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Trace and major metal abundances in the shale and coal of various seams at Okaba coal mine, Kogi State, Nigeria

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ABSTRACT

The distribution of a number of trace and major elements in the shale and coal of differing seams in Okaba, Kogi State, Nigeria, was studied using energy dispersive x-ray fluorescence spectrometer. The study was necessary to compare the quality of Okaba coal to world standards of coal quality. Major elements of Al, K, Ca and Fe showed concentration ranges of 5.93±2.49 – 8.42±0.003 mg/g, 0.18±0.46 – 2.16±0.0 mg/g, 0.53±0.41 – 2.23±0.35 mg/g and 6.05±0.004 – 18.28±1.2 mg/g respectively. The mean concentrations are 7.24mg/g (Al), 1.25 mg/g (K), 0.91 mg/g (Ca) and 11.86 mg/g (Fe). These values are clearly above the recommended concentrations in coal quality standards and for air emission standards by the World health organization. Trace metals of Ti, Cr, Mn, V, Ni and Cu showed concentration range of 0.84±0.007 – 2.98±0.007 mg/g , 0.03±0.0 – 0.12±0.025 mg/g, 0.02±0.11 – 0.30±0.02 mg/g, 0.02±0.44 – 0.2±0.05 mg/g, 0.01±0.075 – 0.12±0.001 mg/g and 0.03±0.02 – 0.62±0.001 mg/g respectively. These results indicate that Okaba coal and shale is enriched in the major elements analysed in comparison to worldwide averages of coal while the trace elements with exception of Ti are below the coal quality standards. Correlations between the various metals were also established. The S content correlated inversely well with the K content of both the shale and coal. Expectedly, the percentage Si content was high in the shale1 (26.70%) and shale2 (26.38%), while the lowest concentration was recorded at Okaba coal seam 5 (6.58%). The absence of Cl, Br, Na, and Mg in the samples clearly indicates the extent of surface leaching on the study area. This is evident by the various mountainous depressions in the study area.

Keywords: Trace metals, EDXRF, coal, shale, major metals, seam.

INTRODUCTION

Over the past few decades, the world has become increasingly wary of coal combustion emissions because of concern about trace, major and minor metal releases into the environment. The fact that coal-fired power plants throughout the world are the major sources of these metals released to the environment has several implications. This suggests that coal combustion is hazardous to health. An accurate and complete emission inventory for atmospheric trace metals on a global scale is needed for both modeler community and policy makers to assess the

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current level of environmental contamination by these pollutants, major emission sources and source regions, and the contribution of the atmospheric pathway to the contamination of terrestrial and aquatic environments (Pacyna and Pacyna, 2001).

Emissions of trace elements to the atmosphere from industrial processes depend upon the concentration of trace elements in the raw materials, processing technology employed and type of control equipment (Nriagu and Pacyna, 1988). Coal is largely composed of organic matter, but it is the inorganic matter in coal minerals and trace elements – that have been cited as possible causes of health, environmental, and technological problems associated with the use of coal (Swaine and Goodarzi, 1997). In order to address these problems, it is important to determine the concentration, distribution and form of trace elements in coal and shale. Toxic or potentially toxic trace and major metallic elements are usually contained in coal and its sediments in various forms. These metals will either stay in the ash or be vapourized during high temperature combustion. Portions of the vapourized metals will be in the form of metal fumes or particulates with diameters less than 1 micron and are potentially hazardous to the environment (Thomas, 1997).

Coal combustion is a major source of energy in many regions of the world. Recent concerns over the impact of atmospheric particulate matter emissions on global climate and human health have prompted a great need to better understand the detailed chemical composition of emissions from the combustion of coal (Charlson et al., 1992). Such measurements are necessary to properly assess the toxic effects of particulate matter from coal combustion and the impact of these emissions on urban and regional air quality problems (Park et al., 2001).

Several studies on trace and major elemental composition of coal have been reported in literature. One of such studies dealt with the concentrations of loadings from coal pile run off. The study established that suspended solids concentration and coal pile volume were significantly correlated with the concentrations of trace metals in the coal pile run off while hydrometereologic variables such as rainfall intensity, rainfall depth, and run off volume were weakly correlated with metals concentrations (Curran et al., 2000). Other works have been reported with heavy metals in suspended solids exceeding guidelines for open water disposal of dredged sediments. The result of this work also showed that Wustite and haematite are good tracers of industrial pollution and their distribution is of importance in determining the particle dynamics (Mayer and Manning, 1990). The modes of occurrence and concentration of trace elements in coal have been reported in previous works (Zhang et al., 2002). Trace and major metal emissions have been reported to be higher in coal and sediments than in fuel oil (Paiva et al., 1990; Srinivasa et al., 2005).

