Assessment of Heavy Metal Pollution in a Columbite/Tantalite Mining Site in Edege-Mbeki, North Central Nigeria

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ABSTRACT: The release of pollutants due to mining activities, especially tailings, has negative consequences on soil and affects agricultural productivity. This study details the assessment of metals (Ni, Mn, Pb, Cd and Fe), physicochemical parameters of the soil and how they affect metal bioavailability and biotoxicity. Metal concentrations were determined using Atomic Absorption Spectrophotometer (AA-6800 Shimadzu). The results of the analysis show that the mean pH varied from a minimum of 7.12 ± 0.36 to a maximum of 7.60 ± 0.28 across all the study area and sampling points. The percent organic matter had an average minimum value of $0.13\pm0.08\%$ and a maximum value of $0.82\pm0.32\%$ in the study area. The heavy metal analysis result shows that concentrations in all the soil and sediments of the study area were all below the maximum permissible limit. Mean concentrations of Ni, Mn, Cd, Pb and Fe had minimum values of 1.45 ± 0.56, 43.3 ± 0.43, 1.11 ± 0.22, 5.50 ± 0.28 and 522 ± 0.88 mg/kg respectively, and the mean maximum concentrations had values of 11.70 ± 0.90, 200 ± 0.17, 20.7 ± 0.11, 31.0 ± 0.78 and 2716 ± 0.83 mg/kg respectively. The findings show no metal contamination. However, the enrichment factor and contamination factor revealed that the presence of Ni, Mn, Cd and Cd in soil samples of the study area may be due to anthropogenic activities of mining.

Since the beginning of the industrial revolution, soil pollution by toxic metals has accelerated dramatically (Nriagu 1996). It is now well recognized that industrial activities like mining, smelting, refining and manufacturing processes led to a substantial accumulation of about 90% of heavy metals in soil on a global scale from industrial activities (Nriagu, 1996). Several chemical industries in the coastal areas have resulted in a significant discharge of industrial effluents, including heavy metals into the coastal water bodies. These toxic effluents released into the environment cause a variety of toxic effects on the food chain (Dembitsky, 2003) by bioaccumulation and biomagnification (Manohar *et al.* 2006). Several researches were prompted due to the adverse effects of heavy metals on both plants and animals. All plants can accumulate both essential metals (Fe, Mn, Zn etc.) required for normal plant growth and metabolism and non-essential metals (Al, Cd, Pb etc.) (Ologundudu *et al.,* 2019). However, when these metals are above the threshold level, there is a possibility of poisoning to individual plants (Garrido *et al.* 2002). For example, elevated level of heavy metals in soil can result in enhanced crop uptake alongside negative effects on plants growth (Schmidt 2003), such as damaging the cell structure and inhibiting a number of cytoplasmic enzymes (Assche *et al.* 1999), and replacement of essential nutrients at cation exchange sites in plants

(Taiz *et al.* 2002). According to Ologundudu (2019), among all the heavy metals, Cadmium (Cd), Lead (Pb), Chromium (VI), and Chromium (III) are highly toxic to plants, animals, and humans as well as soil microorganisms. For instance, high level of Pb in the soil is linked with decreased soil productivity as well as inhibiting important processes such as mitosis, photosynthesis, water absorption, and vegetative growth (Bhattacharya *et al.* 2008). To evaluate the damages that Columbite/Tantalite (COLTAN) mining activities have on the environment, considering that crude methods of mining are still largely used, it is imperative to assess the extent of pollution. Therefore, in order to evaluate the impacts mining activities have on the soil and agricultural productivity, especially considering that old methods of mining activities are still being practiced, the study was aimed at assessing the levels of metals (Ni, Mn, Pb, Cd and Fe) in soil and sediment samples in Columbite/Tantalite mining areas in Edege-Mbeki mining district of North Central Nigeria.

MATERIALS AND METHODS

The study was carried out in a Columbite/Tantalite (COLTAN) mine located in Edege-Mbeki Mining district in Nasarawa State. The site is located in Nasarawa local government, in Edege development

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area. The study and control sites are located on the geographical coordinates of latitude 08 ^{0} 19'30" N and longitude 70^0 50'80" E.

*Soil samples pretreatment***:** Soil and sediment samples were randomly collected at the different mining locations in Edege-Mbeki mining district. Control samples were taken at Maraban-Edege about 15 kilometres away from the mining district. The control site has no record of any mining activities but has human interference. Soil samples were collected at the surface (0-15 cm) and subsurface (15-30 cm) as well as sediments (Bank 1 and 2) using an Auger and a meter rule at both mine and control sites. The collected soil and sediment samples were stored in polythene bags, correctly labelled and transported to the laboratory for further analysis. Upon arrival to the laboratory, the soil and sediment were air-dried for 1 week and sieved on a <2 mm sieve for heavy metals analysis and 0.5 mm for physicochemical analysis. The physicochemical properties (pH and Organic matter) were analyzed using standard methods at the Soil Research Laboratory of the Institute for Agricultural Research (IAR) Zaria.

