

Assessment of Heavy Metal Concentration in Soil Around Owukpa Coal Mine Field, North Central Nigeria.

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ABSTRACT

The evaluation of Heavy metals in the environment around Owukpa coal mine field, Ogbadibo Local Government Area, Benue State Nigeria was carried out to ascertain the degree of contamination resulting from mining activity in the area. The concentrations of selected heavy metals (Cd, Cr, Ni, Fe, Mn and Pb) in soils were investigated. Obtained results from the atomic absorption spectrophotometric (AAS) are as follows: Ni (4.16), Fe (102.91), Cd (1.36), Cr (2.31), Pb (7.15), and Mn (5.46). The result shows most samples had concentration slightly below the WHO standard except for Fe. However, the result obtained for Geoaccumulation index shows the study area fall within uncontaminated to moderately contaminated with PLI value > 1 except Cr (0.1570).

Keywords: Heavy metal, Health Risk, Pollution index, mining, Geo-accumulation.

INTRODUCTION

WHO, 2011 claimed prolonged exposure to environmental pollution is to blame for around a quarter of the illnesses that plague humanity today. Numerous investigations have identified certain heavy metals' natural origins. Naturally occurring heavy metal emissions take place under many environmental circumstances. Forest fires, volcanic eruptions, biogenic sources, rock weathering and wind-borne soil particles are a few examples of these emissions [1]. Industries, wastewater, agriculture, mining and metallurgical operations, and runoff all contribute to the presence and proliferation of pollutants into various environmental compartments. Anthropogenic processes for heavy metals have been found to exceed natural fluxes for a number of elements. The majority of the metals in wind-blown dusts come from industrial environments [2]. Human activities have been observed to be a major contributor of environmental pollution as a result of industrialization, the production of products to meet the fundamental necessities of the huge population [3].

Heavy metals end up being released from their endemic environments through natural weathering processes and end up in various parts of the ecosystem. Zinc (Zn), nickel (Ni), lead (Pb), arsenic (As), chromium (Cr), mercury (Hg), cadmium (Cd), and copper (Cu) among others have high prevalence. Even though they are present in small amounts, they have high tendency to negatively impact human health and the environment in general [4]. According to Athar and Vohora (2001), soils are the main

receiver of the heavy metals that these natural and human-made processes release into the environment. Most of these metals are non-degradable and as a result, they do not go through chemical or microbiological decomposition. In addition, their total concentration accumulates over time after being discharged into the environment [1, 4].

Study Area

The research region is situated between latitudes 6o30' and 7o26'N and longitudes 7o10' and 7o30'E. Owukpa is a region situated within the Ogbadibo Local Government Area in the state of Benue, Nigeria. It has an abundant coal resource with 80 million tons of total reserves, which Owukpa Consolidated Mines Limited is actively mining. Orokam borders Owukpa in the west and has a border with Obollo Eke in Udenu Local Government size, Enugu State. Its total size is approximately 1286 km2. There are two distinct seasons, the rainy season and the dry season, in the study area's tropical sub-humid climate. From April through October, there is a seven-month rainy season. Between 1,200 and 1500 mm of rain fall are recorded annually. In March and April, daytime temperatures are often fairly high. In the summer, the region's daily maximum and lowest average temperatures are 35°C and 21°C, respectively, and in the winter, they are 37°C and 16°C. Although sandstone is the most abundant type of rock in the meta-sediments, they also include shale, siltstone, limestone, and quartzite [5].

