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DISTRIBUTION AND SIGNIFICANCE OF HEAVY METALS IN SOME COALS FROM BENUE TROUGH

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ABSTRACT
The knowledge of the concentration of heavy metals is required when evaluating coals for combustion, conversion and also to evaluate potential undesirable environmental and health impacts resulting from coal use and their geochemical relevance. This research focus on determination of concentrations of Cr, Fe, Cd, Pb, Mn, Zn and Cu in Chikila, Lamja, Lafia Obi, Maiganga and Okaba coals from Benue Trough using Atomic Absorption Spectrophotometry (AAS). Lafia Obi coal has the highest concentrations of Fe, Cr and Mn with values 314.28 mg/kg, 108.60 mg/kg and 103.53 mg/kg respectively. The highest concentrations of Cu (89.23 mg/kg) and Zn (8.17 mg/kg) were found in Okaba coal while Lamja coal has the highest concentration of Cd (1.28 mg/kg). Lead was below the detection limit in all the coal samples while chromium was not detected in Lamja coal only. The concentrations of all the metals in the coal samples, with the exception of cadmium in Chikila coal, are above the approved limits set by the Federal Environmental Protection Agency. Therefore, inappropriate combustion of these coals and the wastes generated may pose a threat to the immediate environment. All the coals investigated are of similar depositional environment.

Keywords: *Coal, heavy metals, geochemistry, Benue Trough.*

INTRODUCTION
Nigeria is blessed with a large coal deposits most of which are reported to be within the Benue Trough (Carter *et al.* 1963; Obaje *et al*., 1994) which is subdivided into Lower, Middle and Upper portions. The Lower Benue Trough, which forms the Anambra Basin, is a major coal producing basin in Southern Nigeria where massive exploration and exploitation activities have been on since 1916 owing to the discovery of commercial coal in Udi near Enugu in 1909 by the Mineral Survey of Sothern Nigeria (Famuboni, 1996). However, the Lafia-Obi coal deposit in the Middle Benue Trough is geologically, the oldest coal deposit in Nigeria so far discovered. This deposit is believed to be Turonian – Coniacian in age (80-95 million years ago) (Obaje and Hamza, 2000).

Coal the most impure of fossil fuels. The impurities range from trace quantities of aluminum and thorium, to larger quantities of aluminum and iron. The metallic elements in coal can have environmental, economic, technological and human health impacts (Jauro *et al*., 2008a). Therefore, knowledge of their concentration is vital when assessing coals for combustion and conversion and also to evaluate potential unwanted environmental and health impacts that may result from coal use as well as their geochemical relevance.

The inorganic aspect of geochemistry which involves heavy metals can give information on source rocks, coals and shales (Onojake *et al*., 2011). The nature of occurrence of trace metals, their distribution patterns and concentration in crude oils and coals can give information on the origin, migration, environment of deposition and maturation of source rocks as well as providing a basis for regional geochemical prospecting (Onojake *et al*., 2011). Metals of proven association with organic matter may be used as reliable correlation tools. Nickel, Vanadium and Cobalt (usually referred to as biophile elements) are such examples (Akinlua *et al*., 2007).

Therefore, in a competitive market environment, detailed knowledge of coal may be a deciding factor in marketing success (Boyd, 2004). The information on the concentration of heavy metals in a prospective coal may be required by the purchaser to better manage the consequent environmental impact requirements and for price bargaining (Boyd, 2004).

As a result of a key relation between energy resources, national development and economic growth, coal industry is improving world-wide and Nigeria should not be left out. Despite the reported occurrences of coal deposits in the above areas, information about them is limited (Jauro *et al*., 2008b). The Federal Government of Nigeria recently announced its plan to generate more power from coals of Benue Trough to end the perennial power outage in the country. Thus, this research investigates the concentration of heavy metals in some coals from Benue Trough, Nigeria.

MATERIALS AND METHODS
Sample collection
The samples were collected from coal seams at Lafia Obi (Nasarawa State), Okaba (Kogi State), Maiganga (Gombe State) as well as Chikila and Lamja (Adamawa State) after scrapping of the top 30 cm lay. The coal samples were pulverized, labeled and stored in a black polyethane bags for subsequent use. The gross sample was reduced to analytical sample by cone and quatery.

