HEAVY METAL CONTENTS OF ONDA TANTALITE MINING AREA, NASARAWA STATE, NIGERIA

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Abstract

Heavy metal contents in soil from Onda tantalite mining area were studied. Thirty and ten soil samples were collected from the mining area and control site, respectively, using a hand auger. The soil samples were analysed for heavy metals; Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni and Zn using atomic absorption spectrophotometer, AAS. The results obtained showed that the mean concentrations for the respective metals above were 9.38 ± 2.98, 18.25 ± 5.32, 40.29 ± 8.47, 34.40 ± 8.77, 1590.57 ± 403.46, 53.10 ± 11.65, 188.57 ± 41.13, ND and 620.44 ± 91.47 mg/kg in soils from the mining area and 6.40 ± 1.99, 21.00 ± 3.68, ND, 36.36 ± 5.26, 1195.95 ± 314.52, 31.24 ± 6.93, 143.23 ± 28.26, ND and 564.15 ± 120.82 mg/kg for soils from the control site. The mean metal contents from the mining site were all higher than those from the control site due to mining activities, except for Co and Cu but were all lower compared to the recommended permissible limits by WHO except for Cd and Zn. The EF, CF, PLI, ERI and PERI evaluated for metals from the mining site show no imminent danger. However, there is the need for constant and regular monitoring of the level of heavy metals in soil from the site because of accumulation overtime, and soil remediation should be employed to take care of cadmium and zinc.

Key words: Tantalite, mining, heavy metals, contamination, pollution

1.   Introduction

Nigeria as a country is endowed with deposits of solid minerals across the length and breadth of the country. The discovery of these minerals and their exploitation has been harnessed very well and has brought about the development of that sector of the economy and also improved the standard of living of the populace in the affected communities [1]. There is also the problem of widespread artisanal mining in different parts of the country, and this has environmental implications and associated human potential health hazards [2]. Invariably, the exploitation of these minerals, such as gold, tantalum, zinc, columbite, oil and gas, has some negative effects on the environment. Mining and agriculture activities are some of the factors that bring about environmental pollution with regard to elevated levels of heavy metals [1].

Mining, whether done artisanally or mechanically, have the same negative effects on the environment. It is a well-known fact that the different components of the environment (rivers, air and soils) have been contaminated by heavy metals from mining. The contamination of the environment by heavy metals is associated with elevated levels of toxic metal concentrations. The weathering of minerals deposits and mines dumps affects the quality of surface and underground waters, air as well as soils in terms of the level of heavy metals. These effects could cause reduced agricultural production, serious threats to the environment and potential health risk in humans [3].

Some of the heavy metals that are associated with mining are Cd, Co,Cr, Cu, Fe, Pb, Mn, Ni, Zn and a few others [4]. The chemical forms of the ore, mode of extraction and the conditions of the environment

determine the effects of mining on the said environment in terms of elevated levels of the mentioned metals. For instance, physicochemical parameters of the soil, such as pH, electrical conductivity, organic matters and cation exchange capacity, as well as the speciation of metals in the soils, affect the mobility and bioavailability of the metals in the soils [1].

Heavy metals are chemical elements with densities above $5.0g/dm^3$ and have potentially toxic effects with associated health risks. These heavy metals are non-biodegradable and persist long in the environment, even in low concentrations and continue to bio-accumulate from where they can enter the food chain through plant uptake (Abiya *et al.*, 2018). Some of the metals such as Fe, Cu, Ni, Mn and a few others are essential to plants because they perform some physiological functions necessary for plant growth, but even at that, at elevated levels beyond the permissible tolerable limits, they could cause deleterious effects. Cd, Pb and some others, are known for their toxic effects both on plants and humans [5].

These heavy metals, which are non-biodegradable, have the capacity to undergo bioaccumulation in any biological system and from there could be found to have undergone translocation into the food chain where it finally gets to humans with their associated health hazards. Minerals deposits are found all over Nasarawa State, and tantalite particularly is mined artisanally in Onda, Nasarawa Local Government Area of Nasarawa State, Nigeria. The area could also be faced with these known problems with mining areas hence the reason for this research work.

