

DISTRIBUTION OF SELECTED HEAVY METALS AND OTHER ELEMENTS IN COAL SAMPLES COLLECTED FROM COAL DEPOSITS IN KOGI STATE, NIGERIA

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Abstract

It is important that emissions of potentially toxic heavy metals and other elements from coal combustion are measured and if necessary, controlled in order to limit any environmental effects. Coal samples were collected from Enjema, Ibibio, and Okaba coal deposits in Kogi state to determine the selected heavy metals and trace elements in the samples. The coal samples were analyzed with the aid of Atomic absorption spectrometry (AAS) and X-Ray fluorescence (XRF) techniques. Heavy metals (Cd, Cr, Mn, Pb and Ni) were determined by AAS while selected trace elements (Fe, K, Ca, S) by XRF. The result shows that the selected heavy metals chromium, manganese, nickel, and lead were present at a high level when compared with heavy metals determined in coal samples collected from Lafia-obi and Chikila in Nasarawa State, North Central, Nigeria. in their previous study. Cadmium was not detected in the samples analyzed; the trace element determined were at lower concentrations when compared to the value of trace elements concentrations found in coal samples obtained from river Ekulu in Enugu State, South East, Nigeria. Sulphur was present at high concentration which can affect the body either when inhaled or absorb. The results indicated that the concentrations of the metals were high and this could have adverse effects on the inhabitant of the area. Apparently, there is need for constant monitoring of the stations to ascertain its pollution status.

Keywords: Coal, metals, soil, x-ray fluorescence, AAS

Introduction

Coal has been found to range from trace quantities of aluminium and thorium, to larger quantities of aluminium. Coal contain organic and inorganic materials, they are physically and chemically heterogeneous, combustible sedimentary rock. Organically, coal primarily consists of carbon, hydrogen and oxygen with lesser amounts of sulphur and nitrogen, while inorganically it consists of a diverse range of ash-forming compounds distributed throughout the coal (Cojocaru, Pantelica, Pincovski & Georgescu, 2006). Various elements in coal have been used to correlate coal beds. The elemental abundances vary between coal basins, within coal beds, and over distances in the same beds. These variations arise from differences in geologic and geochemical processes acting upon the peat and the coal over geologic time. In addition, variations in the plant communities, source material, detrital influx, diagenetic processes and epigenesis do influence the type and abundance of elements in the coal (Orem & Finkelman, 2004).

The metallic elements in coal can have profound environmental, economical, geological, technological and human health effects (Jauro, Agho, Abayeh, Obaje, & Abubakar, 2008). For instance; a few elements in coal (e.g. gold, silver, and uranium) have potential threats to the environments. Coal has been found to be important energy sources required to sustain the standard of living in the United States and many other developing countries such as China and

India, coal will be relied upon as the primary source of energy required to fuel industrialization and to improve standard of living of the populace (Finkelman, Orem, Castranova, Tatu, Belkin, Zhebg, Lerch, Maharaj, & Bates, 2002). In today's industrial society, there is no escaping exposure to toxic chemicals and metals. This is so because somehow, our society is dependent upon metallurgy for proper functioning. It is therefore not surprising that human exposure to heavy metals has risen dramatically in the last 50 years because of an exponential increase in the use of heavy metals or their compounds in industrial and agricultural processes. In the United States for instance, tons of toxic industrial waste are reportedly mixed with liquid agricultural fertilizers and dispersed across America's farmlands. Environmental contamination and exposure to heavy metals is a serious growing problem throughout the world, as both natural sources and anthropogenic processes emit heavy metals into various environmental media. Human exposure to aluminium, for instance, is caused by environmental factors such as soil contamination whereby aluminium can be mobilized as a consequence of soil acidification due to the use of certain fertilizers or acid rain; or as a result of aluminium use in some Industrial processes such as metallurgy, food preservation, water purification (Krewski, Yokel, Nieboer, Borchelt, Cohen, Harry, Kacew, Lindsay, Mahfouz, & Rondeau, 2007), and the use of pharmacological and cosmetic products (Ernst, & Coon, 2000; Ganrot, 1986).

