAHs for ambient water quality criteria to protect human health from the carcinogenic effects of PAH exposure (Table 4). From Table 4, it can be seen that the seven cPAHs highly exceed each of their set maximum contaminant level,

which is high enough to cause harmful effect to various organs in the body and may cause cancer (skin, lung, bladder, colorectal and gastrointestinal) [36] which also depends on mode of exposure [37]. Reactive metabolites of some PAHs bind to cellular proteins and DNA [38], the resulting biochemical disruptions and cell damage lead to mutations, developmental malformations, tumors, and cancer [39].

Table 4. U.S. Environmental Protection Agency (USEPA) maximum contaminant level for carcinogenic PAHs in water and cPAH concentrations in Omaji-Oda Stream

PAHs	Maximum Contaminant Level (µg/L) (USEPA)	Concentrations of cPAHs in Omaji-oda stream (µg/L)
Benz(a)anthracene	0.1	1.42
Benzo(a)pyrene	0.2	1.42
Benzo(b)fluoranthene	0.2	1.40
Benzo(k)fluoranthene	0.2	1.37
Chrysene	0.2	1.30
Dibenz(a,h)anthracene	0.3	1.78
Indeno(1,2,3-c,d)pyrene	0.4	1.51

3.3. Source identification of PAHs in Omaji-oda stream

To discern the sources of PAHs, various researchers [40-42] have used the diagnostic or fingerprint ratios of different PAHs, such as phenanthrene/anthracene (Phe/Ant), benz(a)anthracene/chrysene {B(a)A/Chry} and fluoranthene/pyrene {Fl/Py}, these ratios have been calculated to evaluate both petrogenic and pyrogenic (pyrolytic) origin of PAHs [40,43-44]. In general, no more than two criteria are used to determine possible sources because of different and ambiguous interpretation of the results [45]. In this study, the HMW PAHs are more than the LMW PAHs which suggests pyrogenic origin. It is also taken that when the standard value for LMW/HMW ratio is less than 1, it indicates a pyrogenic source and when the ratio is greater than 1, it suggests petrogenic sources [46]. From Table 5, the diagnostic ratios indicate that the source of PAH concentration in Omaji-oda stream is of pyrogenic origin which could be attributed to the coal mining activity in the community. Continuous erosion and leakage of water from the coal mine field (acid mine drainage) into the stream could heighten the level of the PAHs/cPAHs in the stream, not to forget that this stream is used in day to day activities such as drinking, cooking, washing and bathing in the Okaba-Odagbo community.

Table 5. Diagnostic PAH ratios in water from the mine pond and Omaji-oda stream

Samples	B(a)A/Chry	Phe/Ant	LMW/HMW
L1 (Mine pond)	1.09	1.01	0.51
L2 (Mine pond)	1.09	1.01	0.50
L3 (Mine pond)	1.09	1.02	0.51
L4 (Mine pond)	1.09	0.97	0.54
L5 (Omaji-oda stream)	1.09	0.97	0.51
Pyrogenic	> 0.9	<10	<1
Petrogenic	< 0.4	>10	>1

B(a)A/Chry- benz[a]anthracene to chrysene ratio; *Phe/Ant*- phenanthrene to anthracene ratio; *LMW/HMW* -low-molecular-weight PAHs to high- molecular- weight PAHs ratio

3.4. Proximate and ultimate analyses

Okaba-Odagbo coal in hand specimen is light, partly massive, hard, dull-black to grayish black and slightly brittle.

Proximate analysis (Table 6) shows that Okaba-Odagbo coal on the average contains 3.60% moisture content, 2.93% ash content, 23.66% volatile matter and 69.82% fixed carbon. Using the ASTM [24-25] and previous study by [47] on some Nigerian coals for power generation purposes, the Okaba-Odagbo coal has a low ash content [low ash category (<8.0)], low moisture content, low volatile matter and high fixed carbon. Based on this classification, the Okaba-Odagbo coal is categorized as sub-bituminous coal A. Ultimate analysis (Table 7) shows that

Okaba-Odagbo coal on the average contains 90.09% carbon, 2.22% hydrogen, 2.77% oxygen, 0.42% nitrogen, 0.34% sulphur, 2.7 free swelling index and 7368kcal/kg heating value.

Table 6. Proximate analysis result of Okaba-Odagbo coal

Sample number	Parameters			
	Moisture (%)	Ash content (%)	Volatile matter (%)	Fixed carbon (%)
OK-OD1	3.97	3.25	23.67	69.11
OK-OD2	4.67	2.58	21.79	70.96
OK-OD3	2.98	2.76	24.78	69.48
OK-OD4	3.02	2.98	24.66	69.34
OK-OD5	3.05	2.85	24.49	69.61
OK-OD6	3.89	3.16	22.56	70.39
Average	3.60	2.93	23.66	69.82

Table 7 Ultimate analysis result of Okaba-Odagbo coal

Sample number	Parameters						Free swelling index	Heating value (Kcal/kg)
	Carbon (%)	Hydrogen (%)	Oxygen (%)	Nitrogen (%)	Sulphur (%)			
OK-OD1	86.93	2.09	2.63	0.94	0.89	4.2	7239	
OK-OD2	90.32	2.16	2.74	0.25	0.09	1.6	7312	
OK-OD3	92.45	2.39	2.95	0.14	0.13	2.1	7475	
OK-OD4	91.79	2.34	2.92	0.17	0.15	2.3	7469	
OK-OD5	91.28	2.29	2.88	0.21	0.18	2.4	7453	
OK-OD6	87.76	2.05	2.52	0.79	0.57	3.4	7258	
Average	90.09	2.22	2.77	0.42	0.34	2.7	7368	