2. Materials and Methods

2.1 Study Area

Onda in Nasarawa Local Government Area of Nasarawa State (Home of solid minerals) in the central part of Nigeria is the study area. Nasarawa Local Government Area is located at longitude 7°42'E of the Greenwich meridian and latitude 8°32'N of the equator. The Onda community is inhabited by mainly Afor and others such as Gbagi, Fulani and Hausa people, and they are mainly farmers and a few other, miners. The population of Nasarawa State is 1,863,275 according to the 2006 provisional census, and Nasarawa Local Government Area with a population of 189,835[6] and the Onda people was part of this figure.

The geology of Onda is that which is similar to that of the Afu complex, with the pegmatite associated with older granite emplacement at the younger granite. The selected mining area for the study is the tantalite mining area located in Onda, Nasarawa Local Government Area, Nasarawa State, Nigeria.
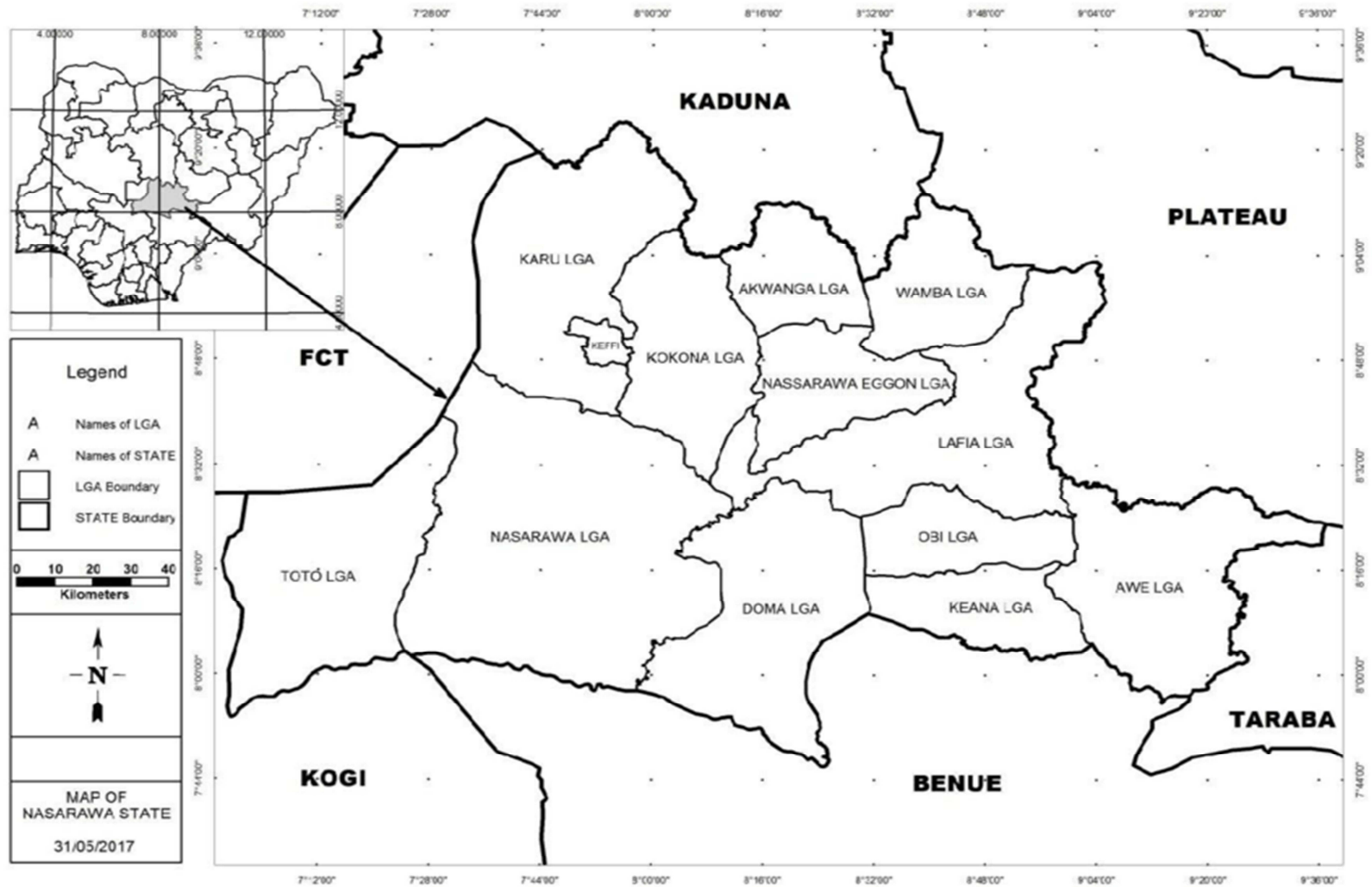
Figure 1: Map of Nasarawa State showing Nasarawa Local Government where Onda is located