The Federal government of Nigeria has a great renewed interest in the coal deposit. The main objectives of these are to diversify the economy which has been solely dependent on crude oil and its refined products. Nigeria has one of the largest coal deposits in Africa. Nigeria coal reserves are large, over 2 billion metric tons of which 650 million tons are proven. If fully resustained, the coal industry could fetch up to 5 billion naira in export earnings annually (Akande, Andreas & Erdtmann, 1992). Coal contains diverse amounts of trace elements in their overall composition (Adaikpoh, Nwajei, & Ogala, 2005). Combustion of coal is a potential source of several trace element emissions to the atmosphere. The electric power sector is the largest source of toxic pollutants, due to coal ash and coal waste, which contain toxins such as heavy metals. The waste left over from burning coal generates tons of coal ash and coal sludge in which 40% of that waste finds its way into new products and 60% is stored in ponds or pits, which can present health and environmental risks when released into ground water (Clean Air Task Force (CATF), 2000).

Equally, a study on Ikorodu, Lagos lagoon area (Ladigbolu, Balogun, & Shelle, 2011) reported higher concentrations of Fe, Cu, Pb, Cd and Zn in sediments when compared with the values in unpolluted sediment as well as the standards of the regulatory authorities (WHO, 1982; Federal Environmental Protection Agency (FEPA), 1988). Thus, there is indeed very high possibility of coal pollution from several environmental pollutants that most probably include some metal forms with equally very high possibilities of human contaminations through the environmental.

With the increasing use of coal, the growing impact on the environment from the potentially hazardous trace elements becomes a great concern. The information about the concentration, distribution and occurrence of trace elements in coal is of great importance (Zhan, Ren, Zhu, Chou, & Zheng, 2004). Only few studies and data on the chemical contents of metals in coal samples on the present sample locations are available. The objective of the present study is to investigate trace metal contents and heavy metal concentrations in coal samples collected from different locations in Kogi state, using AAS and XRF techniques for their metal analysis.

Materials and Methods

Sample Collection

The samples were collected during dry season (2014) from Enjema, Ibiobio and Okaba coal deposit, Kogi state North central zone of Nigeria. The samples were kept in polythene bags, sealed and labelled with a masking tape and transported to the laboratory for further analysis. Detailed record of every sample collected was done by attaching and appropriately inscribing labels showing the site, time and method of collection.

Pre-treatment of samples for ED- XRF analysis

The selected lumps of coal samples were air-dried and then pulverized with clean mortar and pestle and sieved into selected mesh powder. The powdered samples with particles diameter less than 50 μ m were retained for all examinations. The powdered samples were pressed into pellets and analysis of coal samples were performed using ED- XRF (Adedosu, Adedosu & Adebiji, 2007).

Sample preparation for AAS analysis

The coal sample was grinded into smooth particles and was sieved using a 5 mm micro-sieve. 5g of the sieved sample was weighed and kept in a clean dried conical flask. It was moistened with a little distilled water and was digested in different ratio of acid mixtures (5 ml of HNO_3 , 3 ml of HClO_4 , 2 ml of HCl). The mixture was placed on hot plate, heated at 90 $^\circ\text{C}$ until solution was reduced to 20 ml. The solution was allowed to cool and later transferred to 100 ml volumetric flask which was finally made up to the mark with distilled water. The solution was then filtered and kept refrigerated at 4 $^\circ\text{C}$ prior to analysis.

Results and Discussion

Five heavy metals were detected in samples of coal from Enjema, Ibiobio, and Okaba coal deposits in Kogi State using Atomic Absorption Spectrophotometer. These are Pb, Cd, Cr, and Mn and Ni. In addition; the following trace elements were also measured; Fe, Ca, S, K using XRF technique. The results were summarized in the tables 1 and 2 below

Table 1: Mean and standard deviation of heavy metals concentrations (mg/kg) using AAS technique

No	Locations	Cr $\pm$ S.D	Cd $\pm$ S.	Pb $\pm$ S.D	Mn $\pm$ S.D	Ni $\pm$ S.D
1	Enjema 1	0.45 $\pm$ 0.06	ND	0.32 $\pm$ 0.11	3.27 $\pm$ 0.06	1.71 $\pm$ 0.01
2	Enjema 2	0.165 $\pm$ 0.03	ND	0.36 $\pm$ 0.09	2.71 $\pm$ 0.07	0.93 $\pm$ 0.06
3	Ibibio 1	0.105 $\pm$ 0.04	ND	0.47 $\pm$ 0.02	0.54 $\pm$ 0.00	0.35 $\pm$ 0.00
4	Ibibio 2	0.075 $\pm$ 0.03	ND	0.65 $\pm$ 0.05	1.16 $\pm$ 0.05	1.33 $\pm$ 0.13
5	Okaba 1	0.300 $\pm$ 0.00	ND	0.54 $\pm$ 0.02	2.41 $\pm$ 0.01	1.33 $\pm$ 0.02
6	Okaba 2	0.190 $\pm$ 0.02	ND	0.42 $\pm$ 0.04	2.54 $\pm$ 0.03	0.64 $\pm$ 0.02