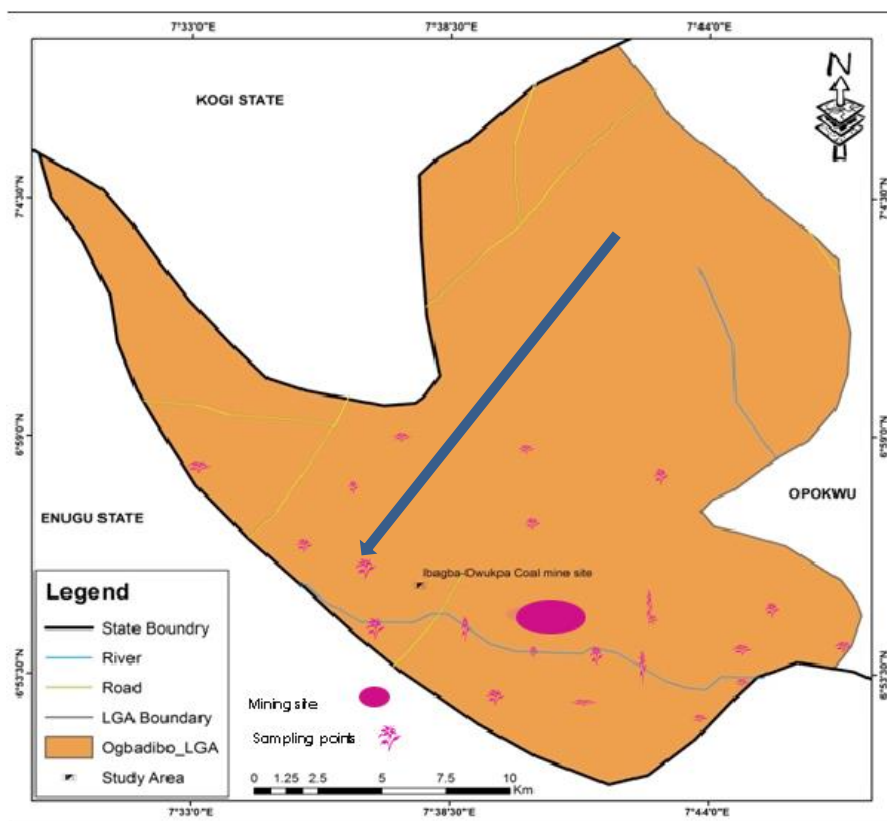


Figure 1: Map of Owukpa

MATERIAL AND METHODS

Material used were Nitric acid, hydrochloric acid (HCl), perchloric acid, distilled water, Filter paper, beaker, conical flask, funnel, measuring cylinder, hot plate, film cardboard, sample bottle, polythene bag, oven, pH meter, weighing balance, black polythene bags, water bottle.

Collection and preservation of Soil Samples

Stratified sampling technique was used for collection of twelve samples. Ten (10) representative samples of top soil (0–15cm) were acquired from various points at the mining site and a control sample from Orokam (10 kilometers from the mine location), using black polythene bags for preservation [6]. The soil samples were conserved in clean, labeled polythene bags and kept at room temperature for laboratory examination after being air dried for 4 days. The samples were then put into a mortar, pounded with a pestle and put through a sieve with a 2 mm diameter to obtain finer samples.

Digestion of Soil Samples

1 g of each sample and 10 mL pure nitric acid was measured into a 100 mL beaker and heated to dryness. In order to keep the pH level low and prevent the precipitation of metal at high pH, 10 mL of 16 M HNO₃ and 3 mL of 11 M HClO₄ were added. The solution was then heated to until it fumed. The residue was then dissolved in 4 mL of hot 6 M HCl (aq), filtered, and diluted to 50 mL mark [6].

Elemental Analysis

The metal solutions were made using water that was deionized. Each 1.0 g solid metal sample was measured into 10 mL of a 1:1 nitric acid solution and then poured into a 1000 mL volumetric flask. The stock solution was then made by adding distilled water. 1000 mg/L stock solution of each metal was used to create standard solutions. Through multiple dilutions of the stock solution, a calibration curve was created. For comparison, working standard solutions of Nickel, chromium, cadmium, lead (Pb), cadmium (Cd), manganese (Mn), and iron (Fe) were utilized. The pH was then lowered to 2.5 by addition of 1 M nitric acid to a 100 mL sample of each metal's reference solution. Each standard solution and sample was then aspirated directly into the flame and absorbance was recorded using Ice 3000 AA02134104 v1.30 Thermo Scientific Atomic Absorption Spectrophotometer equipped with each hollow cathode lamp at 228.8 nm, 357.9 nm, 232.0 nm, 283.2 nm, 279.5 nm and 248.3 nm wavelengths for cadmium (Cd), chromium (Cr), iron (Fe), Nickel (Ni) Manganese (Mn) and lead (Pb), respectively. Every time a sample was taken, deionized water was used to flush the nebulizer, atomizer, and burner. With the highest operating standard solution and a blank, the equipment's stability was periodically tested. In order to get the highest absorbency and linear response while aspirating established standards, the settings were tuned prior to sample analysis.

