

Analysis and Sources of Polycyclic Aromatic Hydrocarbons in Soil and Plant Samples of a Coal Mining Area in Nigeria

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Abstract This study analysed coal, plant and soil samples collected from the vicinity of Okobo coal mine in Nigeria for Polycyclic aromatic hydrocarbons (PAHs) and evaluated the sources of the PAH contamination in the environmental samples. The environmental samples were extracted by sonication using a ternary solvent system and analysed for 16 PAHs by gas chromatography–mass spectrometry (GC–MS). The results of the analysis of the samples identified some of the target PAHs. The ranges of total concentrations (in mg/kg) of PAHs in the coal, plant and soil samples were, 0.00–0.04, 0.00–0.16 and 0.00–0.01 respectively. The evaluation of the results of the PAH analysis of the environmental samples using diagnostic ratios revealed that the PAHs in the soil samples were mainly of petrogenic origin, while those in plant samples indicated mixture of petrogenic and pyrolytic origins.

Keywords Analysis · Coal · GC–MS · PAHs · Plant · Soil

Coal consists of organic and inorganic compounds (Derbyshire et al. 1991). It is very useful in power generation, domestic and industrial heating and in the synthesis of chemicals such as gasoline. Many deleterious compounds are found in coal which may be released into the environment during coal mining and processing. Among the several pollutants associated with coal are the PAHs (Stout and Emsbo-Mattingly 2008). PAHs are aromatic compounds containing

from two to eight conjugated ring systems. More than 30 PAH compounds and several derivatives have been identified, that have carcinogenic and mutagenic effects, making them the largest single class of chemical carcinogens known (Bjorseth and Ramdahl 1985). Okobo is a rural community near Ankpa in Kogi State, Nigeria lying between longitude 7°15'N and 7°30'N and latitude 7°30'E and 7°46'E. There is a coal mine in Okobo and concerns are rising on the potential contamination of the Okobo environment from coal mining activities. Cassava (*Manihot esculenta*) is a major staple food cultivated in a lot of places in Nigeria for its tuberous roots, from which cassava flour, garri, tapioca, and laundry starch, etc., are derived (Cassava 2015). Based on the wide usage of cassava and its extensive cultivation around the mine area of Okobo, this plant was studied for possible contamination with PAHs which might reveal the potential risk of exposure to the chemicals. The soil, from where the plants were uprooted was studied to assess the level of PAHs in the soil. The coal collected from the Okobo mine was also analysed for identification of possible relationship with the studied environmental samples.

No study has been done on the PAHs in the environmental samples at Okobo, hence this research. The aim of this study is to provide a baseline data on the levels of PAH contamination of plant and soil in the vicinity of Okobo. The data may be helpful for putting necessary measures to mitigate adverse environmental effects associated with PAH release possibly from the coals during mining, storage, preparation and transportation. In this study, the coal, soil and plant extracts obtained by extractions with ternary solvent system were analysed using Gas chromatography equipped coupled with mass spectrometry. The target PAHs for this work were naphthalene (nap), acenaphthylene (ace), acenaphthene (acen), fluorene (flu), phenanthrene (phen), anthracene (anth), fluoranthene (fluo), pyrene (pyr), benzo[*a*]anthracene

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(b[a]anth), chrysene (chyr), benzo[b]fluoranthene (b[b]fluo), benzo[k]fluoranthene (b[k]fluo), benzo[a]pyrene (B[a]pyr), dibenz(ah)anthracene (Dib), benzo[ghi]perylene, and indeno(1,2,3-cd)pyrene (indeno). These PAHs are in the list of priority pollutants of the United States Environmental Protection Agency (NRC 1997) due to the extensive amount of data suggesting the toxic and hazardous properties of these compounds (Joa et al. 2009).

Materials and Methods

The extracting solvents, acetone, 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 report published extraction experiment (Ogala and Iwegbue 2011). The standard PAH mixture was purchased from AccuStandard, USA. A gas chromatograph GC system (7890 A, Agilent technologies, USA) with injector (7653 B Agilent technologies, USA) coupled to a mass selective detector (MSD) (5975, Agilent technologies, USA) was also used for this study. We had four sampling points and collected eight cassava plant samples from each of the sampling points.

