OCCURRENCE AND PROFILE OF POLYCYCLIC AROMATIC HYDROCARBONS IN COALS AND SHALES FROM EASTERN NIGERIA

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Abstract

The concentrations and profiles of polycyclic aromatic hydrocarbons (PAHs) in coal and shale samples from eastern Nigeria were examined. The total concentrations of PAHs in the samples ranged from 304 – 4082 µgkg^{-1} and 274 – 1815 µgkg^{-1} for coal and share samples respectively. The profiles of PAHs in the coal and shale samples differed significantly. The coal samples had higher PAHs concentrations than the shale samples. In the coal samples 4-rings PAHs showed predominance over 2, 3, 5-and 6-rings polycyclic aromatic hydrocarbons while 3-rings polycyclic aromatic hydrocarbons showed predominance over 2,4,5 and 6-rings PAHs in the shale samples. The results indicate coal from eastern Nigeria are characterized with high contents of 3 and 4-rings PAHs and poorer in 2,5 and 6-rings PAHs. This suggests that the coal samples are from seams of paralic origin.

Keywords: polycyclic aromatic hydrocarbons; coals; shales; Nigeria.

1. Introduction

Coal is resulted from the accumulation and slow decomposition of plant remains (wood, roots, leaves, spores and seed) in sedimentary strata. It undergoes insitu compaction under water with time, accompanied by biochemical processes such as decomposition due to bacteria actions; dehydration, devolatilization (loss of volatile compounds e.g methane, carbon dioxide, nitrogen and higher hydrocarbons) and densification to form various coal under different environmental conditions (temperature, pH and redox potential) [17].

Coal contains myriad of organic compounds, aromatic clusters, aliphatic bridges and rings, side chains and oxygen functional groups. Some are known to be toxic. The toxic substances found in coal of particular interest are (i) condensed aromatic structures (e.g. polycyclic aromatic hydrocarbons) which are known mutagen, carcinogens and endocrine disrupters (ii) aromatic amines, which have probable nephrotoxic activities and (iii) heterocyclic compounds, which may be carcinogenic and nephrotoxic [10].

Small amounts of PAHs have also be found in geological formation such as hard coal, brown coal, crude oil and butiminous shales [1-3,4,7,12,16]. Studies on the profiles and levels of polycyclic aromatic hydrocarbon in environmental samples have attracted substantial research interest in the last three decades owing to the fact that many of them are carcinogenic, mutagenic and causing irreversible changes in structures and functioning of living organisms [8]. As the molecular weight increases, the carcinogencity of PAHs also increases, and acute toxicity decreases. PAHs known for their carcinogenic and teratogenic properties are benzo(a)anthracene, chrysene; benzo(b)fluoranthene, benzo(j)fluorathene, benzo(k) fluoranthene and benzo(a) pyrene, Indeno (1,2,3 cd) pyrene and dibenzo(a,h) anthracene [13].

Toxic organic compounds can be leached from coal into water supplies; and long term human exposure to these compounds may lead to disease occurrence, including cancer and renal diseases. One example of a disease hypothesized to be linked to coal-derived toxic organic compounds in water is the Balkan endemic nephropathy (BEN) [10]. Despite these potential hazards, little is known about the polycyclic aromatic contents of Nigerian coal. The

purpose of the present study is to evaluate the profiles and levels of polycyclic aromatic hydrocarbon contents of coal and shales from eastern Nigeria.

2. Materials and methods

2.1 Geological setting

The study area falls within latitudes 5°30′ to 8° 00′N and longitudes 6°00′ to 8°00′E (Figure 1). The Anambra Basin is believed to be an extension of the Southern Benue Trough, dated Upper Cretaceous- Lower Tertiary. The Benue Trough was formed as a result of the separation of the African and South American land masses [9,19]. Different views were expressed towards the formation of Anambra Basin, these include the works of [20] that the basin was stressed induced and a tension fractured system set up in the Africa plate as it wedged apart of South American plate during the Mesozoic. However, the precise origin and evolution still remains controversial. Burke et al., [5] proposed a Rift-Rift-Rift (RRR) function model, in which an approximately 200 km wide strip of new ocean crest existed beneath the trough. Nwachukwu et al. [9] , modified the model by proposing that the three arms developed at different times and rate. The southern arm was first active in the Lower Cretaceous followed by Benue arm in the Albian. The northwest arm became active later since there was no complete seaway between the north and south Atlantic until Turonian.