Pollution Level Determination Factor

Pollution Load Index (PLI): The pollutant load index was used to determine the quality of sediments. It is described as the contamination factor (CF) of the n-th root of the metal multiplications of [7]. PLI is an effective tool for assessing heavy metal pollution. PLI values less than 1 demonstrate no pollution, whereas values larger than 1 indicate pollution. [8]

$$PLI = [CF_1 \times CF_2 \times CF_3 \times CF_4 \dots \times CF_n]^{1/n} \dots \dots \dots \text{equation(1)}$$

Geoaccumulation Index (Igeo): The Geo-accumulation Index (Igeo) measures the amount of metal

accumulation in sediments. The geoaccumulation index scale contains seven descriptive groups (0–6) that range from virtually unpolluted to extremely heavily polluted. Igeo values are helpful in dividing soil into quality classes. The hypothesis made by Müller (1969) was used to assess the geoaccumulation index [8].

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \dots\dots\dots \text{equation(7)}$$

RESULT AND DISCUSSION

Table 1: Heavy Metal Concentration (mg/kg) in Soils around Owukpa Coal Mine field

Average heavy metal concentration (mg/kg) in the soil around Owukpa mine fields are presented in table 1 below.

SAMPLE	Cd	Cr	Fe	Mn	Ni	Pb
C1	1.20±0.03a	4.97±0.06d	168.86±0.01f	4.32±0.00e	3.76±0.06c	1.44±0.05b
A	1.21±0.00c	0.04±0.01b	228.38±0.01f	6.95±0.01e	3.73±0.01d	ND
B	1.34±0.04b	7.87±0.00d	122.22±0.02e	4.82±0.08c	4.91±0.03 c	ND
C	1.41±0.01b	0.39±0.02a	91.29±0.03f	13.05±0.05e	4.18±0.03c	8.56±0.02d
D	1.36±0.01a	4.79±0.02c	77.33±0.03f	6.65±0.13d	4.56±0.01b	24.35±0.01e
E	1.42±0.06b	1.05±0.02a	88.54±0.05f	3.32±0.01c	5.35±0.04d	11.09±0.01e
F	1.57±0.01a	3.42±0.01c	115.75±0.08f	4.91±0.04d	3.32±0.01b	7.77±0.04e
G	1.78±0.01b	0.63±0.01a	88.12±0.04e	3.23±0.08c	3.30±0.00c	13.87±0.14d
H	1.27±0.03c	0.70±0.02b	146.83±0.06f	7.24±0.08e	4.91±0.01d	ND
I	1.02±0.01a	2.32±0.06c	42.30±0.05f	4.43±0.01e	3.92±0.04d	1.42±0.06b
J	1.21±0.06b	1.91±0.03c	28.30±0.01f	ND	3.42±0.01d	4.43±0.03e
Mean±SD	1.36±0.02	2.31±0.02	102.91±0.04	5.46±0.05	4.16±0.02	7.15±0.03
Range	1.02 - 1.78	0.04 - 7.87	28.30-228.38	3.23 - 13.05	3.30 - 4.91	1.42 - 24.35

Results are expressed in mean ± standard deviation of triplicate determination. Results with same alphabet superscript show no significant difference while results with different alphabet superscript within the substantial difference in the row at p < 0.05. Where A to J represent Soil sample 1 to sample

10 while C1 control sample.