Cassava plant samples were uprooted with their root, stem and leaf from four sampling points using a stainless steel hoe. Eight plant samples were collected from each of the sampling points during the dry (March) and rainy (October) seasons at between 400 and 500 m from the Okobo coal mine. Sample averages were taken at each sampling point at intervals of 5 m. Soil and dust particles were washed off the plant samples with distilled water and they were wrapped in an aluminum foil under ice and transported to the refrigerator. The plant materials were later cut, sliced, chopped and air-dried at about 27°C inside the laboratory for 72 h. The fibrous materials were discarded while the remaining materials were blended. The plant samples from each point were mixed thoroughly, ground and sieved with a 250 µm sieve and a homogenised composite sample was obtained for each point. Soil samples were collected from the same points where the plants were uprooted, using a trowel. Soil samples were collected from 0–20 cm depth. The samples were put in a sealed aluminum foil under ice and transported to the refrigerator where temperature was maintained at below 10°C prior to extraction. The soil samples were air-dried at about 27°C inside the laboratory for 36 h. Foreign objects such as gravel, pebbles, rocks, sticks and leaves were discarded. The soil samples from each sampling point were mixed thoroughly and sieved with a 250 µm sieve and a homogenised composite sample was obtained for each point. Extraction of the PAHs in the plant and soil samples was done by using ultrasonic extraction

method (EPA Method 3550) (US EPA 2007). Sieved plant samples (30 g) were mixed with anhydrous sodium sulphate (15 g) to further dry the sample and form powder. The mixture was placed in a beaker and 100 mL of mixed solvent comprising DCM-acetone-n-hexane (1:1:1) was added. The mixture was placed in the sonication bath of a sonicator (Model SALD-BS2 beaker type Shimadzu Corporation sonicator with ultrasonic bath). The stirrer and the ultrasonic pulse were activated and the extraction was allowed to proceed for 25 min. Then, the extract was decanted. The same extraction procedure was repeated with sieved soil samples (30 g) to extract the PAHs in the soil samples. The plant and soil extracts from the sonication extraction were separately placed at equal level in tubes in a centrifuge (80-2B Uniscope laboratory centrifuge by Surgifriend Medicals, England). The centrifuge was set at 3500 rpm for 30 min. The extracts were thereafter decanted and filtered. The filtrates were concentrated with rotary evaporator (Model No: RE52 – 2, SearchTech Instruments, England), in which the bath temperature was kept at between 40°C and 45°C.

The coal used in this investigation was obtained from the coal mine at Okobo. The dry coal samples were homogenized by grinding and screening through 250 micron sieve. The undersize samples were collected, mixed thoroughly and packaged in plastic bags, labeled accordingly, and kept in a dark cool cupboard to reduce or prevent volatilization and degradation. The coal samples were subjected to extraction process with solvents using Soxhlet extraction method (EPA Method 3540) (US EPA 1996). Exactly 7 g coal samples were separately wrapped in a tissue paper and placed in the extraction thimble of the Soxhlet extractor. 150 mL of solvents consisting of Acetone: DCM: n-hexane (1:1:1) were added into the flask of the Soxhlet extractor. The extractions of the coals were carried out at 35°C for 8 h. The liquid extracts were concentrated with a rotary evaporator (Model No: RE52 – 2, SearchTech Instruments, England) at 35°C.

To evaluate the extraction efficiency for the target compounds, recovery studies were carried by the spiking method. A spiking solution was prepared by weighing 0.01 g of the PAH standard mixture 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 (plant, soil and coal) and the spiked samples were subjected to the same extraction procedure as described above.

The percent recovery of the spike was calculated as

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

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

The total organic carbon (TOC) was determined following the standard Loss-on-Ignition (LOI) method (ASTM 2000). This involved the destruction of all organic matter in the soil through heating followed by gravimetric determination of sample weight loss. A conversion factor of 1.724 was used to convert organic matter to organic carbon based on the assumption that organic matter contains 58 % organic carbon (Nelson and Sommers 1996).

Analyses of the extracts were performed using an Agilent Technologies 7890A GC system combined with a 5975 MSD Quadrupole GC–MS system in selected ion monitoring (SIM) mode. The GC–MS was equipped with split/spitless inlet and a capillary column (30 m length, 0.25 mm diameter, 0.25 μ m film thickness) used for the separation of the analytes. 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/s. The injection mode was splitless using an auto-sampler. The initial oven temperature was 65°C, held for 1 min, then increased to 140°C at 25°C/min (Ramp 1); and then, increased to 290°C at 10°C/min for 11 min (Ramp 2). The mass spectrometer was used in electron ionization mode at 70 eV. The PAHs were identified using two criteria: comparing the retention time of the samples to the retention time of the external standard used to calibrate the equipment and the matching of mass spectra of the monitored ions 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 (Ragunathan et al. 1999). The mass to charge (m/z) ratios monitored (with the target PAH compounds) were m/z 128 (nap), m/z 152 (ace), m/z 153 (acen), m/z 166 (flu), m/z 178 (phen and anth), m/z 202 (fluo and pyr), m/z 228 (b[a]anth and chyr), m/z 252 (b[b]fluo, b[k]fluo and b[a]pyr), m/z 276 (benzo[ghi]perylene and indeno) and m/z 278 (Dib). The samples were analyzed with method blank samples (solvent) for PAH background correction. This was done to check contamination from prior analysis with the GCMS. The limit of detection and limit of quantification of the GCMS were evaluated using a mixture of the target 16 PAHs standard. This sample analysis was done in duplicate and the data were analyzed using the Pearson's

correlation coefficient in SPSS 16.0 software. This study was carried out between February and December, 2014, at the National Center for Energy Research and Development, University of Nigeria, Nsukka and at the International Energy Services Limited (IESL), Port Harcourt, Nigeria.