A rift developed during the Neocomian as Africa and South America continue to tear apart and gave rise to the Benue Trough.

The Nkporo Formation constitutes the basal lithostratigraphic unit of the Anambra Basin in South-eastern Nigeria. It unconformably overlies the pre-Santonian formations of the Abakaliki Basin. Reyment [14] described the Nkporo Formation as comprising of dark shales and mudstones with subordinate sandstones and shelly limestones. The slowing subsidence and regression in the Maastrichtian, resulted in the deposition of Coal Measures (Mamu, Ajali and Nsukka Formations). The lithology of the Coal Measures consists of rhythmic sequences of sandstones, siltstones, mudstones, and carbonaceous shales. The Mamu, Ajali and Nsukka Formations respectively overlie each other conformably (Figure 1), with the Nsukka Formation being the youngest Cretaceous sequence that occurs in the Anambra Basin. However, a new phase of transgression began in the Paleocene that deposited the Imo Shale, followed by marine regression in the Early Eocene resulting in the deposition of the sandy horizons of the Ameki Formation.
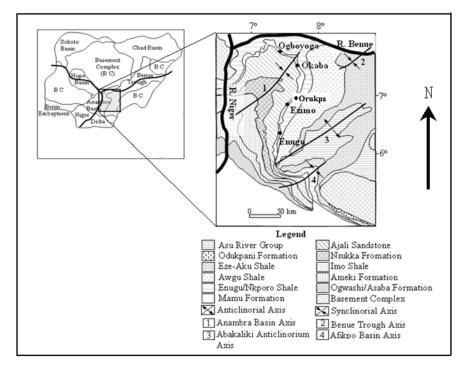

Figure 1: Geological map of Nigeria showing the location of the coal deposits in southeastern Nigeria/Anambra Basin.

2.2 Sampling

9 coal and 8 shale samples were collected from different locations in the eastern Nigeria (Figure 1). 5 g of the waste samples was extracted with hexane (90%) and dichloromethane (99.8% analar grade BDH, Poole, England) in an accelerated solvent extractor (ASE 200, Dionex, Sunnyvale, C.A). Extraction cells were filled with solvent, pressurized to 14 MPa and heated to 120°C for 6mins. Pressure and temperature was held constant for extraction time of 5 mins and cells were rinsed with cold solvent (60% of cell volume) and purged with argon for 150 s. The static extraction and purge step were performed twice for each sample and the extracts were combined [17] [11,18]. The extracts were evaporated to 1 mL and purified by solid phase extraction with 2 g of aluminium oxide (5% deactivated upper part) and 2 g of silica gel (5% deactivated lower part).

The PAHs were subsequently eluted with 15 mL of hexane, 5 mL of hexane and dichloromethane (9:1) and 20 mL of hexane and dichloromethane (4:1). The eluted fractions were combined and evaporated to approximately 0.5mL. Eight deuterated PAHs (NAP-D_8, ACE-D_{10}, FLU-D_{10}, PYR-D_{12}, CHR-D_{12}, PERY-D_{12}, DGHI-D_{12}) as internal standards, to check the recovery of the internal standards FLT-D_{10} was added to extract before injection into gas chromatography. The mean recoveries were greater than 94.8%.

PAHs were detected with gas chromatography (HP 6890 Palo Alto,CA) equipped with a HP5 (cross linked PHME siloxane) (0.25 µm film thickness, 0.25 mm x 30 m) and flame ionization detector (FID). The carrier gas was helium with a flow rate of linear velocity 30 cm/sec. Initial temperature of 100°C and increased finally to 310°C at a rate of 4°C/min. one µL of each sample was injected in splitless mode. The detection limit for PAHs is 1 µgkg^{-1}. All results were calculated at dry weight basis.