The aim of this study is to identify the trace and major elements in the shale and coal of different seams at Okaba in Kogi State Nigeria. Informations from this study will be used to correlate the data from standard trace and major elements compositions in coal. Thus the level of environmental degradation around the mine site due to anthropogenic activities will be recorded. It is also the intention of this work to create awareness on the existence of the coal mine and its attendant effect on the ecology. Mine sites can generate contaminant-bearing materials that can travel with run-off from the mine. It is important for environmental audits to determine whether or not stream sediments are contaminated and might be in need of remediation. This will stimulate more research on the Okaba coal mine especially in the areas of fly-ash for end users.

MATERIALS AND METHODS

Sampling

The Okaba coal mine is located at Lat 7^0 2'N and Long 7^0 43'E (Figure 1 and 3). It is a sparsely populated area with subsistence farming as the main occupation of the inhabitants. The settlement is about 500m from the mine pits of study – panel 10B mine pit (Figure 2). The depths of the seams and shale under observation are approximately at 5m intervals. The method of extraction was by direct excavation of the coal and shale beds using a mechanical excavator. The excavated coal samples are dark in colour and are shiny on exposure to sunlight. The shale samples are dark-brown in colour.

Sample preparation

The coal shale and coal samples were weighed and air dried and the moisture content determined by subtraction. The samples were pulverized to a particle size of < 5µ using a mortar and pestle. Without further treatment, 20 g of the coal and shale samples were individually and intimately mixed with a blinder in the ratio of 5:1 cellulose acetate blinder and pelletized at a pressure of 1.514×10^8 N/m^2 – 2.27×10^8 N/m^2 in a pelletizing machine. The pelletized samples were stored in desiccators for analysis (Plant et al., 1996).

Analytical processes

X-ray fluorescence spectrometry is widely used in the analysis of solid, liquid and gaseous petroleum samples. Simple sample preparation, high accuracy and precision and good detection limits are the principle reasons for this choice and make it an excellent technique for production control. The measurement condition used for the analysis of the elements in the samples is the Kα fluorescent lines for each element were used to set up the calibrations. Calibrating many identical systems for the same application is time consuming. The integrated re-calibration package in the MiniPal PANalytical Epsilon 5 software v 1.0D makes it possible to calibrate only one system and to transfer this calibration to the other systems without re-measuring all standards again (Ingham et al., 2007).

Preparation of standards

A set of toxic heavy elements and non-metals standards from British Geological Standards/ certified reference materials (BGS/CRM) and BGS/Euro standards was used to set up the calibrations. The trace element composition and homogeneity of these standards were assessed using ICP-MS and NAA as independent and reliable analytical methods (Ingham et al., 2007).

Instrumentation

The measurements were performed using a Panalytical B.V. MiniPal 4 model EDXRF spectrometer Lelyweg, Netherlands. It runs on a new version of software for MiniPal spectrometers that adds considerable flexibility for fast elemental analysis across the full spectrum of the entire periodic table. The MiniPal 4 software includes a variety of features that simplify applications set-up and data handling, such as re-calibration, spectra comparison, robust application defaults and extended calibration options. This instrument is equipped with a rhodium anode tube, 5 tube filters, a helium purge facility, high-resolution lithium -silicon drift detector and a 12-position removable sample changer with sample spinner. The tube setting is software controlled with a maximum power of 9 W. The measuring time for each sample is 60 seconds in an air medium (Ingham et al., 2007).

Voltage settings

The voltage settings for the analysis of various metals are in the following range: Na→Cl (4-12 V). The optimised voltage used is 8 V. K→V (12-20 V) has an optimised voltage of 18 V. Cr→Co (20-25 V) with an optimsed voltage of 25 V and Ni→Ag (25-30) with an optimized voltage of 28 V (Ingham et al., 2007).