Table 2: Concentration (mg/kg) of trace elements using XRF technique

Locations	K	Fe	Ca	S
Enjema 1	21.6	7.02	5.36	24.27
Enjema 2	19.9	8.20	5.56	30.01
Ibibio 1	9.8	7.70	3.52	29.88
Ibibio 2	9.2	7.76	3.40	27.81
Okaba 1	6.52	5.10	8.01	68.92
Okaba 2	6.54	5.50	7.65	64.26

The mean concentration of the heavy metals in the coal samples had values of Pb that range from 0.32 mg/kg to 0.65 mg/kg, Cr; 0.075 mg/kg to 0.45 mg/kg, Mn; 0.54 mg/g to 3.27 mg/kg, Cd; not detected, Ni; 0.35 mg/kg to 1.71 mg/kg. All heavy metals measured are harmful and toxic at high concentration to human and can lead to environmental metal poisoning during combustion of coal. The results of this investigation also revealed that heavy metal occurrence are also of natural origin. The negative impacts of heavy metals result from their toxicity to biological processes including those catalyzed by microorganisms.

Manganese was the most abundant metal determined in coal samples from the selected locations. Manganese has the highest concentration in the coal sample at location 1 with a concentration of 3.27 mg/kg and lowest concentration at location 3 with a concentration of 0.54 mg/kg. High values recorded for manganese, this could be due to the presence of different effluents of variable sources e.g. sewage and domestic, agricultural and industrial wastes produced from outlets (Jauro, Agho, Abayeh, & Obaje, & Abubakar, 2008).

The manganese concentration in each location varies as effluents concentration varies in each location. The concentration of manganese recorded in this study was lower than the one recorded by Adekola, Alafara and Buhari (2012) (45.81- 155 mg/kg). Therefore, we can conclude that effluents of variable sources were present in soil of the coal samples resulting in high manganese concentration and this occurred mostly in location 1. Exposure to high levels of Mn (concentrations above 2.22 mg/kg) can affect the nervous system and very high levels may impair brain development in children.

FEPA standard for manganese intake either by exposure to or by inhalation is 2.22 mg/kg (Federal Environmental Protection Agency (FEPA) Act, 1991). Apparently, the use of coal samples collected from location 1, 2 and 5 can pose serious environmental effects to the users. Manganese may be organically bound in coal but is minor in high rank coals like West virginial (Swaine, 1990). Manganese in coal can impact coal mining. Manganese is important in steel alloy, in glass making and permanganate, it is a strong oxidizer used in laboratories and medicine. The next abundant metal in the coal samples was Nickel. Nickel has the highest concentration in the coal samples collected from location 1 with a concentration of 1.71 mg/kg and lowest concentration at location 3 with a concentration of 0.35 mg/kg. In a related research studies the obtained value recorded for Ni ranged between 0.064 - 0.067 mg/kg and this value were very low compared to the values recorded in this study. Accumulation of nickel in the heavy metal is also due to intake of sewages and effluents from industrial companies into water in the soil. . Small amounts of Nickel are needed by the human body to produce red blood cells, however, in excessive amounts, can become mildly toxic. Short-term over exposure to nickel is not known to cause health problems, but long-term exposure can cause decreased body

weight, heart and liver damage, and skin irritation. FEPA standard for Nickel intake either by exposure to or by inhalation is 1.08 mg/kg (Jauro, Agho, Abayeh, Obaje, & Abubakar, 2008) and therefore, at location 1, 3 and 4, the use of the coal samples from these aforementioned locations can be detrimental to human. Nickel inhalation possesses a greater risk than nickel in water. It may cause lung cancer or nasaltumors. Many people also develop dermatitis upon skin contact with nickel (Jauro, Agho, Abayeh, Obaje, & Abubakar, 2008).