2.2   Sample Collection and Preparation

2.2.1   Sample collection

Soil samples were collected randomly at a depth of 0 – 20 cm from the selected tantalite mining sites in Onda, Nasarawa Local Government Area. The samples were collected using the hand auger [7]. Sampling was done randomly but distributed evenly around the main mine pits. A total of thirty (30) samples were collected, with ten (10) samples each from around each of the three (3) main mine pits in the mining site. Ten (10) control samples were taken from a location about 10 – 15km away from the mines, where there are no known forms of anthropogenic activity.

2.2.2   Sample preparation

The samples were air-dried and pulverised or reduced to size using agate mortar and pestle. They were then screened through a mesh size 2.0mm. These were properly packaged in sample bags and labeled appropriately, and kept pending digestion.

2.3   Metal Analysis of Soil Samples

2.3.1   Digestion of soil samples

The air-dried soil sample, 1.00g, was weighed into the digestion flask, and 20.00 cm^3 of aqua regia (1:3, HNO_3: HCl) was added. The mixture was placed on the hot plate and heated for about 3 hours and, if not complete, was heated until a clear digest was obtained. The hot plate was put off, and the digest was allowed to cool. It was then filtered into a 100.00 cm^3 volumetric flask using No. 1 Whatman filter paper, and the filtrate was made up to the mark with de-ionised water. It was transferred into a sample bottle, labeled and kept pending analysis.

2.3.2   Determination of metals in soil samples

The concentrations of Cd, Co, Cr, Cu, Fe, Fe, Pb, Mn, Ni and Zn in the soil samples were determined with an atomic absorption spectrophotometer, AAS (Model NO, AA280 FS) manufactured by Agilent Technologies, USA.

3.   Quality Control/Assurance

Quality control and quality assurance were done through control samples and the use of blank preparations/repetition of samples..

3.1   Control Samples

Control samples were collected from a location about 10 – 15 km away from the study area. It is a location with no form of anthropogenic activities. It has the same geologic features as the study area. It is to help to ascertain that any elevated levels of the metals could actually be from the mining activities.

3.2   Blank preparation /repetition of samples

Blank preparations were made under the same conditions as the above-described digestion methods for metal concentrations. The only difference is that the samples were not part of it. This is to validate the method or test the validity of AAS. There was also the repetition of samples where after every five samples, the fifth was repeated and was done through the entire analysis. This was to find out if the result of the samples repeated and the earlier ones will be within the same range or would be different with a wide range which will suggest a serious error in the results.

4.   Statistical Analysis

The results obtained were subjected to statistical evaluations using tools such as mean, standard deviation, and coefficient of variation.

5.   Methods of Heavy Metal Pollution Assessment

The methods for heavy metal pollution assessment involve the evaluation of the EF, CF, PLI, ERI and PERI.

5.1   Enrichment factor (EF)

This is an index used to assess the presence and degree of deposition of contaminants in soils from human activities (anthropogenic sources). It is evaluated by making a normal one metal concentration in the soils with respect to the concentration of a reference element. A reference element is that which is stable in the soil, not known for vertical mobility [8] and abundant in nature [9]. Iron is selected as a reference element because of its abundance in nature and is one of the widely used reference elements [9]. The index is evaluated in the format adopted [9] is as given by equation (1) below:

$$EF = \frac{(C_m/C_{Fe})_{Sample}}{(C_m/C_{Fe})_{Control}} \qquad\qquad 1$$

Where $(C_m/C_{Fe})_{Sample}$ is the ratio of the concentration of heavy metals to that of Fe in the soil samples and $(C_m/C_{Fe})_{Control}$ value is the reference ratio in the control or background value.