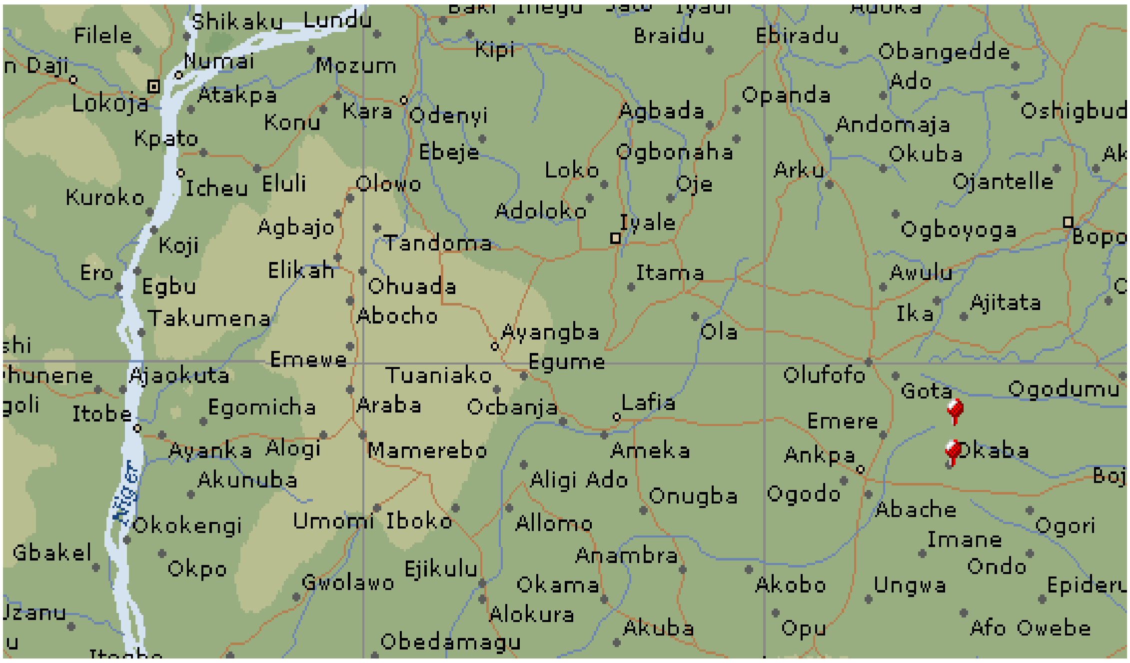

Figure 1: Map of parts of Kogi State, Nigeria, showing Okaba town.


2a
2b

Figure 2: The Figure above shows (a) an approach view of Panel 10B coal mine pit, and (b) a rear view of the mine pit. The overburdens are clearly visible on all sides of the mine pit (location: Lat 7^0 $2^{'}$N and Long 7^0 $43^{'}$E).

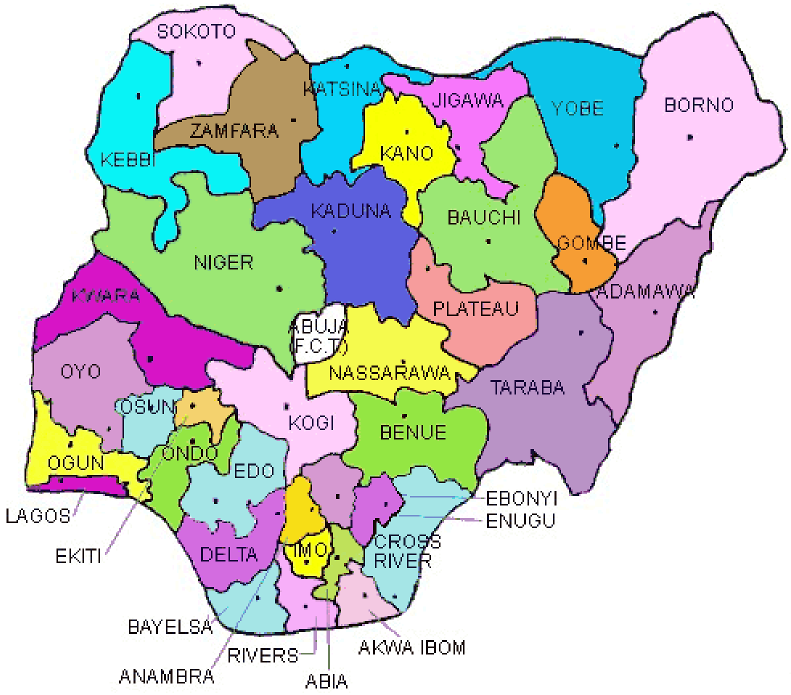

Figure 3: Map of Nigeria showing Kogi State.

RESULTS

The result of the trace and major metals compositions of Okaba shale and coal at different seams are presented in Tables 1a and 1b respectively, while some non-metal contents are presented in Table 2. The Vanadium/Nickel ratio (V/Ni) is presented in Table 3. The spectra of the studied samples are shown in Figures 4 – 10. A correlation between sulphur and potassium is presented in Table 4.

Titanium concentration in the samples ranged from 0.84±0.007 – 2-98±0.007 mg/g. Shale1 and 2 have a Ti content of 1.81±0.095 mg/g and 1.64±0.001 mg/g respectively. At OCS1 the concentration of Ti is 1.79±0.003 mg/g. This value reduced to 0.84±0.007 mg/g at OCS2 and increased sharply to 2.52±1.44 mg/g at OCS3 before peaking at OCS5 to 2.98±0.007 mg/g. Thus, OCS2 could be considered as a transition zone for Ti deposition in the coal seams. Chromium with a mean concentration of 0.06 mg/g showed a slight progressive increase in concentration from Shales1 and 2 (0.03±0.0mg/g), OCS1 and 2 (0.034±0.001 mg/g), OCS3 (0.09±0.005 mg/g) through OCS5 (0.12±0.025 mg/g). OCS4 showed a concentration of 0.08±0.0 mg/g, and thus could be described as exhibiting some transition characteristics. The range of Cr is 0.03±0.0 – 0.12±0.025 mg/g. Manganese concentration ranged from 0.02±0.11 – 0.30±0.02 mg/g.