ND = Not detected

Result of heavy metal analysis of soil samples from Owukpa mine filed shown in table 4.1.2 revealed the following mean concentration and range values of heavy metals: Cd $1.36 \pm 0.02 \text{ mgKg}^{-1}$ ($1.02 - 1.78 \text{ mgKg}^{-1}$), Cr $2.31 \pm 0.02 \text{ mgKg}^{-1}$ ($0.04 - 7.87 \text{ mgKg}^{-1}$), Fe $102.91 \pm 0.05 \text{ mgKg}^{-1}$ ($28.30 - 228.38 \text{ mgKg}^{-1}$), Mn $5.46 \pm 0.04 \text{ mgKg}^{-1}$ ($3.23 - 13.05 \text{ mgKg}^{-1}$), Ni $4.16 \pm 0.02 \text{ mgKg}^{-1}$ ($3.30 - 4.91 \text{ mgKg}^{-1}$), Pb $7.15 \pm 0.03 \text{ mgKg}^{-1}$ ($1.42 - 24.35 \text{ mgKg}^{-1}$). Highest concentration of Fe was determined in the control sample, sample A gave minimum concentration of Cr (0.04 mg/Kg). Pb was not detected in samples A, B and H, while Mn was not detected in sample J.

Table 2: Geological accumulation Index and Pollution Load Index

SAMPLE	IgeoCd	IgeoCr	IgeoFe	IgeoMn	IgeoNi	IgeoPb
C1	0.0217	0.0010	0.8298	0.1553	0.0317	0.0010
A	0.0202	0.000	1.1223	0.1158	0.0746	0.0000
B	0.0223	0.0157	0.6006	0.0803	0.0982	0.0000
C	0.0235	0.0008	0.4486	0.2175	0.0836	0.0571
D	0.0227	0.0096	0.3800	0.1108	0.0912	0.1623
E	0.0237	0.0021	0.4351	0.0553	0.1070	0.0739
F	0.0262	0.0068	0.5690	0.0818	0.0664	0.0518
G	0.0297	0.0013	0.4330	0.0538	0.0660	0.0925
H	0.0212	0.0014	0.7215	1.1207	0.0982	0.0000
I	0.0170	0.0046	0.2079	0.0738	0.0784	0.0095
J	0.0202	0.0057	0.1391	0.0000	0.0684	0.0295
Average	0.0202	0.0046	0.5057	0.0910	0.0832	0.0477
Range	0.0170- 0.0297	0.0000-0.0157	0.1391- 1.1223	0.0000-1.1207	0.0660- 0.1070	0.000- 0.1623
PLI	4.5330	0.1570	25.2850	4.5500	4.1600	2.3830

Result presented in Table 4.11 shows geological accumulation and pollution load index of the soil. Average and Igeo range of elements were presented as follow: Cd 0.0202 (0.0170 - 0.0297), Cr 0.0046

(0.000 – 0.0157), Fe 0.0910 (0.1391 – 1.1223), Mn 0.0910 (0.0000 – 1.1207), Ni 0.0832 (0.0660 – 0.1070), Pb 0.0477 (0.0000 – 0.1623) with increasing magnitude: Fe>Mn>Ni>Pb>Cd>Cr. The highest PLI was observed in Fe with minimum value of PLI for Cr.

Discussion

Concentrations of Heavy Metals in Soil Samples

The concentrations of Nickel (Ni), Iron (Fe), Cadmium (Cd), Chromium (Cr), Lead (Pb) and Manganese (Mn) of the soil samples around coal mines are presented in Table 1. Cadmium concentration (mg/kg) was found to be highest in the sample coded G (1.78) and lowest in I (1.02) with an average concentration of 1.36 ± 0.02 as presented in (Table 1). The mean concentration of Cd in this work was lower compared to the control sample (1.20). Similar the concentration was lower compared to average concentration reported by Afolayan [10] for soils (2.80 mg/kg) obtained beside a battery wastes dumpsite located in Ibadan, Oyo state. However, both concentrations were observed to be lower than the limit of 3.0 mg/kg set by European Union (2016) [11] and 12 mg/kg by WHO [12]. Cadmium is raising concerns due to its potential to have serious negative impacts on plant metabolism, soil biological activity, biodiversity, and human and animal health. It is a non-essential element that has no beneficial or nourishing capacity function in plants, animals, or humans since they are extremely poisonous. It commonly occurs in the lithosphere at values of 0.2 mg/kg. (the upper portion of the earth), in sedimentary rocks, and 0.53 mg/kg in soil. Although this metal is not necessary for any known biological processes, because of how mobile it is in soil, it may be readily absorbed by crops [13]. Some of the known sources of cadmium include burning fossil fuels like coal, municipal trash, and incineration of materials like nickel-cadmium batteries and plastics, which are frequently dumped as solid waste [14].