Determination of soil pH: Determination of soil pH was determined according to the method of Radojevic and Bashkin (2006). Exactly twenty (20) grams of air-dried soil and sediment samples were weighed in triplicate into a 50cm^3 beaker and 20cm^3 of distilled water was added. The mixture was allowed to stand for 30 minutes with occasional stirring using a glass rod. The pH measurement was taken using a Hanna digital pH meter which was initially calibrated using a buffer solution of pH 7. The calibrated pH meter was then inserted into the partly settled suspension and the pH measurement was taken.

Determination of soil organic matter: The organic matter content of the soil and sediment were determined titrimetically (Anderson and Ingram, 1993). Soil/sediment samples were ground with a laboratory mortar to give fine particles that could pass through a 0.5 mm sieve after which they were weighed in triplicate and transferred to an Erlenmeyer flask of 250 cm^3 capacity. Exactly 10 cm^3 of 1M potassium dichromate was pipetted into each flask followed by swirling to disperse the soil, this was followed by addition of 20 cm^3 concentrated sulphuric acid. The flask was swirled gently until the soil and reagents solution have mixed thoroughly. The whole mixture was then allowed to stand for 30 minutes on a glass plate to allow for the oxidation of potassium dichromate to chromic acid. Exactly 100 cm^{3}of deionized water was added followed by the addition of 3 drops of ferroin indicator, after which the mixture

was titrated against 0.5 M ferrous sulphate solution until there was a colour change from dull green to turbid blue. The titration solution was further added in drops until the endpoint was reached indicated by the change of colour to brilliant green. Titration for the blank solution was also carried out in the same manner.

$$\%OC = \frac{B - T}{Mass\ (g)of\ dried\ soil}$$

Where; %OC = Percentage Organic Carbon, B = Blank Reading, T = Titre value or volume of Ferrous Sulphate Used, CF = Conversion factor (1.33)

% organic matter in soil = % organic carbon x 1.729

*Heavy Metal Analysis***:** Digestion of soil/sediment sample was done according to Tsafe *et al* (2012). The soil/sediment sample was ground and sieved on a 2mm sieve at the department of Geology. Exactly 0.5g of soil/sediment was weighed and put into a beaker. Then a measured volume of 15ml of 30% hydrogen peroxide was added. This was left to stand for 60mins until the vigorous reaction ceased. Next 15ml of concentrated HCl was added and the content heated gently at low heat on a hot plate for about 2 hours. The digest was then removed from the digester and allowed to cool to room temperature. The digest was then filtered into 25ml standard flask and made up to the mark with distilled water. Triplicate digestion of each sample was carried out. Determination of the heavy metals as well as the standards were carried out in an atomic absorption spectrophotometer (model AA240FS). The values obtained in ppm after analysis were converted to mg/kg for the soil samples.

The heavy metals of the samples (Ni, Mn, Cd, Pb, and Fe) were carried out using an Atomic Absorption Spectrophotometer (AAS 240FS) at the Multi-User Research Laboratory (MUSRL) of Ahmadu Bello University Zaria.

Assessment of Heavy Metal Pollution: The following parameters were used to assess the pollution level in the soil and sediments;

$$CF = \frac{concentration\ of\ Metal\ in\ Sample}{Concentration\ of\ Metal\ in\ Backgrou\ nd}$$

Where CF = Contamination **Factor**

The USEPA (1993) maximum contaminant limit of heavy metal in soil was used as the baseline or

background metal levels for the calculation of contamination factors of soil and sediment samples.

Pollution Load Index (PLI): This index has been used for pollution assessment of heavy metals in soils and sediments sample (Bhupander *et al.,* 2011). The pollution load index (PLI) for each site was calculated using the following relation**,**

$$PLI = \sqrt[n]{CF1 \; X \; CF2 \; X \; CF3 \; X \; ... X \; CFn}$$

Where CF is the contamination factor of each metal that was examined while **n** equals the number of contaminants evaluated. A PLI value of 1 indicates pollution whereas PLI value less than 1 indicates no pollution (Ong *et al.* 2012).

Enrichment Factor (EF): An enrichment factor is a parameter that is used to evaluate natural or anthropogenic sources of heavy metal content in the soil and water (Ata *et al.* 2009). This index was used to distinguish between natural and anthropogenic sources. To calculate the enrichment factors for the entire elements, Iron (Fe) was used as a reference element.

$$EF = \frac{\left[\left(\frac{Cn}{CFe}\right)\right] Sample}{\left[\left(\frac{Cn}{CFe}\right)\right] Shale}$$

Where (Cn/Cfe) sample is the ratio of the concentration of the element of concern (Cn) to that of Fe in the sediment sample and (Cn/Cfe) shale is the same ratio in an unpolluted reference sample.

