OCCURRENCE, SOURCE APPORTIONMENT AND PREDICTIVE MODEL OF POLYCYCLIC AROMATIC HYDROCARBONS IN A STREAM WATER OF A NIGERIAN COAL MINE AREA

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Abstract
This study investigated the occurrence and levels of selected polycyclic aromatic hydrocarbons (PAHs) in stream water samples collected in two seasons from the vicinity of a coal mine. The organic content of the water samples were extracted by liquid-liquid extraction technique using a binary solvent system. The extracts were analysed for sixteen PAHs using Gas chromatography coupled with mass spectrometry (GC-MS). The range of the mean total concentrations of PAHs in rainy season stream water samples were 0.02-0.69mg/l; and 0.00 – 0.02 mg/l in the dry season samples. The rainy season water samples contained naphthalene, a low molecular weight PAH, while the dry season water samples contained benzo[a]pyrene and pyrene, which were high molecular weight PAHs. These PAHs are toxic, indicating health risk to the stream water consumers. The results of the PAH analysis were evaluated for source apportionment which revealed that the PAHs in the water samples were of mixed sources, petrogenic and pyrolytic. A simple model for predicting total PAH concentrations was proposed. This report provides baseline data which may assist in environmental regulations and control to protect the health of inhabitants of the studied area and for similar areas.

Keywords: analysis, coal, extraction, GC-MS, PAHs, water.

Introduction

Polycyclic aromatic hydrocarbons are a class of complex organic compounds made up of carbon and hydrogen with a fused ring structure containing at least two benzene rings [1]. PAHs are pollutants of serious environmental and human health concerns due to their widespread occurrence, strong persistence, long-range transportation potential, carcinogenic, mutagenic and teratogenic properties as well as their high environmental concentration [2].

Coal, a solid, carbon-rich material, is a primary fuel used to generate electricity and heat, for domestic and industrial uses, such as in steel and cement production [3]. Through coal gasification and liquefaction, coal can be used to produce chemicals such as methanol, hydrogen and ammonia, and is among the natural sources of PAHs [4]. The natural PAHs in raw coal are generated from the biological materials and processes in the transformation of organic matter (plants) to coal [5]. Coal cycle includes operations in handling coal from reserve assessment, through mining, preparation, processing, transportation, to utilization. These processes may affect the ecosystem with huge deleterious impacts on air quality, water and land resources [6].

Since the occurrence and abundance of PAHs in environments represent a risk to organisms and ultimately to humans, there is a constant need for their determination and quantification [7].The monitoring of PAHs presence in the environment is a world-wide activity [8]. The use of water, plants, soil and sediments as qualitative indicators of PAHs contamination in a coal mining environment is a way of assessing the possible risk of exposure to the chemicals [9].

Raw coal particles, which contain PAHs [10], can be released by open pit mining, mine drainage, spills during coal loading, and transport or accidents into the environment [11].

In Nigeria, until 1990s, coal was mined at several locations including Okpara, Onyeama, Ribadu and Orukpa. Today, many of the coal mines are closed, while others, including Okaba and Okobo-Enjema mines were leased to private companies as a way to resuscitate the coal industry. Coal mining commenced in Okobo-Enjema with strip/opencast mining method being used to extract the coals [12]. Environmental concerns of coal mining in Okobo-Enjema are rising due to air, land and water pollution problems. Water associated with the coal mine drains into a nearby stream and the inhabitants of the coal mine vicinity rely on this contaminated for their water needs.   The contamination of the stream by releases from coal mining may have negative implication on the food chain as aquatic organisms, agriculture, human beings and livestock consume the water from the stream [10].

Studies have shown that environmental pollution in some coal mining communities was directly linked to coal mining [13-14]. Literature does not reveal any work on the levels of PAHs in the Okobo-Enjema stream.

This paper therefore presents a baseline data on the levels of PAHs in the water samples collected at Okobo Aji, the only stream in the vicinity of Okobo-Enjema mine and identifies the sources of the PAHs in the water samples. A simple model was produced to simulate the total concentration of the target PAH compounds beyond the boundary where the experimental data were obtained.