The observed concentration range of vanadium is 0.02±0.44 - 0.20±0.05 mg/g with a mean of 0.08 mg/g. The high Fe content observed has a mean concentration of 11.86 mg/g with a range of 6.05±0.004 - 18.28±1.2 mg/g. Nickel showed a range of 0.01±0.075 - 0.12±0.001 mg/g with a mean of 0.06 mg/g. From the results, Al ranged from 5.93±2.49 – 8.42±0.003 mg/g with a mean average of 7.24 mg/g. This observed value increased as the depth of the coal seam increased.

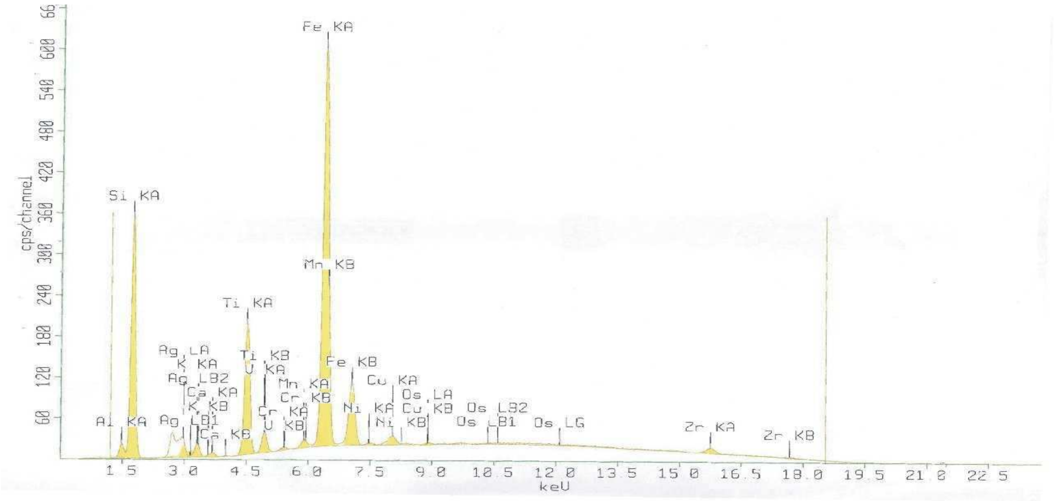

Figure 4: Energy dispersive X-ray spectrum of Okaba coal seam 1 samples: 5m depth from Open pit mine.

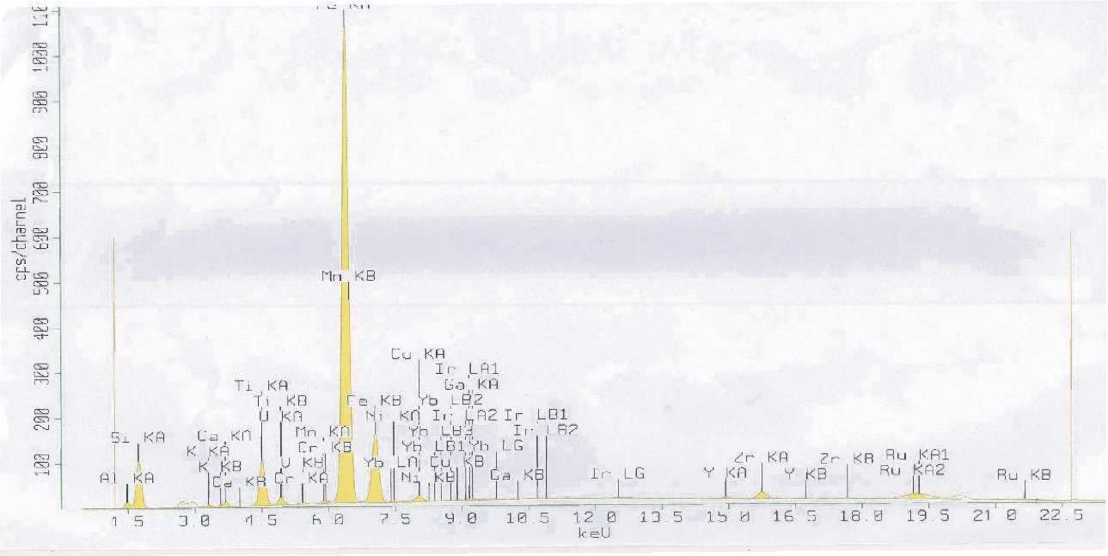

Figure 5: Energy dispersive X-ray spectrum of Okaba coal seam 2 samples at 10m depth from open pit mine site.