RESULTS AND DISCUSSION

The results of physicochemical properties of soil and sediment samples are presented in Table 1. The pH of both the mining and control sites for surface (0-15 cm deep) and subsurface (15-30 cm deep) level in Edege-Mbeki and control is slightly alkaline. According to Mapanda *et al.* (2004), acidic soil aids in the absorption of heavy metals and dissolution of metal carbonates complexes. Hence, the pH may not have played any role in heavy metals absorption or dissolution in the study area. In the control site soil, percentage organic matter was found to be greater than the mining sites at both surface and subsurface levels. At 0-15 cm (subsurface layer), the control site gave a mean value of 0.82 against the mine site 0.18. At the subsurface layer, the mining site gave a mean value of 0.17 against the control site of 0.31. This is probably due to the mining activities that have stripped the mining district soil of its rich organic nutrient in the soil. Generally, the value of the soil and sediment organic matter (% OM) was observed to decrease in moving downward across the soil depth. This is normal since more biological activities usually take place at the upper level of the soil which decreases on moving down the depth of the soil profile (Majiya *et al.,* 2015).

Table 1: Average Physicochemical properties of soil

Soil Parameters	0-15 cm Deep		15-30 cm deep		Sediment	
	Mining Site	Control	Mining Site	Control	Bank 1	Bank 2
pH	7.54±0.40	7.12±0.36	7.52±0.25	7.06±0.41	7.60±0.28	7.48±0.40
% Organic Matter	0.18±0.10	0.82±0.32	0.17±0.10	0.31±0.31	0.19±0.02	0.13±0.08

Mining site = Edege-Mbeki, Control = Maraban-Edege, Bank 1= Mining Pond, Bank 2 = Tailings Pond.

Table 2: Average values (mg/kg) of heavy metals soil and sediment samples

Elements	0-15 cm Deep		15-30 cm deep		Sediment	
	Mining Site	Control	Mining Site	Control	Bank 1	Bank 2
Ni	5.38±0.72	6.64±0.10	11.7±0.9	4.73±0.39	1.45±0.56	2.25±0.18
Mn	119±2.62	105±0.19	71.0±1.9	43.3±0.43	134±0.6	200±0.17
Cd	2.18±1.03	20.7±0.11	1.11±0.22	14.7±0.47	1.45±.00	1.35±0.07
Pb	16.3±0.22	16.2±0.64	5.50±0.28	14.6±0.34	ND	31.0±0.78
Fe	2716±0.83	887±0.40	1676±0.4	522±0.88	539±0.94	578±0.94

Mining site = Edge-Mbeki, Control = Maraban-Edege, Bank 1= Mining Pond, Bank 2 = Tailings Pond, ND- Not detected.

Heavy Metals Level in Soil: The mean values of heavy metals in soil and sediment samples from the study area is shown in Table 2. The values obtained for all the soil/sediment samples were far lower than the US-EPA (1993) maximum contaminant limit of 75mg/kg for Nickel (Ni) in the soil. The highest concentration of Mn (200±0.17 mg/kg) at the entire study area was obtained in sediment sample "Bank sediment 1" of Edege-Mbeki mining pond. The values obtained for all

the soil/sediment samples were below the US-EPA (1993) maximum contaminant limits of 850 mg/kg. This implies that all the samples analyzed in this study area are not contaminated with manganese. Generally, there was a downward decrease in the concentration of Mn across all the soil depth profile (0-15cm, 15-30cm) in the entire sampling site. The values obtained for Cadmium decreases downward across the soil depth profile (0-15 cm, 15-30 cm) at all the sampling sites.

The highest concentration of Cd (20.71 ±0.11 mg/kg) was observed at 015cm depth of Mararaban-Edege and the lowest concentration of Cd (1.33 ±0.04 mg/kg) was observed at the mining pond sediment "Bank sediment 2". The values obtained for all the soil and sediment samples were below the US-EPA (1993) maximum contaminant limits of 85 mg/kg. The highest concentration of Pb (31.0±0.78 mg/kg) was obtained at Edege-Mbeki (Bank sediment 2) while the lowest concentration (5.50±0.28 mg/kg) was obtained at the depth of 15-30 cm. In this research work, all the soil and sediments samples were below the US-EPA (1993) maximum contaminant limits of 450 mg/kg for Pb in the soil. The highest concentration of Fe (2716 ±0.83 mg/kg) was observed at 0-15 cm soil depth (Edege-Mbeki) and the lowest concentration of Fe (522.91±0.88 mg/kg) was observed at 15-30 cm soil depth of control (Mararaban-Edege). The values obtained for all the soil/sediment samples were lower than the US-EPA (1993) maximum contaminant limit of 47200 mg/kg. Heavy metals contamination of soil can hinder microbial activities leading to low organic matter mineralization that is required for plant growth (Dai *et al.,* 2004). The apparent increase of heavy metals concentration (not in all cases) in mine site and sediment compared to the control site points to the fact that mining waste is a potential source of soil contamination. An increasing level of these metals presents the site as potentially hazardous and could alter the food chain and biological life in the environment (Ologundudu *et al.,* 2019).