Materials and Methods
Study area
This study focused on the Okobo Aji water at the immediate neighbourhood of Okobo-Enjema coal mine in Ankpa Local Government Area of Kogi State, Nigeria. Okobo-Enjema, is an agrarian rural community lying between longitude 7º15´N and 7º30´N and latitude 7º30´E and 7º46´E, and is in the Benue trough in the geology of Nigeria.

Water sample collection, preparation and analysis
Experimental design was employed in this research and the samples were collected with sterilized 1L amber glass sample bottles in a modified method of Anyakora and Coker [15]. Each bottle was rinsed thoroughly with site water prior to collection.

Water samples were collected during the rainy and dry seasons in 2014 from this stream [16] at between 5cm and 60 cm depth and from three sampling stations (A1, A2 and A3) at different distances from the coal mine. A1 sampling station was located within 400 m from the coal mine. A2 sampling station was located between 400 m and 500 m from the coal mine, while A3 covered areas between 500 m and 600 m from the coalmine. Each sampling station consisted of eight sampling points. The chosen sampling points were at downstream as it was suspected that discharges were washed into the stream and transported downstream.
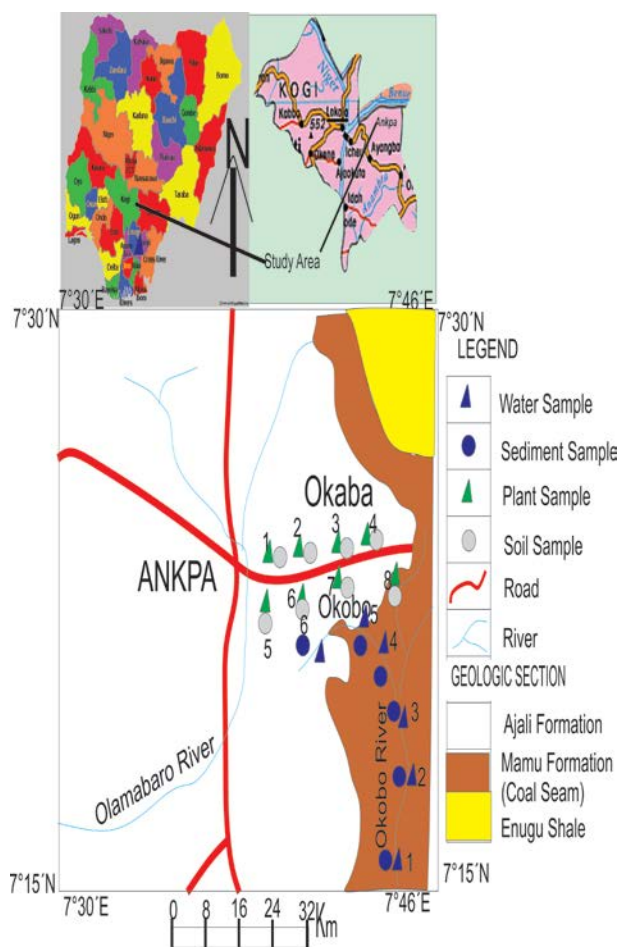
Replicate samples were collected from each sampling point with the sterilized 1L amber glass sample bottles. These samples were acidified at point of collection with conc.HCl to render inactive any microorganism that may cause biodegradation of the samples [15]. The initial pH of water samples was measured using a pH meter.

The water samples were stored in the bottle covered with screw caps and placed under ice for transportation to the laboratory of the National Centre for Energy Research and Development at the University of Nigeria, Nsukka where they were preserved in a refrigerator prior to analyses. Control samples were collected from Onuiyi stream at Nsukka, Enugu state, which was far from influence of any coal mining.

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Control samples were collected from Onuiyi stream at Nsukka, Enugu state, which was far from influence of any coal mining.

Map of the study area showing the sampling points [16].

Liquid-liquid extraction (LLE) of PAHs in water
As the best pH for extraction of a broad range of dissolved organics is around 6.5 [17], pH adjustments of the water samples were done with concentrated hydrochloric acid (HCl) and sodium hydroxide (NaOH)

solutions. Liquid-liquid extraction method was used to extract PAHs from water as described in ALPHA [18]. The extracting solvents, dichloromethane (DCM) and n-hexane were analytical grade reagents supplied by Sigma Chemical Limited, Germany. These solvents have relatively low boiling points, are readily available and had been used by other researchers to publish PAH extraction experiments [19]. The standard PAH mixture solution of sixteen PAHs was purchased from AccuStandard, USA.

