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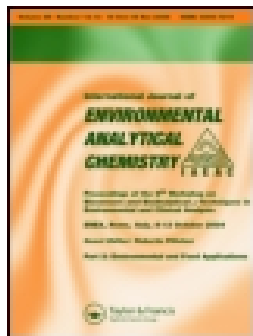
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# Assessment of the Selected Heavy Metals Contamination of Fossil Fuel (Coal) within Okaba, Onyeama and Ribadu Mining Sites, Nigeria

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## ABSTRACT

**Aim:** The concentration levels of selected trace metals in coal samples collected from three different locations, namely Okaba coal deposit Kogi State, Onyeama coal deposit and Ribadu both in Enugu state, were investigated in this study.

**Method:** The representative coal samples were analysed for the presence of trace metals such as Cadmium, Chromium, Lead and Copper using an Atomic Absorption Spectrophotometer.

**Result:** The mean concentrations of  $0.043 \pm 0.007$ ,  $0.020 \pm 0.006$ ,  $0.032 \pm 0.006$  and  $7.245 \pm 0.557$  (mg/kg) were observed for the selected metals. The concentration of the selected metals investigated with the exception of Lead was found to be above detection limit for EPA – NBS standard and compared to the previous work done globally.

**Conclusion:** The emission of coal has been attributed to the release of critical heavy metals such as Cadmium, Chromium, Lead and Copper, into the environment thereby posing a threat to human health and endangering the ecosystem.

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Coal; toxicity; heavy metals; Okaba; Onyeama; Ribadu

## 1. INTRODUCTION

Fuel may be defined as any substance capable of being ignited with the tendency of generating heat when combusted in air and obtainable in the large amount used for domestic purposes such as power generation, cooking, and heating [1].

They are products of natural processes of anaerobic decay of buried dead organisms and are carbonaceous materials. Organisms with their corresponding fossil take mostly over millions of years and in most cases exceed 650 million years [2]. The assumption that fossil fuels are products of fossilised remnants of dead plants [3] as a consequence of high temperature and pressure on biosphere over millions of years, thereby referred to as biogenic theory was first devised in 1556 by the duo George Agricola and Mikhail Lomonosov [4].

The utilisation of coal had been known for long in China before it was introduced to Europe. They were essentially utilised in North-Eastern China as a source of heat for

smelting Cu in 1000BCE. The initial allusion to the exploit of coal as a fuel could be traced to Europe by the Greek scientist Theophrastus [Circa 71–287BC] [5].

Electricity and heat generation had been the primary uses of coal through the combustion process.

Coal was the earliest fossil fuel that played a pivotal role in economic development before the advent of crude oil production globally, most especially in Nigeria in the early 1950s. An estimation of about 1.8 billion tonnes for both coal and lignite resources was observed, globally [6–8]. Palaeobotanical specialists concerned with the historical basis of a deposition while the petrographic characteristics of coal have helped to determine the usefulness for a variety of economic purposes [8] may study it. A diverse amount of heavy metals was observed in coal in their overall composition [9]. It is composed mainly of rings of carbon, hydrogen with some traces of oxygen, sulphur and less nitrogen as indicated in Figure 1.

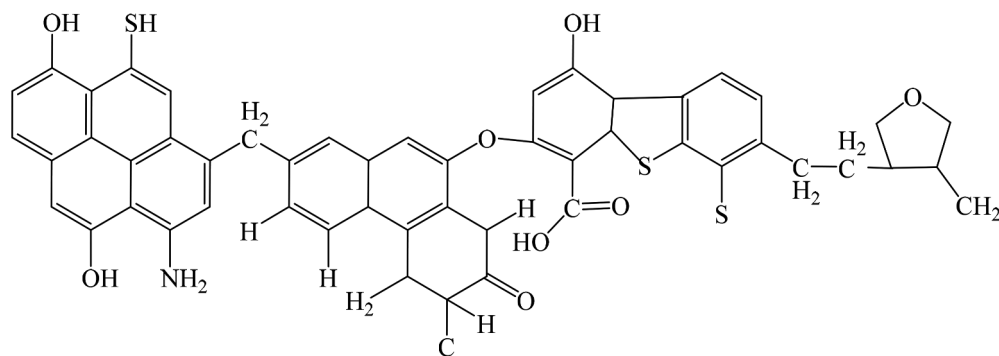
The effects of geological processes such as temperature and pressure on dead biotic materials over time, under suitable conditions, have been reported to lead into the successful transformation into peat, lignite (brown coal), sub-bituminous coal, bituminous coal, steam coal anthracite and graphite [1,10–14].