Sample digestion
The sample (1 g) was digested using 10 cm^3 of conc. nitric acid (69.5%, BDH) and 2 cm^3 of conc. perchloric acid (70%, BDH) until the brown fume disappeared. The mixture was then filtered through Whatman No. 1 filter paper into a 100 cm^3 volumetric flask, which was made to the mark with distilled water and each sample was prepared in triplicate. For the blank sample, a mixture of 10 cm^3 of conc. nitric acid (69.5%, BDH) and 2 cm^3 of conc. percholoric acid (70%, BDH) was heated until a dense white fume and a clear solution

appeared. Upon cooling, it was diluted and made to mark in a 100 cm^3 volumetric flask.

Analysis

The concentrations of the heavy metals were determined using an Atomic Absorption Spectrophotometry (SensAA, GBC). The results of each sample was in triplicate. Data were reported as Mean ±SD (standards deviation). Statistical treatments were done using Minitab Statistical Package. One-way ANOVA was used to test the significant difference between the coal samples, using Turkey test at 95% confidence level ($\alpha = 0.05$).

RESULTS AND DISCUSSION

The results obtained from the heavy metal analysis in all the coals are presented in Figure 1-7.

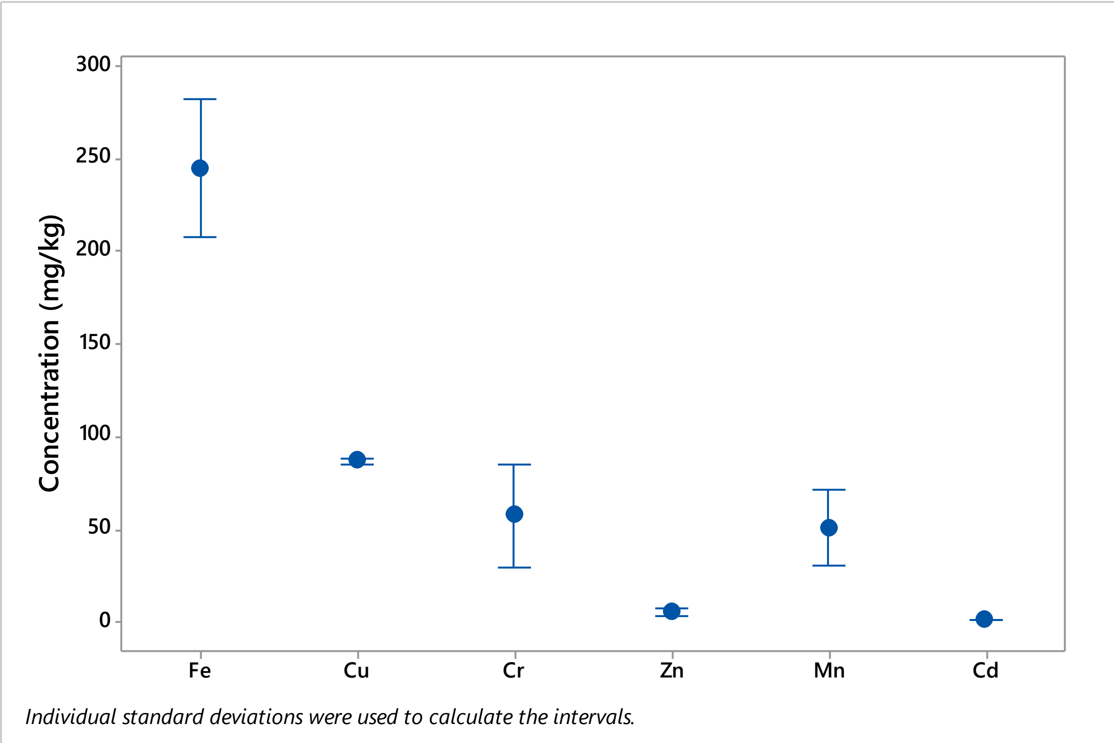

Figure 1: Concentrations of Heavy Metals in Coal Samples

Fig. 1 shows that iron has the highest concentration in all coal samples with a mean value of 244.99 mg/kg followed by copper with a mean value of 86.68 mg/kg while cadmium is the lowest with a mean value of 1.16 mg/kg. All the samples have high iron content (Fig. 2) with Lafia Obi having significantly ($p < 0.05$) higher concentration compared to other samples. Chikila and Lamja coals have similar iron content ($p > 0.05$). Maiganga coal has the lowest content of iron. For Cu (Fig. 3), all the samples have similar ($p > 0.05$) copper content.