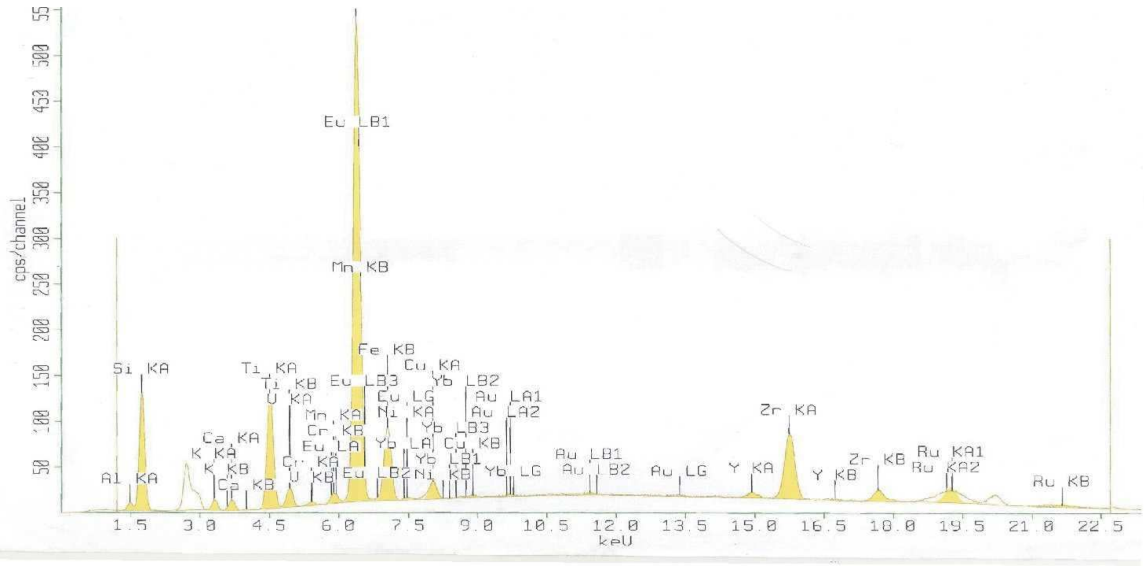

Figure 6: Energy dispersive X-ray spectrum of Okaba coal seam 3 samples at 15 m depth from open pit mine site.

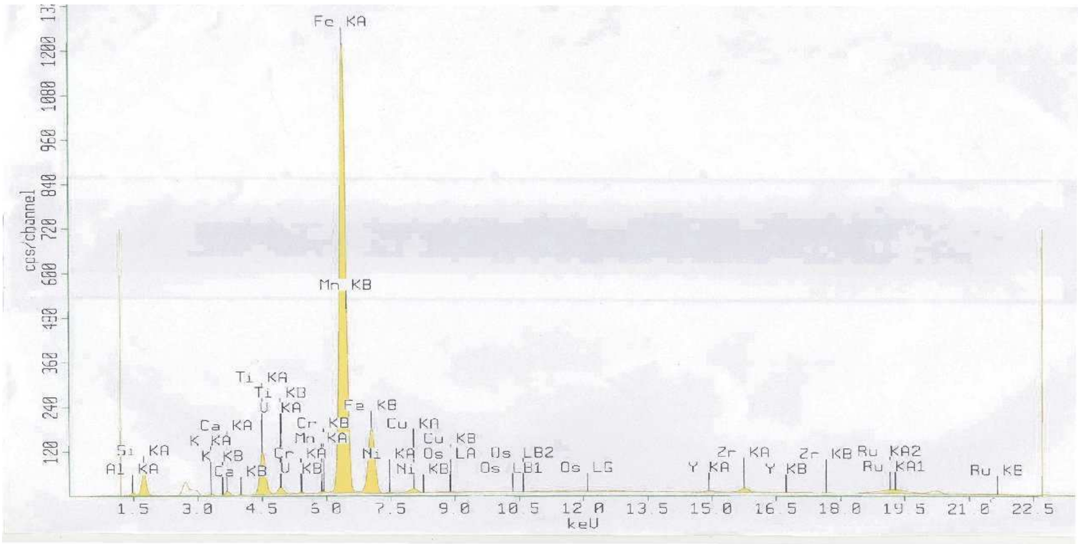

Figure 7: Energy dispersive X-ray spectrum of Okaba coal seam 4 samples at 20m depth from open pit mine site.