By definition, heavy metals are a group of metals and metalloids with an atomic density exceeding  $6 \text{ g/cm}^3$ . These metals include elements like cadmium (Cd), copper (Cu), lead (Pb), chromium (Cr), manganese (Mn), zinc (Zn), iron (Fe), nickel (Ni), cobalt (Co), arsenic (As) known for their toxicity and pollution tendencies to human, environment, although, these metals play a significant role in the support of life at a lower or trace level [15]. Additionally, their toxicities are apparent based on their increased concentration in the physiological system in humans. Heavy metals are ubiquitous in the environment, which may arise as a consequence of both natural and anthropogenic pathways.

The tendency of heavy metals to increase in concentration and bioaccumulate within the environmental samples over time had been observed [15].

They are sufficiently bounded and increase in the number of quantity over a period of time by sediments but are also subject to inequitable discharge into the human environment [16].

Aerial transportation of acid rain agents causes leaching of heavy metals to sediments. Metals transported in the soil as a result of deposition are cadmium, zinc, arsenic, and selenium [17–20].



**Figure 1.** Structure of Coal.

The quest to assess and detect the constituents and the presence of heavy metals in coal, within the selected hot spot zone in Nigeria prompted this present study.

This work is aimed at evaluating the concentration levels of the selected heavy metals, determining the best digestion method for the analysis of the Nigerian coal samples, and assessing its environmental impact along with the selected locations as compared to the international best protocols and the reported literature globally. This present study is critical due to the predominance of coal deposits within the catchment areas. The relationship with the contamination source of heavy metals associated with coal could have a significant impact on the quality of soil, and water as well as environmental degradation in general. It is important to carry out this type of study in order to unravel the pollution source associated with inorganic contaminants such as the selected heavy metal concentrations, which have the potential to pose serious threat to the environment and humans.

## **2. EXPERIMENTAL**

### ***2.1. Sampling sites and collection***

The study areas for this present study were Ribadu coal deposit site, Onyeama in Enugu State at specific coordinates of (6° 24 '92 "N 7° 27 '12 "E and 6° 28 '18.70 "N 7° 26 '47.53 "E) respectively. Another sample collected at Okaba coal deposit site in Odagbo village is located at latitude 7° 24 '0 " N and longitude 7° 42 '0 " E, within Kogi State Nigeria. These sites were selected due to the historical coal depositions and the reported cases of poor water quality supply and shortages as a major problem being faced with the inhabitants in these areas [21,22]. In addition, it has been reported that some localities within the Enugu area that are associated with coal mine have been faced with acid mine drainage pollution from underground coal mines which require further investigations that prompted this current study.

Representative samples (three samples were collected from each site that form the composite sample) were taken at 0–5 cm, 5–10 cm below the earth's surface from each site. The samples were collected using aluminium foil, wrapped and packed in polythene bag and transported safely into the laboratory.

### ***2.2. Sample preparation and preservation***

The coal samples were air-dried, ground to a fine powder using pestle and mortar at the Chemistry Laboratory complex, Department of Science Laboratory Technology, Ladoké Akintola University of Technology, Ogbomoso, Nigeria. The air-dried samples were sieved using stainless steel particle analysis with mesh No 4 (425 µm) into a sampling bottle prior to the preservation and then stored in a refrigerator at temperature below 4°C prior to digestion.

### ***2.3. Sample digestion***

In this study, the wet digestion process was observed for the coal samples. The following digestion procedures were carefully observed. A 0.2 g of the coal sample was weighed and 7.5 mL of nitric and perchloric acid was added in the ratio 2:1, respectively, to the weighted sample in 200 mL conical flask. A glass filter funnel was placed in the neck of the digestion tube during pre-digestion as a cover and to reflux acid fumes generated during digestion. It

was left for a few hours at a temperature of 5°C. In some cases, they may be on hot plates for a few minutes and then relocated to the fume cupboard and were left overnight without heat [23]. The tube was placed in a heating block and rotated so that the nitric acid is driven off as uniformly as possible. The time at which the tubes had reached the dense white fume stage was noted and tubes were thereby removed and cooled to about 100°C.