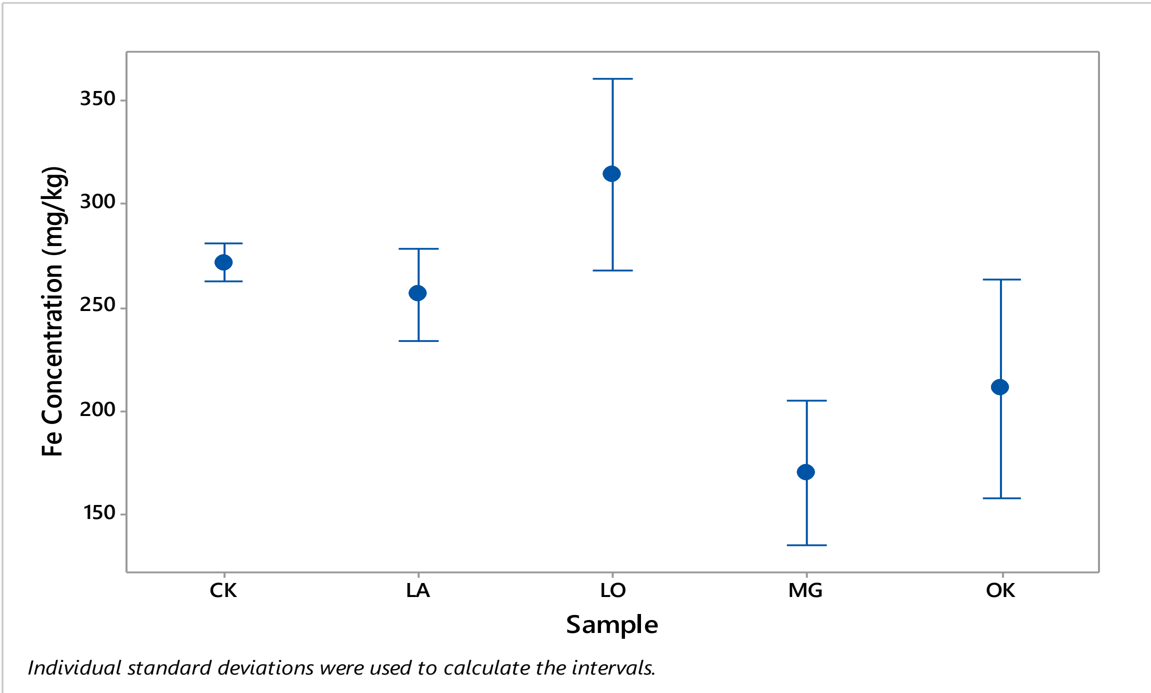

Figure 2: Concentration of iron in coal samples

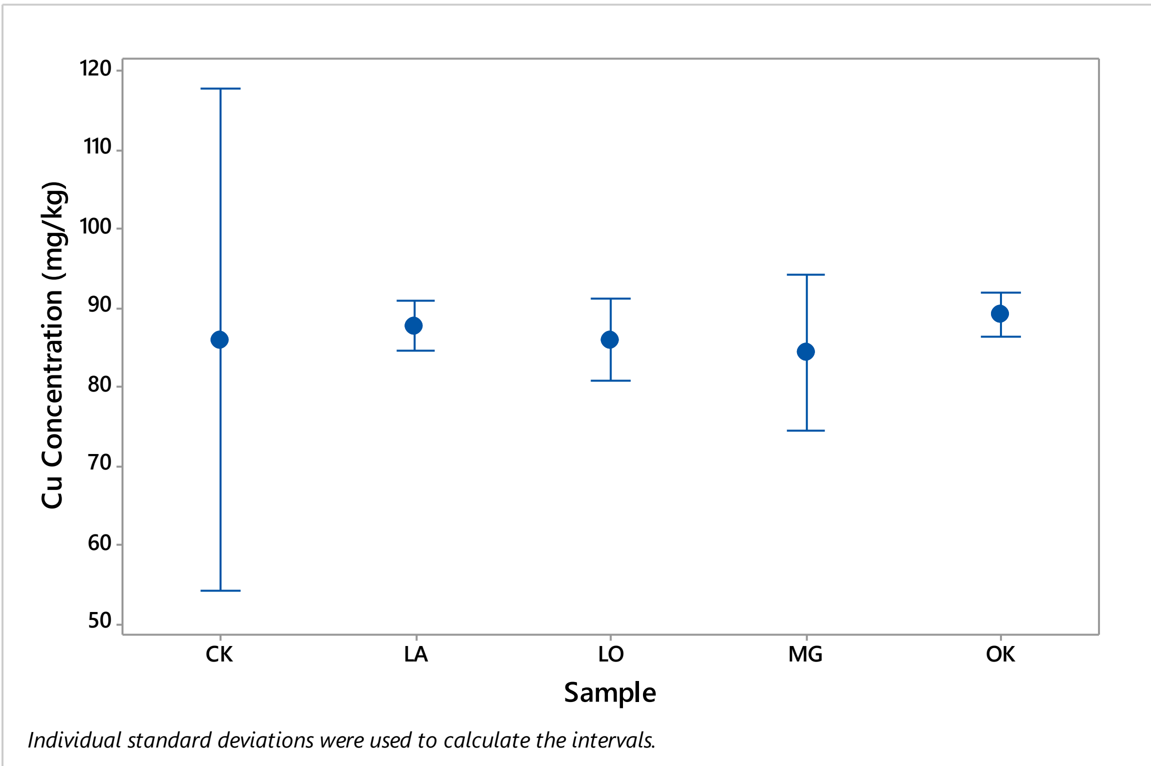

Figure 3: Concentration of copper in coal samples

All samples have significantly ($p < 0.05$) different Cr content (Fig. 4) ranging from 0 to 108.60 mg/kg. Lamja, Maiganga, and Okaba coals have similar ($p > 0.05$) Zn content (Fig. 5) which are significantly ($p < 0.05$) higher than Chikila coal. Lafia Obi coal has the lowest content of Zn. For Mn (Fig. 6), Lafia Obi coal has significantly ($p < 0.05$) higher concentration compared to other samples. Chikila, Lamja and Maiganga coals have similar ($p > 0.05$) Mn content. Okaba coal has the lowest content of Mn. All samples have similar ($p > 0.05$) Cd content (Fig. 7). Pb was below the detection limit.