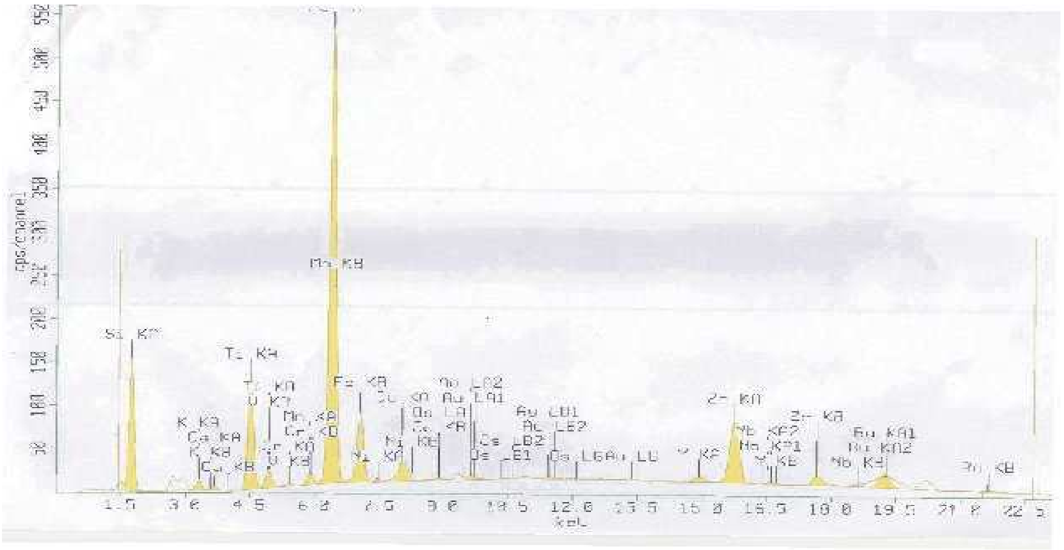

Figure 8: Energy dispersive X-ray spectrum of Okaba coal seam 5 samples at 25m depth from open pit mine site.

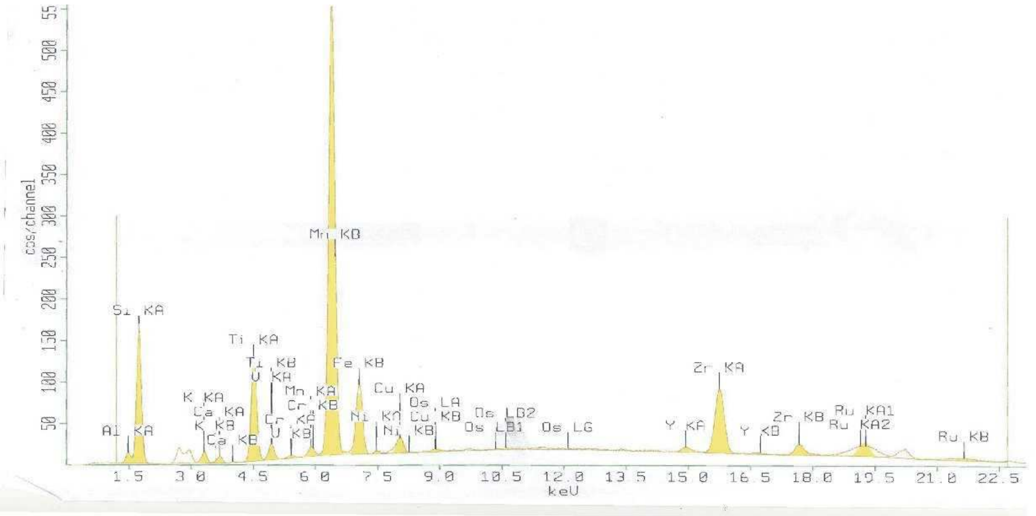

Figure 9: Energy dispersive X-ray spectrum of shale 1 sample 5 m above coal deposits from Open pit mine at Okaba.

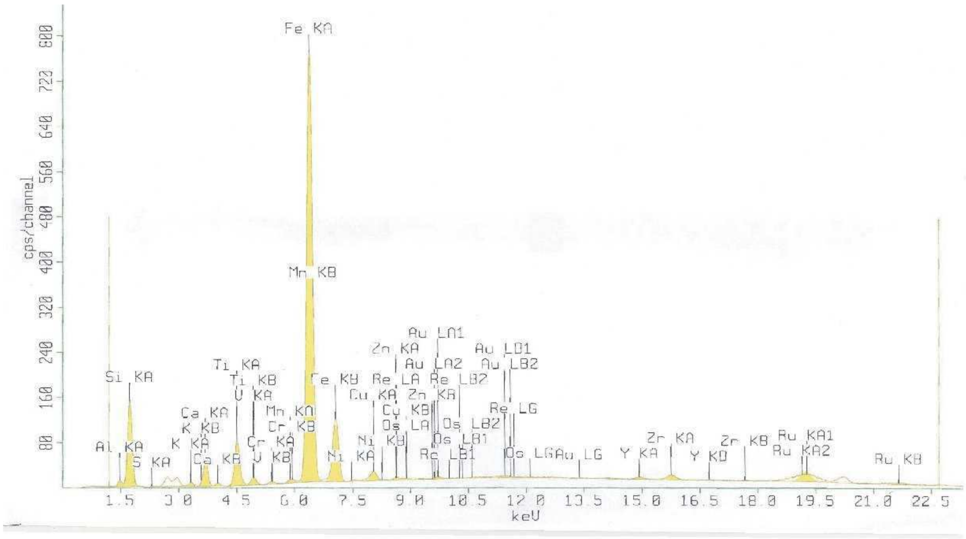

Figure 10: Energy dispersive X-ray spectrum of shale 2 samples 10m above coal deposits from open pit mine site.

Table 1a: Trace metals concentrations in the shale and coal at Okaba, Nigeria (mg/g).