The dry ashing method (pipette digests for analysis of metals) was adopted as thus. A 0.2 g of fairly ground coal sample was weighed and oven-dried at 60°C into a 30 mL porcelain crucible. The sample was later ignited in a muffle furnace for 6–8 hours at a temperature of 450°C. It is pertinent to note that white ashes should be obtained, otherwise indicating incomplete ignition. Another sample was weighed and ignition repeated. The sample was later cooled on top of asbestos and 5 mL of 1 M HCl solution added. The resultant sample mixture was later evaporated on the hot plate at low heat under ventilation for five (5) min. 10 mL of 1 M HCl solution was added and the solution filtered into 100 mL volumetric flask, i.e. the cooling solution was made up to 100 mL in volumetric flasks with deionised water and later stored in the refrigerator prior to heavy metal analysis using atomic absorption spectrophotometry (AAS).

The crucible and the filter paper were washed with distilled water, a portion of 1 M HCl (three times), made up to volume with 4 mL distilled water and stir the filtrates for Ca, Mg, Na, P, K micronutrient and heavy metals determination.

## **2.4. AAS analysis of digested coal samples**

The filtered solution from digested coal samples was collected for AAS analysis. Standard stock solutions (1000 mg/L) of Cr, Cd, Pb and Cu solutions were prepared upon which lower concentrations of 0.60, 0.30, 0.10 and 9.00 ppm for Cr, Cd, Pb, and Cu were prepared from the stock and used to generate the calibration point for each of the metals. The set of standard solutions and the filtrate of the digested samples were analysed by a Shimadzu AA-6200 AAS. The detection limit of the heavy metals in the sample was calculated in parts per million (ppm). Chromium, zinc, cobalt, iron, nickel, arsenic cathode lamps were used for the analysis of Cr, Cd, Pb, and Cu, respectively. Also, absorbances were read in triplicates for reproducibility. All the quality controls were carefully observed and all reagents used are of analytical grade.

## **3. RESULTS**

### **3.1. Concentration of heavy metals in coal samples**

Based on the result obtained from AAS analysis, it was observed that coal samples had a varying concentration of heavy metals analysed in this study. The concentration of each heavy metals present in the coal samples based on their digestion modes was summarised in Tables 1 and 2 for wet and dry digestions, respectively.

bdl = Below detection limit.

bdl = Below detection limit

NBS: National Bureau of Standards.

EPA: United States Environmental Protection Agency.

Significant at  $p = 0.05$  level

## 4. DISCUSSION

### 4.1. Cadmium

The concentration of cadmium in the Ribadu coal sample was found to be below the detection limit based on the modes of digestion as shown in Tables 1 and 2. As a result of this, it was deduced that the coal site is deficient in cadmium.

In the case of the Onyeama coal sample, the cadmium levels were found between the ranges of 0.03–0.04 mg/kg. The concentration level of cadmium was found to be higher in Okaba coal sample as the range falls between 0.04 and 0.06 mg/kg which depicts the presence of trace metals as shown in Table 2. Moreover, its concentration exceeds the NBS – EPA tolerable limit [24,25] as illustrated in Table 4.

The sources of cadmium emissions could be attributed to anthropogenic conditions due to human activities, which are basically as a result of unmonitored combustion of wastes on dumpsites, non-ferrous metal production, cement, and steel manufacturing processes. Combustions of coal, oil, and production of iron along with steel could as well be the greatest cadmium emanation sources along with the sites. The marine sources of cadmium are chiefly from the non-ferrous industry (24.9%) [26].

Abiogenic deposit in the form of coal contains significant concentrations of the trace elements. The utilisation of coal is increasing both nationally and industrially in the global sense, in which the evaluation of environmental penalties is noteworthy. Among these, one of the environmental concerns is the poisonous metallic discharges. Concentrations of various trace metals in coal vary from mining sites in tonnes in different countries. It was approximated that the standard concentration of cadmium in coal ash may be more than 5.0 ppm [27].

### 4.2. Chromium

Based on the digestion modes, chromium was observed to be below the detection limit in the Ribadu sample. The negligible concentration range of 0.01–0.03 mg/kg was observed in Onyeama and Ribadu samples.