The extracts were combined and concentrated to 5 cm^3 using a rotary evaporator (Model: RE52 – 2, SearchTech Instruments, England), with bath temperature at between 40 °C and 45 °C. The extracts were thereafter analysed. This analysis was carried out at the International Energy Services Limited (IESL) Laboratory, Port Harcourt, Nigeria, using a GC-MS instrument. This system comprised of 7890A GC/5975 MSD system by Agilent Technologies in selected ion monitoring (SIM) mode. The GC-MS was equipped with a capillary column (30 m length, 0.25 mm diameter, 0.25µm film thickness) and a split/splitless inlet. The carrier gas was helium at a flow rate of 1.0493 mL/min, pressure of 9.0855 psi and average velocity of 37.604 cm/sec. The initial oven temperature was 65ºC, held for 1 min, then increased to 140ºC at 25ºC/min (Ramp 1); and then, increased to 290 ºC at 10ºC/min for 11 min (Ramp 2). The run time was 30 min and the injection mode was splitless, using an auto-sampler. The mass spectrometer was used in electron ionization mode at 70eV. The mass spectrometer quadropole analyzer and source temperatures were set at 150 ºC and 230ºC respectively. The PAH standard was analyzed in scan mode first in order to see the fragmentation pattern of each PAH. All the ions between 50 and 550 amu were scanned. After scanning the standard, target and qualifier ions were determined for each PAH compound.

The reported mean concentrations of the target PAHs for each sampling station were calculated from the total concentrations of the target PAHs in the eight sampling points in a sampling station.

Quality Assurance/Quality Control procedures
Limit of detection (LOD) and the Limit of quantification (LOQ)
The quality control procedures carried out included establishing the performance of the instrument with the LOD and the LOQ of the GC-MS. The detection limits were determined for each of the sixteen target PAHs based on the calibrations using several concentrations of the standards.

Recovery test using standard addition method
As a procedure for recovery studies, the water was analyzed for PAH content before spiking. Then, the recovery studies were carried by standard addition method to determine the extraction efficiency for the selected PAH compounds

A spiking solution was prepared by weighing specific amount of the PAH standard into a 100 mL volumetric flask. The mixture was dissolved and made up to the mark with n-hexane to obtain 100 µg/ml PAH standard stock solution. Specific volume of the spike solution was added to a measured volume of each of the samples and the spiked samples were subjected to liquid-liquid extraction procedure as described above.

The volume of spike solution added to each sample was determined as follows:

$$\text{Volume of Spiking Solution} = \frac{A \times B}{C}$$

Where   A= spike concentration desired
   B= volume of sample to which spike
       is added
   C= concentration of the spiking
       solution

The percent recovery of the spike was calculated as

$$\% \text{ Recovery} = \frac{(X-Y)}{Z} \times 100$$

Where   X = concentration of the spiked sample
Y = concentration of the unspiked sample, Z = concentration of the spike solution added

Analysis of blanks
Blanks (solvents only) were analyzed for PAHs using the GC-MS.
Source apportionment
Source apportionment or source identification is essential in PAH studies, to determine the origins of PAHs present in environmental samples [20]. Major sources of PAH contamination are the natural and the anthropogenic sources. The natural are mainly due to volcanic activities. Anthropogenic sources consist of petrogenic and the pyrolytic sources. Petrogenic contamination is characterized by the predominance of the lower-molecular-weight PAHs, while the high–molecular-weight PAHs dominate in the pyrolytic source [21-23].This study identified the main sources of the PAHs in the stream water samples by finding the predominate molecular weight of the PAHs in the samples and also comparing the results of analysis with literature.
Simulation model for predicting total PAH concentrations in the stream water
A simple model was used to predict the total target PAH concentrations in the stream water at distances from the coal mine. The mean concentrations of the target PAHs were analytically obtained at various sampling stations, which represented various distances from the coal mine. Graphical plot of the total mean PAH concentrations (y)

versus distances from the coal mine (x) was used to facilitate curve fitting. A non-linear logarithmic regression type was used to find the equation of the curve with the R-squared value using the Microsoft Excel computer software.