Lead was detected at high concentrations lower than manganese and nickel in the coal samples, but in location 4 highest concentration for lead was recorded (0.65 mg/kg) and lowest concentration (0.32 mg/kg) was recorded in location 1 respectively. Lead has the highest concentration in the coal samples. The observed values for lead was found to be within the acceptable FEPA limit (0.32-0.65 mg/kg) and the acceptable limit according to FEPA is <1.00. The obtained results were compared with their related studies, in Jauro et al., lead was not detected at all in the samples analyzed. In Adaikpoh, Nwajei and Ogala (2005). The value recorded for lead ranged between 0.013 – 0.0017 mg/kg which was very low to the results obtained in this study. Accumulation of Lead as heavy metal in coal is through deposition of sewages and gaseous effluents etc. High Lead concentration recorded in the fourth location could be due to natural and anthropogenic sources. Others sources include, the use of lead containing ceramics dishware, metal plumbing, food and lead solder (White, Cory-Slechta, Gilbert, Tiffany-Castiglioni, Zawia, Virgolini . . . , 2007). Human being can get exposed to lead contamination from industrial sources such as lead smelting and manufacturing industries (White, Cory-Slechta, Gilbert, Tiffany-Castiglioni, Zawia, Virgolini . . . , 2007; Goyer, 1996).

Various effects occur over a broad range of doses, with the developing foetus and infant being more sensitive than the adult. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system. FEPA standard for lead intake either by exposure to or by inhalation is 0.45 mg/kg (Federal Environmental Protection Agency (FEPA) Act, 1991). and therefore, at location 3, 4 and 5, the use of the coal samples from locations 3, 4 and 5 are be detrimental to human and can lead to human poisoning. The acceptable limit for chromium according to FEPA standard is < 1.00. Apparently, from these results it can be inferred that concentration falls within the acceptable limit of FEPA. Chromium has the highest concentration in the coal sample at location 1 with a concentration of 0.45 mg/kg and lowest concentration at location 4 with concentration of 0.075 mg/kg. Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration and long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. FEPA standard for chromium intake either by exposure to or by inhalation is 0.24 mg/kg (Federal Environmental Protection Agency (FEPA) Act, 1991).

Cadmium was not detected in all coal samples at each location. In the current study cd was not detected in the sample analyzed. Accumulation of Cadmium as heavy metal in coal is through deposition of sewages, atmospheric deposition and fertilizer application on the soil (Goyer, 1996). However, with the absence of cadmium, we can say that no agricultural activities was done near the coal deposits because, fertilizer would have been applied to boost growth of crops and that would have been the source of our cadmium as heavy metal.

The most significant use of cadmium is in nickel/cadmium batteries, as rechargeable or secondary power sources. Cadmium coatings provide good corrosion resistance, particularly in high stress environments such as marine and aerospace applications where high safety or reliability is required. Cadmium is also present as an impurity in several products, including phosphate fertilizers, detergents and refined petroleum products. In humans, long-term exposure is associated with renal dysfunction, obstructive lung disease and lung cancer. Cadmium may also produce bone defects in humans. FEPA standard for Cadmium intake either by exposure to or by inhalation is 0.18 mg/kg (Federal Environmental Protection Agency (FEPA) Act, 1991) or therefore, it is not risky to human health.

The major elements in soil are derived from inorganic and organic sources (Swaine, 1990). Most of these trace elements are useful in low concentration in human but in high concentration; they can be toxic to human and can affect the body. These trace elements have been proven dispensable for normal growth and reproduction of all higher plants (Bowen & Kratky, 1983).

The concentrations of trace elements in most of the samples analyzed were found to be less than the levels in most U.S and China coals (Finkelman, Orem, Castranova, Tatu, Belkin, Zhebg, Lerch, Maharaj, & Bates, 2002). This has been shown not dangerous to human health. Thus, proper use of the coal should not result in significant health concerns regarding exposure to these trace elements. Sulphur, the most abundant trace element found in the coal samples from these locations. The highest concentrations of sulphur were recorded in location 6 with a concentration of 56.2 mg/kg while lowest concentration was recorded at location 1 with a concentration of 24.27 mg/kg (Ryoo, Choi, & Hong, 2000).

The sulphur content of coal varies considerably with the nature and origin of the fossil deposits. When coal is burnt, its sulphur content combines with oxygen to form sulphur dioxide, which contributes to both pollution and acid rain (Liu, Cao, Luo, & Chen, 2009). Sulphur in coal cannot be removed by physical means and the existing chemical processes are costly. Short term exposure to high level of sulphur causes breathing difficulties and obstructing airways while long term exposure results in chronic bronchitis and respiratory illness.