Chromium is a micronutrient is recommended for crop production and other agricultural practices like livestock farming. Although caution should be taken to avoid the

**Table 1.** Concentration of heavy metals in coal sample (mg/kg) using a wet digestion method.

Samples	Cd	Cr	Pb	Cu
Ribadu	Bdl	Bdl	Bdl	6.00
Onyeama	0.03	0.01	0.02	6.50
Okaba	0.04	0.01	0.03	9.00

**Table 2.** Concentration of heavy metals (mg/kg) in coal sample using dry digestion method.

Samples	Cd	Cr	Pb	Cu
Ribadu	Bdl	Bdl	0.01	6.02
Onyeama	0.04	0.03	0.05	6.55
Okaba	0.06	0.03	0.05	9.40

**Table 3.** NBS-EPA standards for Coal ash.

ELEMENTS	Concentration (mg/kg)
Cd	0.00088–0.006
Cr	0.0000002–0.001
Pb	0.01870–0.110
Cu	1.00–2.00

**Table 4.** Comparison of the result with NBS-EPA Standards for coal ash.

Elements	EPA-NBS Concentration (mg/kg)	Real samples (mg/kg)	Remark
Cd	0.00088–0.006	0.03–0.06	Above limits
Cr	0.0000002–0.001	0.01–0.03	Above limits
Pb	0.0187–0.110	0.01–0.05	Below limits
Cu	1.00–2.00	6.00–9.40	Above limits

emergence of heavy metals bioaccumulation. Besides, its value exceeds the standard limit as proposed by NBS – EPA as indicated in [Table 3](#).

#### 4.3. Lead

It was found that Okaba sample has the highest concentration of lead (0.03–0.05 mg/kg), the presence of lead could only be observed using dry ashing digestion method, and however, the level of metals in Ribadu sample could not be determined using wet digestion. This could be attributed to the fact that its trace metal value does not exceed 0.01 mg/kg in this sample which was found below the detection limits.

The concentration range for Onyeama coal was 0.02–0.05 mg/kg as shown in [Tables 1](#) and [2](#). Because of this, it could be concluded that the Ribadu coal site has a concentration gradient below EPA and NBS standard limits which are 0.0187–0.11 mg/kg for Pb [[24](#)]. To avoid bioaccumulation apart from coal deposit contamination, other sources of deposit should be prevented such as airborne lead from automobile exhaust and paint chips.

#### 4.4. Copper

Copper was found to be the most abundant trace metal in all the coal samples collected with an average concentration of 7.245 mg/kg, with Okaba having the highest concentration of copper metal followed by the Onyeama coal sample.

When copper exceeds its toxic limit, it could be harmful. If swallowed, it is very toxic causing violent vomiting, diarrhoea, and eventual collapse.

#### 4.5. Statistical analysis of the data

The data generated were subjected to statistical analysis and expressed as group means standard error (SE) analysed using SPSS version 21.0 (IBM SPSS statistical software 21.0). A p-value of less than 0.05 signifies that there is a significant difference and good correlation and values greater than 0.05 mean a very weak significant difference. The



levels of selected heavy metals along the sampling points were compared for any significant differences for both wet and dry digestion as indicated in Table 5. It was found that Cd, Cr, and Pb in Ribadu were significant with both Onyeama and Okaba sites and good correlation but result for Cu did not follow these patterns; as Ribadu was found to be weakly significant with Onyeama but not significant to Okaba site. This observation was found to be peculiar to both wet and dry digestion methods, although, there are little significant differences in terms of detection capacity while comparing wet and dry digestion methods, which indicated that, dry digestion was able to trap more trace metals investigated compared to the wet digestion method. The high concentration of Cu found in all the samples could be responsible for the difference observed compared to other metals in this study. The elevated level of Cu found in the samples relative to others in this study is less to worry about as Cu has a low toxicity effect within the concentration range observed therefore pose low health and environmental concern

The concentration levels of selected heavy metals in coal ash obtained in this study were compared with the results reported by various authors in the literature globally as shown in Table 6. The concentrations of heavy metals obtained in this work were found to be lower compared to the results obtained in most of the study done across the globe, although the number of sites investigated was found to be more compared to what was done in this study. Generally, the concentration of Cu was found to be higher in all the studies across the countries except for the work done in China and Malaysia by [34] and [35], respectively. The concentrations of Cd and Cr were found to be relatively lower compared to Cu across the countries, this is consistent with this present study, although [36] reported a very high concentration of Cr across the 19 sites investigated in Indonesia likewise [37] who reported an elevated value of Cr across the six sites studied in Turkey. The presence of Cr and Pb at elevated concentration is cause for concern as Cr has serious health and environmental consequences. The presence of Cr in the Shengbei Coalfield of China has been associated with lung cancer [38]. Also, the presence and emission of lead could lead to Pb poison and Cu has a low toxicity effect within these concentration ranges therefore, it poses low health and environmental concern.