Heavy Metals Contamination Factors (CF) of Soil Samples and Pollution Load Indices (PLI): Calculated contamination factors of the heavy metals under study and their pollution load indices (PLI) are shown in Table 3. Generally, except for Cadmium (Cd) in Edege-Mbeki (7.2767) at a soil depth of 0-15 cm, there was low contamination of these metals (Ni, Mn, Pb, Cd and Fe) in all of the soil and sediment samples of Edege-Mbeki. However, there was very high contamination (CF>>6) of Cd in all the soil samples of Mararaban-Edege while all the other metals recorded low contamination of these metals (Ni, Mn, Pb, and Fe). The highest contamination of Cadmium (69.043) was observed at Mararaban-Edege at a soil depth profile of 0-15cm, while the soil samples of Edege-Mbeki recorded the least contamination (3.6767) of Cd. The PLI value >1 indicates pollution whereas PLI <1 indicates no pollution (Ong *et al.* 2013). In the entire soil sampling site, PLI value calculated for heavy metals was ranged between 0.1793 and 0.3826, which indicates that there was no serious overall load of heavy metals pollution or contamination in the entire sampling site.

Table 3: Heavy metals contamination factors (CF) and pollution load indices (PLI) of the soil and sediment samples

Location/site	Contamination factor (CF)					PLI
	Ni	Mn	Pb	Cd	Fe	
Edege – Mbeki						
0 – 15cm	0.0747	0.141	0.0816	7.2767	0.0576	0.2048
15 – 30cm	0.1713	0.0835	0.2750	3.6767	0.0355	0.2198
Average	0.1604	0.1123	0.1783	5.4767	0.0466	0.3826
Edege Mining ponds						
Bank sediment 1	0.0331	0.2359	0.5513	4.50	0.0123	0.2319
Bank sediment 2	0.0213	0.1579	-	4.8333	0.0114	0.1793
Average	0.0223	0.0898	2.0237	4.5833	0.0174	0.2096
Mararaban – Edege						
0 – 15cm	0.0978	0.1247	0.0811	69.043	0.0188	0.2641
15 – 30cm	0.0696	0.0509	0.7332	48.833	0.0111	0.2689
Average	0.0837	0.0878	0.4072	58.938	0.0149	0.3047

Table 4: Heavy metals Enrichment Factors (EF) of soil samples using Iron (Fe) as a reference element.

Location/site	Enrichment factor (EF)			
	Ni	Mn	Pb	Cd
Edege – Mbeki				
0 – 15cm	1.375	2.444	14.309	125.87
15 – 30cm	4.826	2.351	7.741	103.84
Average	3.101	2.396	11.025	114.86
Mining Ponds sediments				
Bank sediments 1	2.701	19.24	126.47	366.59
Bank sediment 2	0.436	3.069	123.26	154.19
Average	1.667	12.037	124.87	314.67
Mararaban – Edege (Ref)				
0 – 15cm	5.192	6.628	43.476	3670.58
15 – 30cm	6.286	4.602	66.765	4408.48
Average	5.739	5.615	55.121	40.39.53

The enrichment factor of heavy metals understudy in the soil and sediment samples was calculated using Iron (Fe) as a reference element and the results obtained is shown in Table 4. EF values ranging between 0.5 and 2 can be considered in the range of natural variability whereas a value greater than 2 indicates some enrichment corresponding mainly to anthropogenic inputs (Hernandez *et al.* 2003; Ata *et al.* 2009). Generally, the enrichment factors (EF) for Ni, Mn, Pb and Cd in all of the soil samples of the study area were greater than 2, highlighting the anthropogenic origin of these metals. The results of heavy metals were subjected to 1-way analysis of variance and indicated that there was no statistically significant difference (P > 0.05) in the Mn, Pb, Cd, Ni, and Fe contents across the depth profile of soil in all the villages of the study area. There was also no significant difference (P > 0.05) in the heavy metals content among the six sediments obtained from the mining ponds in Edege-Mbeki.

Conclusion: The concentration of heavy metals (Ni, Mn, Cd, Pb and Fe) in the soil samples analyzed were below the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) permissible limits. Hence, the soil at Edege-Mbeki at the time this research was carried out does not pose a significant threat or level of contamination. Despite all of these, the geochemical parameters show that the soil/sediment samples were contaminated with Pb, Cd, and Mn which have their origin from anthropogenic activities.

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