Sulphur is required in the body for detoxification. Sulphur bonds are required for proteins to maintain their shape and the bond determine the biological activity of the proteins. Potassium was the next abundant elements in the selected coal samples. Potassium has its highest concentration in the coal sample at location with a concentration of 21.6 mg/kg and lowest concentration at location 5 with a concentration of 6.52 mg/kg. Industrial activities and plants or sewages deposits in the surrounding water and oil are sources of potassium in coal. Kidney disease is the most common symptoms of exposure to high level of potassium. Low level of potassium can also lead to breakdown of red blood cells, muscle tissues and other tissue injury. Potassium in the body helps muscles to move, nerves to work and kidneys to filter blood.

Highest concentration of iron in the coal sample was recorded at location 2 with a concentration of 8.2 mg/kg and lowest concentration at location 5 with a concentration of 5.1 mg/kg. In a related study carried out by Jauno et al., on Lafia-Obi and Chukka coal samples in Nasarawa State. The concentration of iron recorded ranged between 21.95 - 49.555 mg/kg. The values were higher than FEPA limit of 70 mg/kg. Therefore, the value recorded for iron in this study found within the acceptable limit. Iron is mainly produced by industrial activities, and deposit slowly in the surrounding water and soil. Since Iron is present, its high concentration indicates

the presence of iron bearing minerals such as iron pyrite, and a kerinite (Liu, Cao, Luo, & Chen, 2009). Exposure to high level of Iron concentration causes nausea and vomiting, abdominal pain and diarrhoea, gastrointestinal bleeds, serious overdose, which causes hepato cellular necrosis (jaundice, hepatic failure) and gastric outflow obstruction, which may be a late complication. Calcium, the least abundant elements determined in the coal samples from the selected locations has its highest concentration in coal samples from location 5 with a concentration of 8.01 mg/kg and lowest concentration at location 4 with a concentration of 3.4 mg/kg.

Calcium is used in the body for the production of bones. Exposure to high level of calcium can cause damage to kidneys, kidney stone, nausea, vomiting, constipation, poor appetite, weakness and weight loss. The heavy metals and trace elements determined were compared with results of a study of environmental metals pollutants load of a densely populated and heavily industrialized commercial city of Aba, Nigeria (Tobias, Ndubuisi, Ezejiofor, Udebuani, Ezeji, & Ayalogbu, 2013) which generally revealed that the mean concentrations for most of the metals including such toxicants as lead, nickel, chromium, cadmium, etc. were all found to be quite high relative to those of the control sites where (except iron, manganese and copper) most of them were either not detected at all or the concentration of the detected ones were relatively low which is in concord with the concentration of heavy metals and trace element determined except in cadmium which was not detected in the coal samples.

Trace elements concentration was compared with concentration result of the physico chemical characterization and speciation of sulphur of Nigerian coal samples carried out by Adekola, Alafara and Buhari (2012) and was found relatively low to concentration of trace elements in the coal samples from the present study. The data also shows that all metals investigated in these coals have mean content lower than the Chinese Pernian coals (Shifeng, Deyi, Yuegang, Mei, & Liming, 2005). The concentrations of heavy metals and trace elements determined in this study were found to be higher than trace elements determined in coal sediments from river Ekulu in Enugu (Adaikpoh, Nwajei, & Ogala, 2005). In general, the result of the trace elements recorded in this study, it was observed that Ca, Fe, and Sulphur was found as a major elements, similar case was observed in this study.

Conclusion

The study of heavy metals and trace elements content needs to be considered and studied for the interest of geochemical studies and economic interest. The selected heavy metals were all present except cadmium. The other elements were also present both in small and larger percentage. Therefore, the monitoring and assessment of the environmental quality of coal plays an important role in restoring damaged ecosystems, protecting soil environmental quality, and developing a scientific basis for sustainable coal mining with improved human health impact. Thus, heavy metals determined and found in the coal samples are detrimental to human beings, residents of these areas are at great risk of environmental metal poisoning, and the selected trace elements was found in the coal sample. The heavy metals and trace elements bioaccumulation in plants and especially in human can lead to serious health challenges. From the findings, it shows that coal combustion is a source of toxic heavy and trace elements and the use as fuel should be minimized.

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