This study was carried out between March and December, 2014, at the National Center for Energy Research and Development, University of Nigeria, Nsukka, Nigeria.

Results and Discussion

The initial pH of the stream water samples ranged from 8.02 to 8.79. On acidification at the point of collection, the pH of the samples were brought to between 4 and 4.29, while pH of the samples during extraction ranged from 6.46 to 6.50.

The target PAHs were naphthalene (Nap), acenaphthylene (Ace), acenaphtene (Acen), fluorine (Flu), phenanthrene (Phen), anthracene (Anth), fluoranthene (Fluo), pyrene (Pyr), benzo(a)anthracene (B[a]anth), chrysene (Chry), benzo(b)fluoranthene B[*b*]fluo, benzo(k)fluoranthene (B[*k*]fluo, benzo(a)pyrene B[*a*]pyr, indeno(1,2,3-cd)pyrene (indeno[1,2,3-*cd*]pyr, dibenz(a,h)anthracene (Dib[*a,b*]Anthr) and benzo(g,h,i)perylene (B[*ghi*]pery). These PAHs are in the list of priority pollutants of the United States Environmental Protection Agency (US EPA) due to the extensive amount of data suggesting their toxic and hazardous properties [24].

The PAHs were identified by comparing the retention time of the samples with the retention time of the external standard used to calibrate the equipment and by matching the mass spectra of the monitored ion ratios of the compound in the sample with the National Institute of Standards and Technology (NIST) library database spectra. The instrument automatically calculated the concentrations from the areas of the peaks and compared the analytes' data with data from the external standards which were used to calibrate the equipment.

All the 16 PAH standards were recovered at extraction efficiency range of 72% to 96 % with RSDs 3 % to 6.2 %. Only dibenz[a,b]anthracene recorded 96 % recovery. Nap was 94%, while Acen was 83%. About 85 % were recovered with fluo, pyr and B[ghi]pery. Indeno [1,2,3-cd]pyr , B[k]fluo and B[b]fluo recorded 72 % recoveries. Recoveries were clearly dependent on the individual PAHs in the samples. No PAH was detected in the blanks analyzed.

Table 1 shows the mean total concentrations of target PAHs in the water samples collected in Okobo-Enjema stream at various stations (A1-A3). Eight sampling points made up each station and the mean of the PAH concentration in the points is presented for each of the stations.

Table 1 Mean total concentrations of target PAHs in rainy season stream water samples at sampling stations (distances) from the coal mine

PAHs	A1 (400 m)	A2 (500 m)	A3 (600 m)
Nap	0.69±0.13	0.19±0.06	0.02±0.01
Acen	Nd	Nd	Nd
Phen	Nd	Nd	Nd
Anth	Nd	Nd	Nd
Fluo	Nd	Nd	Nd
Pyr	Nd	Nd	Nd
B[a]anth	Nd	Nd	Nd
Chry	Nd	Nd	Nd
B[b]fluo	Nd	Nd	Nd
B[k]fluo	Nd	Nd	Nd
B[a]pyr	Nd	Nd	Nd
B[g,h,i] pery	Nd	Nd	Nd
Indeno[1,2,3 -c,d]pyr	Nd	Nd	Nd
Dib[a,h] anthr	Nd	Nd	Nd
TOTAL	0.69±0.13	0.19±0.06	0.02±0.01

Nd signifies not detected, and figuratively connotes 0.00

The PAH composition in the Okobo-Enjema water collected in the rainy season comprised of only naphthalene, while pyrene and benzo[a]pyrene were detected in the dry season water samples (Table 2). The average total PAHs concentrations in the Okobo-Enjema rainy season water samples ranged between 0.02-0.69 mg/l, while the average total PAHs concentrations in the Okobo-Enjema dry season water samples ranged between 0.00-0.02 mg/l.

Results of analysis of rainy season water samples show some degree of PAH contamination based on the World Health Organization (WHO) classification. According to the World Health Organization study [25], the concentration of individual PAHs in surface and coastal waters is generally in the neighborhood of 0.05 µg/L and concentration above this point indicates some contamination. Benzo[a]pyrene, the most carcinogenic pollutant of all PAHs [26], was detected in the dry season water samples, with concentration of 0.01 mg/l. The level was higher than those of the EPA National Recommended Water Quality Criteria for the protection of aquatic life $(0.010 \mu gL^{-1})$ [27], and may therefore have an adverse ecological effect in the Okobo-Enjema aquatic organisms. The U.S. Environmental Protection Agency has established drinking water criteria for benzo[a]pyrene, not to exceed 200 ng/l [28].