Table 1 PAHs contents (µgkg^{-1}) of coals from Eastern Nigeria

PAH	Acronyms	OG1	OG2	EZ1	EZ2	ORK1	ORK2	OKB1	OKB2
Naphthalene	NAP	nd	nd	167	199	nd	nd	nd	nd
2-methylnapthalene	2MNAP	nd	nd	239	nd	nd	nd	nd	nd
Acenaphthalene	ACY	nd	97	641	144	179	nd	96	185
Acenaphthene	ACE	116	62	151	63	126	nd	86	117
Fluorene	FLU	nd	nd	233	nd	nd	nd	nd	nd
Phenathrene	PHE	320	68	154	115	238	178	nd	114
Anthracene	ANT	nd	188	130	164	344	127	164	237
Fluoranthene	FLT	154	191	460	674	138	nd	nd	nd
Pyrene	PYR	nd	118	1,761	294	nd	nd	nd	nd
Benzo (a) anthracene	BAA	258	165	146	186	194	nd	500	226
Chrysene	CHY	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(b) fluoranthene	BBF	nd	nd	nd	137	nd	nd	nd	nd
Benzo(a) pyrene	BAP	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(k) flouranthrene	BKF	nd	nd	nd	nd	nd	nd	nd	nd
Indeno(1,2,3) perylene	IND	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a) anthracene	DBA	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i) perylene	BGHI	nd	nd	nd	nd	nd	nd	nd	nd
Total PAH$_S$		848	889	4082	1976	1310	305	846	879

Table 2 PAHs contents (μgkg^{-1}) of shale

PAH	Acronyms	OG1	OG2	EZ1	EZ2	ORK1	ORK2	OKB1	OKB2
Naphthalene	NAP	nd	nd	nd	nd	nd	nd	nd	nd
2-methylnapthalene	2MNAP	nd	nd	nd	107	nd	612	nd	nd
Acenaphthalene	ACY	188	nd	73	140	183	194	42	60
Acenaphthene	ACE	134	nd	47	62	140	nd	nd	nd
Fluorene	FIDI	nd	nd	nd	70	nd	nd	nd	nd
Phenathrene	PHE	856	nd	nd	174	131	264	59	nd
Anthracene	ANT	293	122	75	252	363	120	117	144
Fluoranthene	FLT	210	nd	nd	nd	191	118	nd	nd
Pyrene	PYR	nd	nd	nd	nd	nd	nd	nd	nd
Benzo (a) anthracene	BAA	199	145	269	139	268	232	71	70
Chrysene	CHY	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(b) fluoranthene	BBF	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(a) pyrene	BAP	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(k) fluoranthrene	BKF	nd	nd	nd	nd	nd	nd	nd	nd
Indeno(1,2,3) perylene	IND	nd	nd	nd	nd	nd	nd	nd	nd
Dibenzo(a) anthracene	DBA	nd	nd	nd	nd	nd	nd	nd	nd
Benzo(g,h,i) perylene	BGHI	nd	nd	nd	nd	nd	nd	nd	nd
Total PAH$_S$		1815	264	463	945	1 276	1 541	290	274

3. Results and discussions

The content of PAHs in the coal result firstly from enrichment caused by digenetic alterations (compaction, decrease in porosity, dehydration), resulting in carbon content increase and a decrease in volatiles and water. Secondly, it is caused by alteration of substituted PAHs to unsubstituted PAHs [1]. The total contents of polycyclic aromatic hydrocarbon in coal samples from eastern Nigeria ranged between 305 μgkg^{-1} and 4082 μgkg^{-1} with a mean content of 1391.88 μgkg^{-1} while the total PAHs contents of the shales ranged between 274 μgkg^{-1} and 1815 μgkg^{-1} with a mean content of 858.5 μgkg^{-1}. The contents of PAHs in this coal samples were similar to 2.74 to 4.894 ppm range reported as the contents of unsubstituted PAHs in brown coal from Poland [1] but were lower than levels reported for hard coal samples (4.110 - 6.619 ppm) from Poland [2]. Quantitative relations between individual hydrocarbons in this group are variable in these coal deposits.

The distribution of PAHs in coals is a function of several factors which include:
(i)Type of sediments (autochthonous or allochthonous), vegetation spectrum, sedimentary environment (boggy, limnic or brackish-marine), nutrient levels (eutrophic or oligotrophic), physico-chemical conditions of the environment (pH, redox potential, temperature);
(ii) the biochemical evolution (processes such as rotting, mouldering, alteration to peat and decay, depends on redox conditions) and
(iii) the geochemical conditions during conversion into coal as temperature and pressure increases [1].

PAHs in coal developed from natural compounds, mainly terpenoids. The precursors of PAHs might be diterpenoids found in resins, then altered to substituted PAHs such as pimanthene or retene or triterpenoids in plant tissues, altered into dimethylchrycene or trimethylpicene. Other PAHs precursors might be hopanoids present in the bacteria remnants, tetraterpenoids

found in green sulphur bacteria and steroids, which might alter into dimethyl phenanthrene [16]. Some substituted PAHs alter to unsubstituted compounds during digenesis.