Results and Discussions

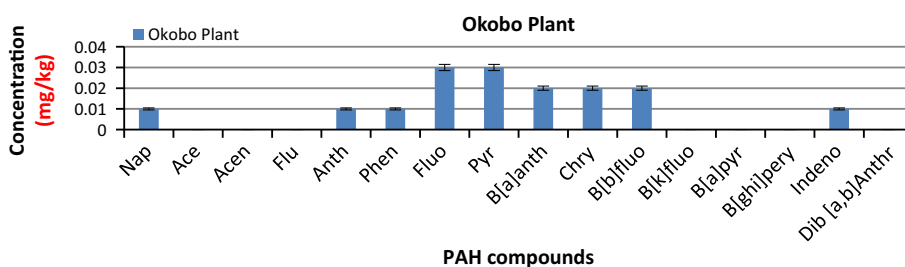
The recovery percentages of the different PAHs for extraction efficiency and quality control, at a spike concentration level of 100 mg/kg varied between 67 % and 89 % with relative standard deviation (RSDs) between 6.23 % and 15 % for coal samples; 68.02 % and 91.11 % with RSDs ranging from 6.92 % to 13 % for soil samples; 68.83 % and 92.21 %, with RSDs ranging from 7.12 % to 13 %, for plant samples. Recoveries were clearly dependent on the individual PAHs in the different samples. PAH background contamination was not found in the solvent blanks, indicating that analytes were not carried over from previous analyses.

The LOD values calculated for PAHs in the coal, soil and plant samples varied from 0.01 to 5.0 mg/kg, 0.01 to 3.0 mg/kg, and from 0.01 to 5.0 mg/kg respectively. The LOQ for PAHs in the coal, soil and plant samples varied from 0.03 to 12.5 mg/kg, 0.03 to 8.7 mg/kg, and from 0.03 to 10.5 mg/kg respectively.

Figure 1 shows the average amount (in mg/kg) of the target PAHs in the cassava plants extracts obtained with ternary solvent system of acetone, DCM and n-hexane.

These solvents were used for enhanced extraction efficiency, because they comprised of water-miscible and immiscible solvents. While the water-miscible solvent (acetone) facilitated the penetration into the matrice, the water-immiscible solvents (DCM and n-hexane) dissolved the analytes into the solvent system. Nine out of the sixteen PAHs studied were found in the cassava plant samples within the detection limit of the instrument used. All of them were in a concentration range from 0.01 to 0.03 mg/kg. The highest concentrations in the samples were found for flu and pyr (0.03 mg/kg), followed by b[a]anth, chyr and b[b]fluo (0.02 mg/kg), and then nap, anth, phen and indeno (0.01 mg/kg). Ace, acen, flu, B[a]pyr, b[ghi]perylene and Dib

Fig. 1 Mean PAH compounds in Okobo composite plant samples (PAHs with no bars were not detected) ($n = 16$ and 5 % error bars)



were not detected in the plant samples. Based on International Agency for Research on Cancer qualitative classification of PAH carcinogenicity (IARC 2009), some carcinogenic PAHs, namely, benz(a) anthracene, chrysene, benzo(b)fluoranthene, and indeno (1, 2, 3-cd)pyrene were found in the samples. There was an indication of uptake of PAHs from the soil since these PAHs were not detected in the soil where the plants were uprooted from. This may imply that the PAHs in the soil were present at very low levels, and the plants concentrate them, up to measurable levels in the plants. This study has revealed that the cassava plant in this mining area has been contaminated by PAHs. There is concern that the food chain may have been contaminated with toxic PAHs which might be really dangerous for human health. The results from the analysis of PAHs in the plants showed that high molecular weight (HMW) PAHs (>3 rings) were prevalent in the samples. These HMW PAHs are generally derived from pyrolytic origin (Qiao et al. 2006; Sanders et al. 2002). Diagnostic ratios are widely used to determine the origins of PAHs present in environmental samples (Liu et al. 2005). Many researchers have developed and used specific values of PAH ratios to determine the origins of PAHs present in environmental samples (Liu et al. 2005; Yunker et al. 2002). In this study, the ratio benz[a]anthracene/(benz[a] anthracene + chrysene) was 0.5. The ratio benz[a] anthracene/(benz[a] anthracene + chrysene) <0.20 usually implied petrogenic origin; 0.20–0.35 indicates mixed petrogenic and pyrolytic origin, while >0.35 indicates pyrogenic origin (Yunker et al. 2002). This ratio definition meant that the source of the PAHs in the studied plant samples was pyrolytic in origin. Pyrolytic source is referred where source was as a result of combustion, an anthropogenic activity. Here, low molecular weight (LMW) PAHs was identified as well as HMW PAHs. The implication is that there was a mixed source of the PAHs in the studied samples, with the pyrolytic source predominating.