Table 2 Mean total concentrations of target PAHs in dry season stream water samples at sampling stations (distances) from the coal mine

PAHs	A1 (400 m)	A2 (500 m)	A3 (600 m)
Nap	Nd	Nd	Nd
Acen	Nd	Nd	Nd
Phen	Nd	Nd	Nd
Anth	Nd	Nd	Nd
Fluo	Nd	Nd	Nd
Pyr	0.01±0.001	Nd	Nd
B[a]anth	Nd	Nd	Nd
Chry	Nd	Nd	Nd
B[b]fluo	Nd	Nd	Nd
B[k]fluo	Nd	Nd	Nd
B[a]pyr	0.01±0.001	Nd	Nd
B[g,h,i]pery	Nd	Nd	Nd
Indeno[1,2,3-c,d]pyr	Nd	Nd	Nd
Dib[a,h]anth	Nd	Nd	Nd
TOTAL	0.02±0.002		

Nd signifies not detected, and figuratively connotes 0.00

The composition pattern of PAHs by ring size for the water samples around the Okobo-Enjema coal mine suggested that 2-5 aromatic ring compounds were PAHs present in the water samples. The high-molecular-weight PAH of four rings, Pyr, and five rings, B[a]pyr were detected in the dry season water samples at A1, while the low-molecular-weight PAH of two rings, Nap, were detected during the rainy season.

This high concentration of naphthalene is perhaps due to its high solubility in water compared to other target PAHs. Except for naphthalene, PAHs have very low water solubility but are lipophilic and therefore, their concentration in water is very low [29-30]. At the aquatic environment, some PAHs are taken up by organisms, while a large proportion is deposited to the sediments. Volatilization, photolysis, hydrolysis, biodegradation, and adsorption to particulate matter followed by sedimentation are the main processes governing the fate of PAHs in water [31]. Due to the propensity of PAHs to biodegrade in water, half-lives have been estimated to range from 0.5 to 20 days for naphthalene and from 0.6 to 5.2 years for pyrene under aerobic conditions [32]. The low molecular weight PAHs, which are more soluble, are susceptible to evaporation and microbial degradation [33]. Nap disappeared in the Okobo-Enjema dry season water as it is soluble and susceptible to evaporation due to higher temperatures in the dry season [34]. Pyr and B[a]pyr are less water-soluble and less volatile than low molecular weight naphthalene but higher resistance to degradation [35].

High molecular weight PAHs such as benzo(ghi)perylene,dibenz(a,h)anthracene and indeno(1,2,3-cd)pyrene are rarely found in water samples unless there is a presence of dissolved solids that have these compounds attached to them [15]. This study result corroborated a work by Atwater and Mavinic [36], which analyzed wastewater and sludge samples from 11 coal operations across Canada. Only naphthalene and phenanthrene were detected at levels >10 µg/L.

It was observed that the total amount of target PAHs decreased as the distance from the mine increased. This implies that at some distance beyond the boundary of our sample collection, the target PAHs may not be detectable.

Naphthalene was the only target PAH detected in the control stream water samples at mean concentration of 0.35 mg/l.

Source Apportionment of PAHs in the studied water
The studied dry season water samples had higher proportion of HMW-PAHs which indicated that the PAHs were of pyrolytic origin, that is, from combustion sources, which were likely derived from anthropogenic activities [37]. This corroborated a study of stream water of Fuglebekken in Norwegian Arctic where coal mining and excavation activities took place for a long time, the source of PAH contamination of the Fuglebekken stream, indicated that more than 70% of the samples were of combustion origin; the remainder was as a result of petrogenic influence [38]. The rainy season water sample contained only naphthalene, a low molecular weight PAH, which indicated petrogenic source. The predominance of the lower-molecular-weight PAH in the rainy season water samples suggested a relatively recent local PAHs source which entered into the water from natural source [39].