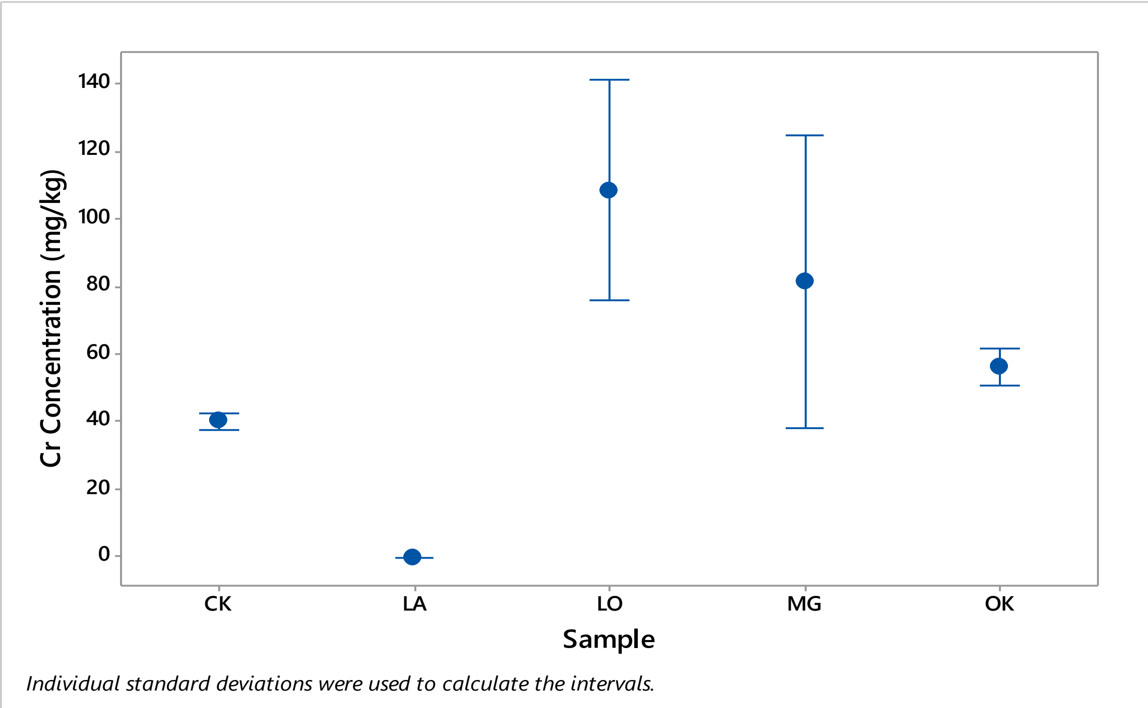

Figure 4: Concentration of chromium in coal samples

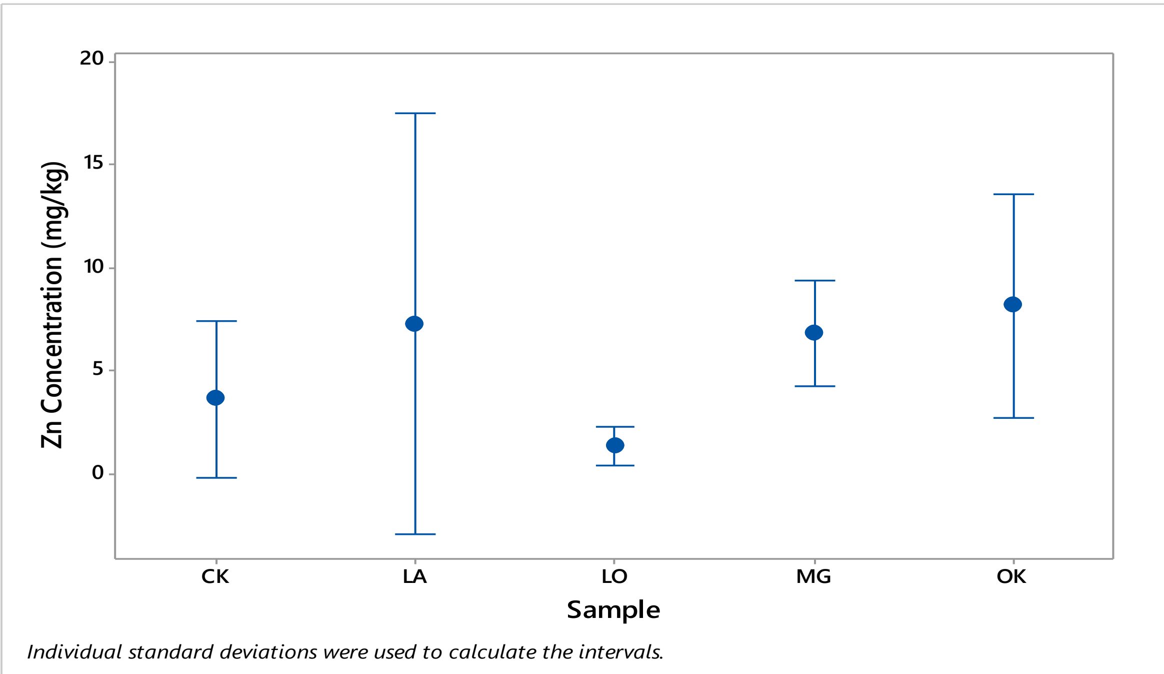

Figure 5: Concentration of zinc in coal samples

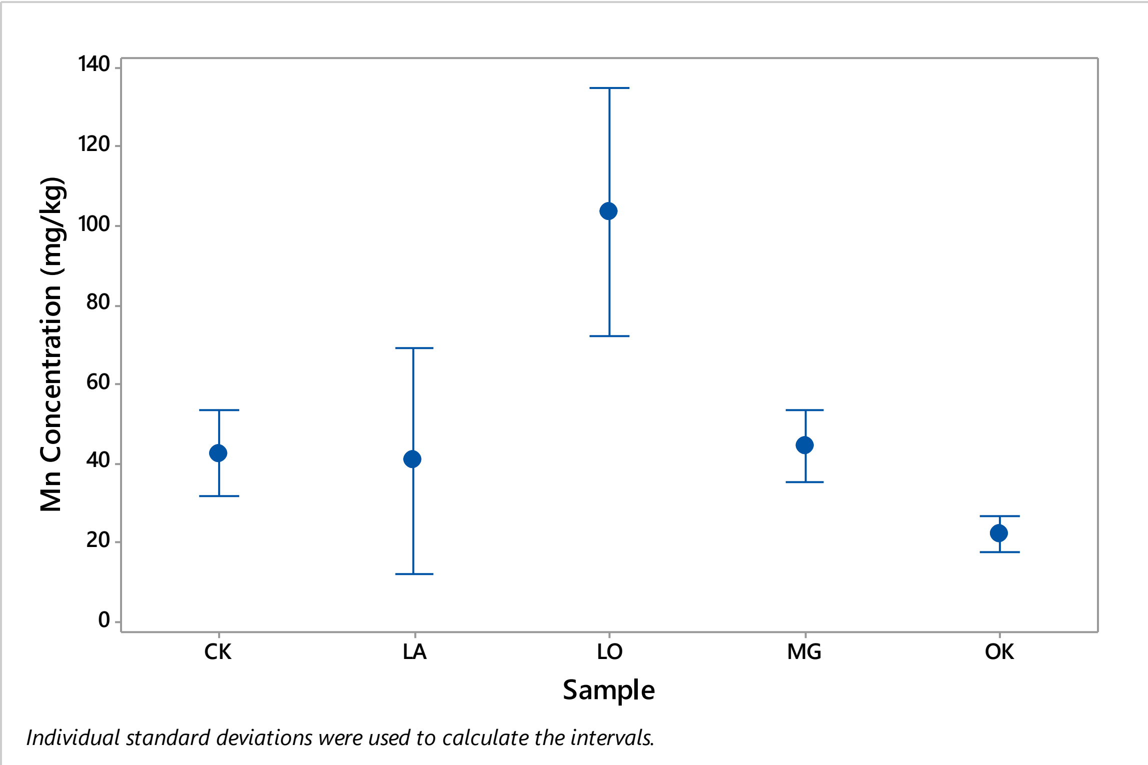

Figure 6: Concentration of Manganese in coal samples

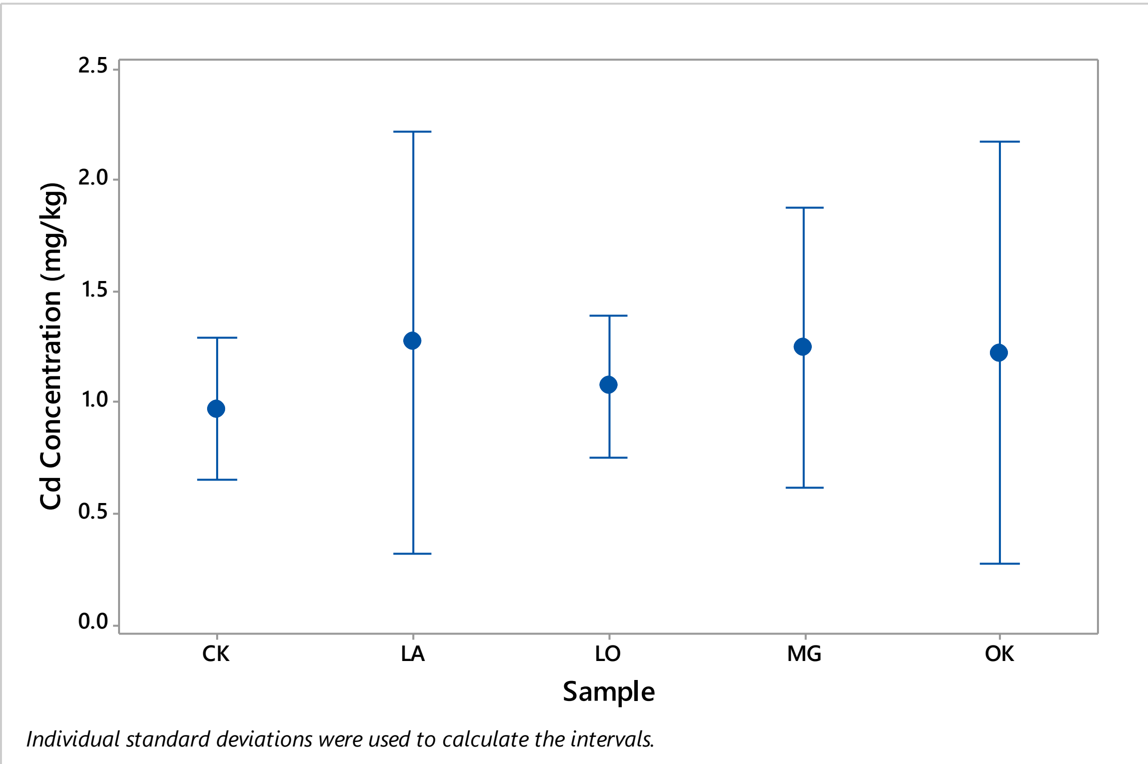

Figure 7: Concentration cadmiun in coal samples

Cr was not detected in Lamja coal and Pb was not detected in all the coal samples analysed. This is in agreement with Jauro *et al*. (2008a) where Pb was not detected in Chikila and Lafia Obi coals. Fe is stable in coal due to its multiple forms of occurrence in coal. It exists as oxides, in clay and in organic association (Frinkelman, 1993). The mean concentration of iron is lower than the concentration of six coal samples from South African power stations (Kelanga, 2011) and it's not within the range reported by Goodarzi et al. (2006). High iron concentration in coal is undesirable as chronic inhalation of iron oxide dust or fume may result in development of siderosis and enhances the risk of lung cancer (Jauro, *et al*., 2008a). The iron may be present in form of iron bearing minerals like siderinite, ankerinite and pyrite which have been shown to be the major minerals of iron found in coal. The concentration of copper is higher than the concentration in some South African coals (Kalenga, 2011) and it's not within the range reported by Willis (1983).