	Fe	Ti	Cr	Mn	V	Ni	Cu	Zn
Shale1	6.80±0.69	1.81±0.10	0.03±0.01	0.03±0.01	0.06±0.01	0.01±0.08	0.05±0.02	ND
Shale2	6.05±0.01	1.64±0.01	0.03±0.01	0.02±0.01	0.06±0.01	ND	0.03±0.02	ND
OCS1	7.14±0.48	1.79±0.01	0.034±0.01	0.02±0.11	0.06±0.01	ND	0.06±0.01	ND
OCS2	15.12±2.7	0.84±0.01	0.034±0.01	0.03±0.81	0.02±0.44	0.12±0.08	0.42±0.09	ND
OCS3	18.28±1.20	2.52±1.44	0.09±0.01	0.22±0.02	0.20±0.05	0.07±0.02	0.46±0.01	ND
OCS4	16.38±0.01	2.16±0.01	0.08±0.01	0.24±0.01	0.09±0.02	0.07±0.01	0.55±0.01	ND
OCS5	13.30±0.01	2.98±0.01	0.12±0.03	0.30±0.02	0.06±0.01	0.12±0.01	0.62±0.01	ND
Mean	11.86	1.96	0.06	0.12	0.08	0.06	0.31	ND
Range	6.05-18.28	0.84-2.98	0.03-0.12	0.02-0.30	0.02-0.2	0.01-0.12	0.03-0.62	-
SCQ	0.73	0.06	16	15	23	10.8	5.9	

Table 1b: Major metals concentrations in the shale and coal at Okaba, Nigeria (mg/g).

	Al	**K**	**Ca**	**Mg**	**Na**
Shale1	8.11±0.0	2.13±0.075	ND	ND	ND
Shale2	8.42±0.003	2.08±0.005	ND	ND	ND
OCS1	8.37±0.0	2.16±0.0	ND	ND	ND
OCS2	6.37±0.0	1.50±0.01	0.53±0.41	ND	ND
OCS3	7.09±3.98	0.28±0.13	1.78±0.62	ND	ND
OCS4	6.38±0.0	0.40±0.001	1.85±0.004	ND	ND
OCS5	5.93±2.49	0.18±0.46	2.23±0.35	ND	ND
Mean	7.24	1.25	0.91	ND	ND
Range	5.93-8.42	0.18-2.16	0.53-2.23	-	-
SCQ	0.855	0.0748	0.13		

OCS1 – Okaba coal in seam 1, OCS2 – Okaba coal in seam 2; OCS3 – Okaba coal in seam 3, OCS4 – Okaba coal in seam 4; OCS5 – Okaba coal in seam 5, SCQ – Standards for coal quality. ND – Not detected

Table 2: Some non-metallic composition of Okaba coal and shale (%).

	S	**P**	**Si**	**Cl**	**Br**
Shale1	2.69	ND	26.17	ND	ND
Shale2	2.97	ND	26.38	ND	ND
OCS1	2.20	ND	25.19	ND	ND
OCS2	4.28	ND	19.88	ND	ND
OCS3	5.42	ND	11.66	ND	ND
OCS4	6.68	0.17	9.11	ND	ND
OCS5	8.64	0.17	6.58	ND	ND

Table 3: Trace metal ratios in Okaba coal seams and shale.

	V (mg/g)	**Ni (mg/g)**	**V/Ni**	**V/(V+Ni)**
Shale1	0.06	0.01	6.00	0.86
Shale2	0.06	ND	-	-
OCS1	0.06	ND	-	-
OCS2	0.02	0.12	0.17	0.14
OCS3	0.20	0.07	2.86	0.74
OCS4	0.09	0.07	1.29	0.56
OCS5	0.06	0.12	0.50	0.33

Table 4: Correlations between sulphur and potassium.

		S	**K**
S	Pearson Correlation	1	-.927**
	Sig. (2-tailed)		.003
	N	7	7
K	Pearson Correlation	-.927**	1
	Sig. (2-tailed)	.003	
	N	7	7

**. Correlation is significant at the 0.01 level (2-tailed).

DISCUSSION

Trace metals concentrations

The result for Ti concentration agrees with previous report on Okaba coal (Ewa, 2004). When compared to the worldwide averages of coal, these shale and coal samples are not enriched in Cr. These low values are closely correlated with the presence as recorded. An increase in Ca in different genetic types of calcite in coal and shale can accumulate different trace elements like Cr and Ni. These elements are in higher concentrations in calcite deposited from low – temperature hydrothermal fluid than in that deposited from ground water (Zhang et al., 2002). The result of Cr concentration agrees with the work previously carried out on Okaba coal (Adedosu et al., 2007).

The trend observed for Mn showed a progressive increase as the coal seam is increased. The low value of Mn may be attributed to part of fine – grained detrital minerals which are homogenously distributed in the organic matter of coals (Querol et al., 1997).