Yang et al [40] suggested that the high concentration of naphthalene might result from the large amount of raw coal particles. On the average, the PAH contamination in Okobo-Enjema water samples was from mixed sources, petrogenic and pyrolytic. The petrogenic source may be due to contamination from the coal mine in the area.

Simulation models for predicting total PAH concentrations in the Okobo-Enjema stream water
Figure 1 is the graph of mean total PAH concentrations of rainy season water samples at various locations from Okobo-Enjema coal mine.
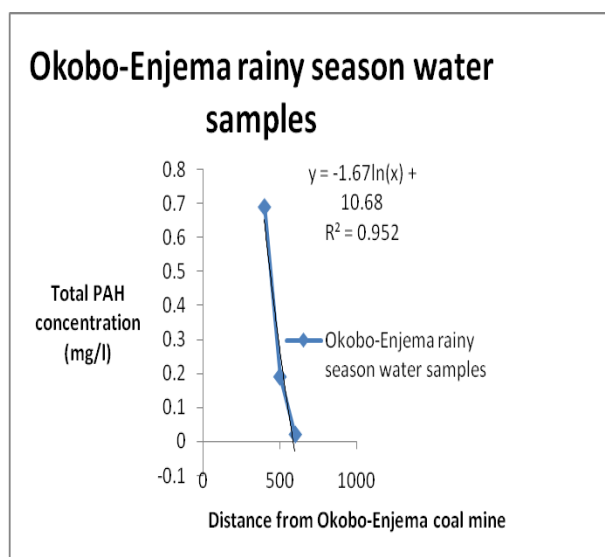
Figure 1 Graph of mean total PAH concentrations of rainy season water samples at various locations from Okobo-Enjema coal mine

The estimated total target PAH concentrations at different distances from the coal mine may be estimated from the graphs. The deviation of the experimental and the estimated results were not significant.

Conclusions

The water samples were extracted by liquid-liquid extraction method. Only naphthalene was detected in the rainy season water samples, while pyrene and Benzo[a]pyrene were detected in the dry season samples. These PAHs are toxic to human beings and are therefore of health concern as the inhabitants and their animals drink from that Okobo Aji stream water, while also using the water for other domestic and agricultural purposes. The sources of PAH contamination of the Okobo-Enjema water is mixed, petrogenic and pyrolytic. The petrogenic source could be traced to the coal mine in the area. Simple models based on non-linear logarithmic equations were produced to simulate total concentration of PAHs in the portions of the stream water where samples were not taken.

The equation of the graph and the R^2 value obtained for the rainy season mean total PAH concentrations are as follows:

$$y = -1.674 \ln (x) + 10.681$$
$$R^2 = 0.9528$$

The equation of the graph and the R^2 value obtained for the dry season mean total PAH concentrations (Figure 2) are as follows:

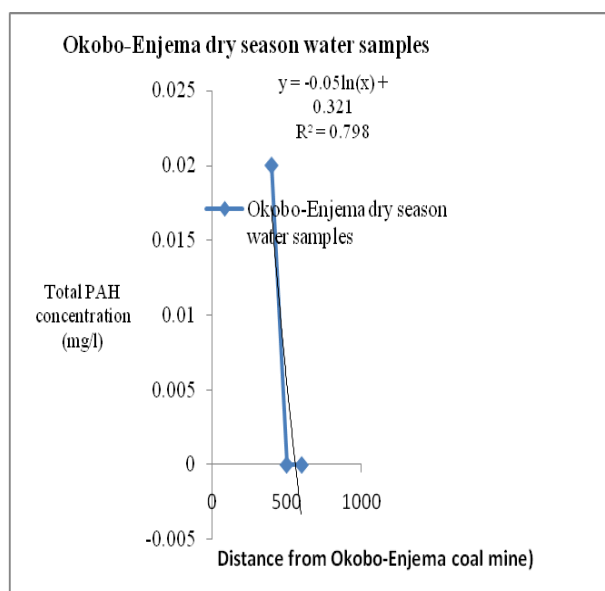$$y = -0.051 \ln (x) + 0.3217$$
$$R^2 = 0.7985$$

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Figure 2 Graph of mean total PAH concentrations of dry season water samples at various locations from Okobo-Enjema

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