## 5. CONCLUSION

The concentration levels of some selected heavy metals (Cr, Cu, Pb, and Cd) were evaluated from coal samples collected within the coal-rich sites in Nigeria (Ribadu coal deposit in the coal city and Onyeama, a few kilometres away from Enugu metropolis both located in Enugu State, and Okaba, extracted from Okaba coal deposit site in Odagbo village, Kogi State) in this study. The coal samples were found to contain varying concentrations of heavy metals investigated.

The concentration of cadmium and chromium in the Ribadu sample was found below the detection limit but present in other sites (such as Okaba and Onyeama coal sites in Odagbo village).

Based on the modes of digestion, dry ashing method was found to be the most effective in this study. This could be attributed to the fact that this procedure was able to extract a significant amount of Pb from the sample media as well as cost-effectiveness.

**Table 5.** Descriptives Mean with the standard error of correlation for selected heavy metals along with Ribadu, Onyeama, and Okaba coalsites.

Sample location	Wet digestion (Descriptives Mean with standard error) N = 3			Dry digestion (Descriptives Mean with standard error) N = 3		
	Cd	Cr	Pb	Cd	Cr	Pb
Ribadu	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.000 ± 0.000	0.0097 ± 0.00033
Onyema	0.0333 ± 0.00882	0.0113 ± 0.0186	0.0190 ± 0.00379	0.0443 ± 0.00644	0.0960 ± 0.0620	0.0523 ± 0.00617
Okaba	0.0413 ± 0.00353	0.0097 ± 0.0014561	0.0293 ± 0.00233	0.0623 ± 0.00561	0.0357 ± 0.00567	0.0523 ± 0.00617

**Table 6.** Comparison of selected heavy metal concentrations in coal-related samples (mg/kg) from different studies around the world.

Location of coal samples	Total number of coal samples collected	Heavy Metals investigated concentration (mg/kg)				References
		Cr	Cd	Cu	Pb	
Nigeria	3	bdl–0.01 <sup>a</sup>	bdl–0.04 <sup>a</sup>	6–9.0 <sup>a</sup>	bdl–0.03 <sup>a</sup>	This study
Nigeria	3	bdl–0.03 <sup>b</sup>	bdl–0.06 <sup>b</sup>	6.02–9.40 <sup>b</sup>	0.01–0.05 <sup>b</sup>	This study
Global samples*	24	3.6–30.2	0.09–1.1	4.2–24.3	2.39–32.0	[28]
Malaysia	8	7.72–460	-	0.91–364	<1.0–7.64	[29]
Indonesia	19	87.57–5649.81	nd–0.33	9.40–131.49	8.41–35.29	[36]
Nigeria	9	41.07–47.14	0.1–0.1	43.2–64.14	18–29	[30]
India	4	-	-	9.8–30.35	5.08–24.13	[31]
India	27	17.9–55.5	0–5	2.8–40	2.4–13.7	[32]
Malaysia	27	bdl–71	bdl–bdl	17–82	90–362	[35]
China	34	52.62–101.20	0.62–5.37	35.51–104.31	46.02–108.0	[34]
Botswana	4	36.8–45.5	-	15.1–28.1	16.2–19.2	[33]
Turkey	6	8.14–266.70	1.10–15.92	160.70–372	34–201.85	[37]

**Note:** a- wet digestion, b- dry digestion, bdl- below the detection limit, nd- not detected, \*- samples collected across the world such as United States of America, South Africa, India, China, Colombia, Japan and Australia.

The outcome of this study suggested that the Ribadu coal site is less prone to heavy metal contamination resulting from Cd and Cr.

Also, coal samples obtained from Onyeama, Enugu exterior, and Kogi were found above allowable limits with Cd, Cr and Cu as stipulated by the US EPA standard limit and NBS with the exception of Pb that is below detection limits. In addition, the concentrations of the selected heavy metal investigated in this study were lower compared to other studies done in other countries across the world.

From our results, it could be concluded that coal combustion can have a significant impact on the environment by the discharge of heavy metals such as Cr, Cu, Pb, and Cd into the air, soil, and aquatic environments.

Thus, precautionary measures must be ensured during the combustion of coal to protect the human ecological system from the harmful consequences of heavy metals within these areas. Also, further monitoring of these trace metals and others that are known to pose serious threat to the environment are encouraged to be investigated periodically in order to save guard the health of humans and aquatic lives that might be exposed to these toxic heavy metals.

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