For vanadium, there is a narrow variation in their concentrations among the samples studied. This may however be associated with the formation of soil horizon before the accumulation of peat in the basin (Zeng et al., 2005). The high value of Fe is characterized by a high S content as reported in literature (Zhuang et al., 2000). The results observed in the S agreed with previous work on the correlation with Fe. This value however increased with an increase in the depths of coal seams. The result of this high Fe content may also suggest that Okaba coal is rich in mineral containing iron and thus of economic value. The increase in the concentration of Ni as the depths of the various seams increased agreed with previous work carried out on Ni. Such study in Heshan coal fields’ southern China indicated that Ni was concentrated in the upper and lower parts of the coal mines (Zeng et al., 2005). This result showed a close agreement with the result of Ni obtained with Okaba coal. In the case of Cu determination, a weak trend associated with the mineral matter was observed. This was also corroborated by the works of previous authors. Observed mean concentration is 0.3 mg/g while the range is 0.03±0.02 - 0.62±0.001 mg/g. The concentration however increased with increasing seam depth. This increase may be ascribed to the fact that Cu appeared to be partly complexed with organic matter (Given and Miller, 1987). Zinc was not detected in the samples plausibly showing a negative correlation with the organic matter (Querol et al., 1997).

The differences in the concentrations of Al may be explained partly by variations in the composition of the pore waters permeating the strata, and partly by the mobility of silica and alumina from different sources within the peat deposit (Ward, 1992). The values agreed with previous works on Nigerian coals (Ogugbuaja et al., 1999; Moses et al., 2002). As a neurotoxin, Al has been found to be bioaccumulated on the tissue of rabbits where coal combustion is in use in Nigeria (Ogugbuaja et al., 2004).

Major metals concentration

Potassium concentration ranged from 0.18±0.46 – 2.16±0.0 mg/g with a mean average of 1.25 mg/g. This value decreased as the depths of coal seams increased. Potassium is known to enhance the desulphurization process in coal in which the inorganic and organic sulphur were removed preferentially (Ratanakandilok et al., 2001). In correlation with sulphur content as shown in Table 2, the observed S concentrations decreased with an increase in the K content in the samples. Sample OCS5 with the lowest K concentration of 0.18±0.46 mg/g has the highest sulphur content of 8.64%, while sample OCS1 with highest K content of 2.16±0.0 mg/g has the lowest sulphur content of 2.20%. This abnormally sulphur contents as shown in Table 2 may however suggest that the Okaba coals accumulated in low-lying marine influenced palaeomires, developed on carbonate platforms. Many of these characteristics have also been recorded in the Heshan coals southern China (Longyi et al., 2003). The analysis of Ca in the various samples showed an increase in its concentration as the coal seam increased. However, Ca was not detected in Shale1, Shale2 and OCS1. Its concentration was observed at OCS2 (0.53±0.41 mg/g), OCS3 (1.78±0.62 mg/g), OCS4 (1.85±0.004 mg/g) and OCS5 (2.23±0.35 mg/g). The increase in these values with depth may be ascribed to leaching. In geochemical sense, these values of Ca reflect its common association with carbonate minerals for medium – to high – rank coals (Wang et al., 2008).

Non-metal concentration

Mg, Na, Cl and Br are not detected. This may be the result of leaching from overlying carbonates. However P was not detected in the Shale samples but was only observed in sample OCS5. This may be ascribed to leaching. Silicon showed a decrease in concentration with an increase in depth. This decrease from 26.17% in Shale1 to 6.58% in OCS5 may be attributed plausibly to organic activity within the seams as the depths are increased.

Trace metal ratio

Vanadium deposition in coal provides information on the maturity of such coals. This information can be sourced in the form of V/Ni ratios as shown in Table 3. This Ratio agrees with the work of Adedosu et al. (2007) on Nigerian coals. Correlation of this information with observed vanadium/nickel (V/Ni) ratio falls within the range of 0.17 – 1.29 for the coal samples while the calculated V/(V+Ni) ratio has a range of 0.14 – 0.56.

Conclusion

The result of this work showed that metallic compositions of coal and shale are necessary to predict the impact of emissions from different coal-fired combustion processes. Although these elements are also present in the exhaust of fuel-powered plants, the distribution of these metals is different and more importantly its impact on the environment is necessary to ascertain the level of air pollution. It is important to recognize however that these tracer and major elements are not present in the same distribution and concentration in emissions from industrial scale combustion of coal. The total metal in Okaba coal is greater than the shale overburden. This result may suggest that the mineral matter in Okaba coal may be derived primarily from a source similar to that of the shale overburden.

There is a correlation in the concentration of K and S as previously reported. All the major metals are above the coal quality standards for trace and major metals and are therefore potential sources of air pollution with its attendant health risks. Of all the trace metals studied, only Ti showed an average higher than the recommended standard for coal quality. To this end, quantitative analysis of minerals contributes significantly to coal quality. Informations from this can aid stratigraphic correlation between seams in a coal-bearing sequence or between subsections within an individual coal bed. This work, however, has identified the mobility of some trace and major elements in Okaba coal including their potential toxic ones. This study can also be used to evaluate the behaviour of Okaba coals from different seams in different utilization processes. Knowledge of these quality characteristics of Okaba coal deposits may allow the use of this coal as essential energy resource and effectively with less undesirable environmental impact.

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