Chromium highest concentration was observed in sample B (7.87 mg/kg) and the least Cr concentration was seen in sample A (0.04 mg/kg). The average mean concentration of Cr was 2.31 ± 0.02 as revealed in Table. 4.1.2 and were lower than the permissible limit of 100 mg/kg for Cr set by WHO [12] and 150 mg/kg by European Union Standard [14-15]. However, the control sample had higher concentration of 4.97 mg/kg than the mean concentration for chromium obtained in this study. Cholesterol, glucose, and fat are all broken down by the chromium molecule. Its lack results in increased body fat, hyperglycemia, and a reduction in the number of sperm, while its excessive concentration makes it poisonous and cancer-causing [16]. The poisonous metal Cr is known to harm both plants and animals severely. The phytotoxic concentration of Cr in soil according to Kabata-Pendias [17] is between 5 to 30 mg/kg. At this level, Cr could inhibit degradation of pigments, seed germination, nutrients imbalance and induction of oxidative stress [18]. Cr poisoning can change the ultrastructure of the chloroplast and membrane in plants [19]. Chromium is hazardous to plants, affects their growth and development, however some plant species can tolerate it (hyper-accumulators) without exhibiting any morphological abnormalities [20].

The highest concentration of Fe was observed in sample A (228.38 mg/kg) while lowest Fe concentration was found in sample J (28.30 mg/kg). The mean concentration of Fe which was 102.91 ± 0.04 mg/kg were found to exceed the WHO limit of 40.7 mg/kg for Fe in soil samples by WHO (2011) as reported by [21]. This includes the control sample. A similar investigation was carried out on soil around abandoned Pb-Zn mines in Yelu, Alkaleri LGA, Bauchi State. The result obtained showed that Fe (0.58 – 0.78 mg/kg) was between the permissible limit which was attributed to the fact that mining activities were suspended over years [22].

Iron (Fe), a component of myoglobin, hemoglobin, cytochromes, and other proteins, acts as a catalyst in a number of metabolic events and is crucial for the transport, storage, and consumption of oxygen. It is a coenzyme for several enzymes, and its shortage causes anemia and other diseases [21]. Anthropogenic activities including mining, smelting processes, transportation, the chemical industry, and agriculture, among others, are common sources of heavy metal contamination in soils [21-22].

The concentration of Manganese found in soil samples was highest in sample C (13.05 mg/kg) and least in sample G (3.23 mg/kg) with an average concentration of 5.46 ± 0.05 mg/kg as presented in Table 4.2. The mean concentration of Mn observed in this work were lower than the acceptable limit of 12 mg/kg (WHO, 2011) [12]. However, Mn was not detected in soil sample J. Manganese is a trace element that is recognized to be crucial for the growth of plants and animals. In animals, its lack results in severe skeletal and reproductive problems. Human lungs and brains can suffer dangerous repercussions from high manganese (Mn) concentrations [23]. Compared to other micronutrient toxicity, manganese poisoning is a rather prevalent issue. Industrial activities such as Ferroalloy production among others can lead to Mn contamination of the soil.