Cr with a mean concentration of 57.29 mg/kg is lower than the concentration in some South African coals (63.65 mg/kg) (Kalenga, 2011) but within the range reported by Wagner and Hlatshwago (2005). Cr in form of –Cr (IV) and Cr (VI) may have genotoxic and carcinogenic effect (Akinsola, 2007). Cd (1.16 mg/kg) may cause painful degenerative bone disease called *Itai-itai* in older women who had many children (Kevin and Lewis, 1995).

The combustion of all the coals investigated in a coal power plant may pose a threat to the environment due to their presence in high concentrations.

Zinc occurs in the environment primarily in inorganic forms, either dissolved or as insoluble complexes and compounds (USPHS, 2000). In soils, it often remains strongly sorbed, and in the aquatic environment it will predominantly bind to the suspended material before finally accumulating in the sediment (Bryan and Langston, 1992). If plants and animals are exposed to high concentrations of bioavailable zinc, significant bioaccumulation can arise with possible toxic effects such as interveinal chlorosis in new leaves of plants and leg paralysis in birds (USPHS, 2000).
Mn occurs in most Fe ores, in coal and, in much lower concentration in crude oil (Speight, 2005). Because of its low volatility, Mn settles mostly in the immediate vicinity of its source of release. It has been widely accepted that elemental constituents play significant role in designing coal combustion systems and also affect coal liquefaction and gasification processes (Speight, 2005).

The distribution of heavy metals in coal can give information on the geochemical environments during coal formation (Liu et al., 2001). The absence of Pb and the similarity in concentration of all sampling sites with regards with Cu and Cd signified the same depositional environment which is in agreement with the work of Usman (2015) using biomarker parameters where it was indicated that the coals are of terrestrial environment under oxic condition.

The observed disparity in the concentration of the individual metals in the various samples may be due to minerals compositional difference arising at the epigenetic phase or syngenetic phase of the coal formation (Speight, 2005). Disposal and/or any use of coal ash are becoming a major issue because of its potential to contaminate surface and ground water with metals. The stipulated limits set by the Federal Environmental Protection Agency for Cr, Cd, Zn, Cu and Pb is less than 1 mg/kg while for Fe and Mn is 20 mg/kg and 5 mg/kg respectively. The concentrations of all the metals in the coal samples analysed with the exception of cadmium in Chikila coal are above the agreed limits set by the Federal Environmental Protection Agency (FEPA, 1991). Therefore, the combustion of these coals and inappropriate disposal of the wastes may pose a threat to the environment.

CONCLUSION

This research investigated the concentration of heavy metals in Lamja, Chikila, Maiganga, Lafia Obi and Okaba coals from Northern Nigeria. The result revealed that lead was below the detection limit in all the coal samples while chromium was not detected in Lamja coal. The concentrations of all the metals in the coal samples analysed with the exception of cadmium in Chikila coal are above the stipulated limits set by the Federal Environmental Protection Agency (FEPA, 1991). Therefore, the combustion of these coals and the wastes generated may pose a threat to the environment. The coals investigated are of similar depositional environment.

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