No 2-rings polycyclic aromatic hydrocarbon was found in the coal samples except for coal samples from Ezimo (EZ1 and EZ2). The concentrations of 2-rings PAHs in these samples were 406 µgkg^{-1} and 199 µgkg^{-1} for EZ1 and EZ2 respectively, whereas, in the shale samples only 2-methylnalpthalene was found in EZ2 at a level of 107 µgkg^{-1} and ORK2 at a level of 612 µgkg^{-1}. The percent composition of 2-rings PAHs in coal and shale samples never exceeded 11.34 %.

In the coal samples 4-rings PAHs showed predominance over 3-rings, 2-rings and 5-ring PAHs. The contents of the 4-rings PAHs differs significantly. No clear predominance of a species amongst 4-rings PAHs was observed. For example, benzo (a) anthracene was the predominant species of 4-rings PAHs in OG1 (258 µgkg^{-1}), ORK (194 µgkg^{-1}), OKB1 (500 µgkg^{-1}), OKB2 (226 µgkg^{-1}). Flouranthene showed predominance in OG2 (191 µgkg^{-1}) and EZ2 (647 µgkg^{-1}) and pyrene in EZ1 (1761 µgkg^{-1}). Three rings PAHs such as acenapthalene, acenaphthene, phenanthrene and anthracene was detected in at least 6 - 7 of the coal samples examined. However, fluorene was found only in sample EZ1 at a level of 233 µgkg^{-1}. Similarly fluorene was also detected in only one of the shale sample studied (EZ2, 170 µgkg^{-1}). The concentrations of acenapthalene acenaphthene, phenanthrene and anthracene in coal samples ranged from not detected (nd) to 641 µgkg^{-1}; nd to 151 µgkg^{-1}; nd to 320 µgkg^{-1} and nd to 344 µgkg^{-1}, respectively. The contents of 3-rings PAHs found the coal samples were comparable to 3-rings cyclic hydrocarbon found in coal in Poland (Bajakwoska and Sokolowska, 2001b). For the shale samples, 3-rings PAHs showed predominance over 2-rings, 4-rings and 5 to 6-rings PAHs in most of the samples. For example, in samples OG1, EZ2, ORK1, ORK2, OKB1 and OKB2 3-rings PAHs showed predominance while 4-rings PAHs show predominance in OG2 and EZ1. Among the 3-rings PAHs in shale samples phenanthrene showed higher concentrations in OG1 (856 µgkg^{-1}), and ORK2 (264 µgkg^{-1}) whereas anthracene was the predominant species of 3-rings PAHs in OG1, EZ1, EZ2, ORK1, OKB1, and OKB2. Anthracene is the most widely distributed 3-rings PAHs in the shale samples. The concentrations of anthracene ranged between 75 and 363 µgkg^{-1}. Acenaphthene was detected only in four shale samples while acenapthalene was found in all shale samples except for OG2. The contents of acenapthalene in the shale samples ranged from not detected in (OG2) to 194 µgkg^{-1} in ORK2. Within the 4-rings PAHs, benzo(a) anthracene was found in all the shale samples analyzed with concentrations ranging from 70 µgkg^{-1} in OKB2 to 296 µgkg^{-1} in EZ1 while flouranthene was detected in 3 shale samples (OG1, ORK1 and ORK2).

4. Conclusion

The PAH 'profiles' varies within the Anambra basin. The coals collected from the mines in the eastern Nigeria are characterized by high contents of 3-rings and 4-rings PAHs and poorer in 2-rings, 5 and 6-rings. This implies that the coal samples are from seams of paralic origin. Low contents of 5 and 6-rings polycyclic aromatic hydrocarbons are characteristics of carboniferous hard coals. The difference in the amounts and composition of the PAHs in Palaeozoic and younger coals probably result not only from the intensity of digenesis, but also from the composition of the accumulated vegetal materials. In the Tertiary, conifers, angiosperm tree and perennial herbs with subordinate ferns, mosses and water plants represents the primary material. Angiosperm herbs and sphagnum mosses with subordinate trees are dominant in recent coal forming environments whereas in Carboniferous, lycopods, horsetails, ferns and cordaites, together with mosses and herb lycopods, ferns and primitive conifers were the main coal producing plants [1].

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