The highest concentration of nickel (Ni) was discovered in E (5.35 mg/kg) and lowest in G (3.30 mg/kg) with average concentration of 4.16 ± 0.02 mg/kg as revealed in Table 4.2. The control sample was noticed to be slightly above the mean concentration. However, the values of Ni concentrations observed in this work were below the WHO limit for nickel in soil (WHO 2011) which is 10 mg/kg [24]. Similar investigation was carried out in Kwara North central. The findings revealed that soil samples' Ni concentrations ranged from 1.83 to 14.87 mg/kg with mean concentration of 8.35 mg/kg which is also below the acceptable limit set by WHO [25]. The findings thus revealed that the soil was polluted as a result of release of Nickel during mining activities in the study area through atmospheric emissions from trucks and other machines used by the miners. Nickel (Ni) is necessary for human health and functions as a cofactor for several enzymes and hormones. However, at some concentrations, Ni may be toxic and cause cell damage, changes in enzyme and hormone activity, oxidative stress, and neurotoxicity [26]. Nickel often only occurs in the environment at extremely low quantities [27].

Lead mean concentration was observed to be highest in sample D (24.35 mg/kg) and lowest in sample I (1.42 mg/kg) with mean concentration of 7.15 ± 0.03 mg/kg as shown in Table 4.2 which is below the WHO permissible limit. However, Pb was not detected in the control sample, similarly in sample A, B and sample H. When compared to the average concentration of 40.0 mg/kg reported by Afolayan (2018), the values obtained were lower [28] for soils obtained near a battery wastes dumpsite in Ibadan, Oyo state. The average concentrations obtained in this study were lower when compared to WHO (2011) safe limit of 30mg/kg [29] which suggest Pb only polluted the soil at a low level. The potential health risk associated with accumulation of Lead (Pb) over time cannot be taken for granted. Lead can be present in the soil, water and air, human activities such as fossil fuel burning, use of lead-based paint in homes and industrial processes such as mining are good source of lead in the environment.

Geoaccumulation Index (Igeo) and Pollution Load Index (PLI)

The amount of heavy metal pollution in the soil was estimated using the Geo-accumulation Index (Igeo) and Pollution Load Index (PLI). Using the Tomlinson approach, the pollutant load index for each sample location was evaluated. [9].

The geoaccumulation index was divided into the following five classes: Class 0 = $I_{geo} < I_{geo} < 1$

(uncontaminated to moderately contaminated); Class 2 = 1 Igeo 2 (moderately to heavily contaminated); Class 4 = 3 < Igeo < 4 (heavily contaminated); Class 5 = 4 < Igeo < 5 (heavily to extremely contaminated); and Class 6 = 5 < Igeo (extremely contaminated). Class 6 is an open class that includes all index values that are higher than Class 5 [30].

The mean geo-accumulation index for the analyzed metal increased in the order: Fe>Mn>Ni>Pb>Cd>Cr with mean Igeo values of 0.5057, 0.0910, 0.0832, 0.0477, 0.0227 and 0.0046 respectively as shown in Table 2. The range of geo-accumulation index for Cd, Cr, Fe, Mn, Ni and Pb were 0.0170 to 0.0297, 0.000 to 0.0157, 0.1391 to 1.1223, 0.0000 to 1.1207, 0.0660 to 0.1070, and 0.0000 to 0.1623 respectively. The above geo-accumulation index results presented in Table 2, shown that the field soils sampled in this study were uncontaminated to moderately contaminated with Cd, Cr, Ni and Pb with slightly to moderate contamination by Fe and Mn respectively.

From the results in Table 2, it is interesting to note that Fe, had the maximum pollution load index (PLI) of 25.2850, while Cr recorded the minimum pollution load index (PLI) of 0.1570. All metal recorded values of PLI greater than unity (1.0) except Cr. PLI value > 1 is polluted as noted with all analyzed metal in the increasing order Fe>Mn>Cd>Ni>Pb except Cr (0.1570) with PLI value < 1 which indicates no pollution.

CONCLUSION

Results of the AAS analysis of the heavy metals in soil reveal increasing order of: Fe>Pb>Mn>Ni>Cr>Cd. It was observed that the concentration of Cr, and Fe, were higher in the control sample compared to the mean concentrations obtained in this study. All metal recorded PLI values greater than 1 (value > 1) and increased in the order (Fe>Mn>Cd>Ni>Pb) except Cr (0.1570) indicating pollution of the soil.

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