With the exception of naphthalene, no other target PAHs was detected by the GC–MS analysis in any of the soil samples. The concentration of naphthalene in the composite soil sample collected during the rainy season at ambient temperature of 27°C and dry seasons at ambient temperature of 39.5°C were 0.25 and 0.01 mg/kg respectively. Based on the classification of soil pollution according to Maliszewska-Kordybach (1996), Okobo soil is weakly contaminated. This result does not rule out the possible presence of other PAHs in the soils which may have been degraded by the high temperature (Wilcke 2000) and microbes (Sadler et al. 1993) or possibly absorbed by the biota, including the vegetation on the top soil (Zuydam 2007). The organic carbon content in the studied samples was between 4 % and 8 %. The influence of organic matter was explained by Adamczewska et al. (2000), who observed that in soils with

more organic matter, the PAH concentration is higher than those with less organic matter. The TOC in the studied Okobo soils was low indicating that the soils have less organic and therefore less PAH. These values of detected PAHs in the soil samples were higher than total PAH concentrations of 1–10 ppb (diagenic source), as higher values indicated that the PAHs were likely from anthropogenic sources (Olajire and Brack 2005). Petrogenic contamination is characterized by the predominance of the LMW PAHs, while the HMW PAHs dominate in the pyrolytic origin (Benner et al. 1990). The soil samples contained only LMW naphthalene which implied that the PAH in the soil samples were of petrogenic origin. Yang et al. (2008) suggested that high concentration of naphthalene might result from large amount of raw coal particles.

The ternary solvent system extracted 9 out of the 16 target PAHs in Okobo coal (Fig. 2). The extracted PAHs included 2–5 ring compounds such as nap, flu, pyr, chry, fluo and pyr. Phen and fluo were the most extracted PAHs at average of 0.04 mg/kg while nap followed at average of 0.03 mg/kg before the trio of b[a]anth, chry and b[b]fluo. Results of blanks (solvents) extracted under the same conditions with the samples were below detection limits.

There was significant positive correlation between PAHs in coal and plant samples (0.762) and between PAHs in coal and soil samples (0.367) using Pearson's correlation coefficient. This software was also used for the analysis which produced the results in Table 1. The implication of the positive correlation between the PAHs in the coal and plant samples, and between the PAHs in coal and soil

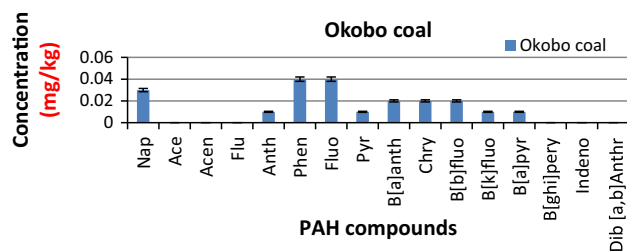


Fig. 2 Mean PAH compounds in Okobo coal samples (PAHs with no bars were not detected) (n = 8 and 5 % error bars)

Table 1 Results of statistical analysis of target PAHs in Okobo samples

Samples	Mean (ppm)	Standard deviations	Std. Error	Statistically significant at 0.05 level of significance
Coal	0.013	0.01	0.004	No
Plant	0.010	0.01	0.003	No
Soil	0.017	0.06	0.016	No

samples is that the sources of the PAHs in plant and soil samples are similar.

Low concentrations of toxic PAHs were measured in the soil and plant samples collected from the vicinity of Nigerian Okobo coal mine. Some of the identified PAHs in plant samples were carcinogenic and there is reasonable concern that these chemicals may enter the food chain. While it is possible that some of these PAHs are linked with other sources of anthropogenic activities, the use of diagnostic ratios for source identification and apportionment strongly suggested the contamination have input of coal. The statistical analysis showed positive correlation between the coal and the environmental samples. These PAH composition profile and concentrations figures will provide a very useful baseline data for evaluating future trends in PAH concentrations in Okobo as well as similar investigations elsewhere.

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