These values are also similar to those of Wyoming (USA) sub-bituminous coal (A sub-bituminous coal from Wyoming has the following elemental composition: 75% C, 4% H, 19% O, 1.5% N and 0.5% S), indicating that Okaba coal is sub-bituminous coal. From the results, based on the heating value (exceeding 6200kcal/kg in the classification of Indian coal) and low sulphur content, Okaba-Odagbo coal can be classified under sub-bituminous coal A. Sulphur is commonly present in most Nigerian coal in the form of pyrite and marcasite [48]. Though the sulphur content of Okaba coal (0.34%) falls within the ratings for coke-making, its pyritic nature makes it unsuitable for coke production. Also, the higher the carbon content, the higher the calorific (heating) value which is an indication of the maturation of the coal and the better the quality of the coal for power generation. Metallurgical coals according to [49] are commonly divided into three categories according to their content of volatile matter: low, medium, or high-volatile content. Lower-volatile coals are strongly expanding and create strong pressure during coking. If used alone, many low-volatile coals make a strong coke due to high fixed carbon and other coking characteristics, but could break the walls of a coke oven if used alone. Therefore, it is invariably necessary to blend with either medium or high-volatile coals to prevent excessive expansion of coke in the ovens [50]. Blackmore [49], also recommended an ash content of 6.8% and moisture content of 6% for a good coking coal thereby making Okaba-Odagbo coal with 2.93% ash and 3.60% moisture content (Table 5) unsuitable for coke production. Free swelling index (FSI) is a traditional and quick measurement of a coal's overall coking characteristics. According to [49], coals are generally considered to have coking properties if their FSI is over four. However, coals that are classified as metallurgical coals generally have a FSI of seven (7) or more (the top of the scale is nine). Based on this rating, Okaba-Odagbo coal, with FSI of 2.7 on the average, does not possess metallurgical quality. Quality assessments based on sulphur content and proximate analysis indicate that the coal is of medium quality, non-coking and sub-bituminous. These put together suggest that none of the six coal samples possesses some coking qualities suitable for coke making blends. However, it is suitable for electric power generation and as a domestic fuel, rich in

resinous and waxy materials and is therefore a suitable raw material for the chemical industry and also for use in the manufacture of plastics, when fractionally distilled.

4. Conclusions

The research work showed that concentrations of PAHs in water samples from the coal mine ponds (16.82-17.28 $\mu\text{g/L}$) and Omaji-oda stream (16.93 $\mu\text{g/L}$) were much higher than the guidelines set by WHO (2.00 $\mu\text{g/L}$), Standard Organization of Nigeria for Drinking Water Quality (7.00 $\mu\text{g/L}$) and European Union (0.10 $\mu\text{g/L}$) for PAHs in water. From the source identification of PAHs in Omaji-oda stream using various diagnostic ratios; it revealed that high level of PAHs in the surface water is from pyrogenic source which could be attributed to the coal mining activity in the community. Physicochemical assessment of water samples from the coal mine ponds and Omaji-oda stream in Okaba-Odagbo community was carried out. Most of the physical parameters are within the W.H.O safe limit. However, some of the results indicate high levels above the standard set by W.H.O safe limits; this could pose health risk to the inhabitants of the areas that use these water sources for drinking and other domestic purposes without treatment. Quality assessments based on sulphur content and proximate analysis indicate that the Okaba-Odagbo coal is of medium quality, non-coking and sub-bituminous coal, based on the low moisture content, low volatile matter and high fixed carbon, the Okaba-Odagbo coal is categorized as sub-bituminous coal A. Okaba-Odagbo coal is not a good coking coal but rather suitable for electric power generation, gas fuel and as a domestic fuel. Okaba-Odagbo coal also is rich in resinous and waxy materials and is therefore a suitable raw material for the chemical and plastic industries.

5. Recommendations

It is recommended that policy measures must be put in place by the government to ensure that anthropogenic activities (coal mine) that led to the release of PAHs and cPAHs into the Omaji-oda stream are checked and there should be a regular monitoring regime to assess PAH levels in surface water in the community and also the groundwater. Several researchers have been able to biologically degrade PAHs by increasing their availability to microbial metabolism in the media [11]. This is usually achieved using various methods such as biostimulation, bio-augmentation, use of surfactants, solvents and other solubility enhancers (so that recalcitrant PAHs can be readily available for degradation). Government is therefore advised to look into this area. As the results indicated, some of the parameters analyzed showed higher concentration above the WHO contaminant level therefore relevant agencies should make effort to regulate and educate the community on indiscriminate waste disposal from domestic and industries within the study area. With the power supply problem currently affecting Nigeria and her economy, electricity generation from coal is a more approachable and feasible solution to this problem. It is important for the Nigeria government to seize the opportunity of the vast coal reserves in the study with appropriate proximate and ultimate values for this purpose.

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To whom correspondence should be addressed: Dr. O. C. Adeigbe, Department of Geology, University of Ibadan, Nigeria, E-mail: olukris2009@gmail.com