The classes of enrichment factor are as follows; EF≤1 - background concentration, EF 1 – 2 = minimal enrichment, EF 2 – 5 = moderate enrichment, EF 5 – 20 = significant enrichment, EF 20 – 40 = very high enrichment and EF >40 = extremely high enrichment [8].

5.2   Contamination factor (CF)

CF is a quantitative evaluation of the level of contamination and sources of pollution. CF makes use of conservative elements as the reference element [1]. The CF is evaluated as the quotient as adopted [9] given by equation (2)

$$\frac{c_S}{c_C} \qquad\qquad 2$$

Where C_S = concentration of metal in samples, C_C = concentration of metal in the control sample and for a location, it can be evaluated as follows, as adopted [3] given by equation (3).

$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \qquad\qquad 3$$

Where the mean concentration of the metal from the soil samples is C_{0-1}^i and C_n^i is the average concentration of elements from control/background values.

The classes of contamination factor are as follows; CF<1 = low contamination factor, 1 ≤CF<3 = moderate contamination, 3≤CF<6 = considerable contamination CF, CF≥6 = very high contamination factor [1].

5.3   The pollution load index (PLI)

The pollution load index is used to determine the magnitude of heavy metal contamination in soils. It is an important tool used to evaluate heavy metal pollution. It can be expressed as given below in equation (4).

$$PLI = (CF_1 \times CF_2 \times \ldots \ldots \times CF_n)^{1/n} \qquad\qquad 4$$

Where CF_1 is the contamination factor and n is the number of heavy metals. The extent of heavy metal risk that is evaluated by PLI has the following classes; PLI =0 (perfect situation), PLI = 1 (Baseline levels of pollutants present) and PLI>1 (progressive deterioration of the site) [1].

5.4   Ecological risk index (ERI)

This parameter is utilised in evaluating heavy metal pollution in soils to associate ecological and environmental effects with their levels of toxicity and the toxic response factor (T_r) of Cd, Cr, Cu, Pb, Ni and Zn being 30, 2, 5, 5, 5, and 1 mg/kg respectively. ERI could be expressed as given by equation (5) below;

$$Er = T_r \times Cf_i \qquad\qquad 5$$

Where T_r is the toxic response factor for a given substance and Cf_i is the contamination factor. The extent of heavy metal risk as expressed by ERI has the following classes; $E_r^i < 30$ (low risk), E_r^i: $30 - 60$ (moderate risk), E_r^i: $60 - 120$ (considerable risk), E_r^i: $120 - 240$ (high risk) and E_r^i: >240 (significantly high risk) [10].

5.5   Potential ecological risk index (PERI)

This is employed to determine the semi-quantitative evaluation of regional pollution levels. It is expressed as given by equation (6) below;

$$PERI = \sum_{i=1}^{n} E_r^i \qquad\qquad 6$$

Where E_r^i is the ecological risk factor of the element i. The degree of heavy metal assessment by PERI is categorised into four classes; PERI<110 (low risk), PERI: $110 - 220$ (moderate risk), PERI: $220 - 440$ (high risk) and PERI>440 (significantly high risk) [11].

6. Results and Discussion

Table 1

Mean metal concentrations (mg/kg) in soils from tantalite mining site

Parameters	Study Site	Control Site	CV for Study Site	WHO [12]
Cd	9.38±2.98	6.40±1.99	31.77	3.00
Co	18.25±5.32	21.00±3.68	29.15	50.00
Cr	40.29±8.47	ND	21.02	100.00
Cu	34.40±8.77	36.36±5.26	25.49	100.00
Fe	1590.57±403.46	1195.95±314.52	23.37	50,000.00
Pb	53.10±11.65	31.24±6.93	21.94	100.00
Mn	188.57±41.13	143.23±28.26	21.81	2000.00
Ni	ND	ND	ND	50.00
Zn	620.44±91.47	564.15±120.82	14.74	200.00

ND = Not Detected, CV = Coefficient of Variation

Table 2

Pollution indices

Parameters	EF	CF	ERI
Cd	1.09	1.50	45.00
Co	0.65	0.87	NA
Cr	NA	NA	NA
Cu	0.73	0.95	4.75
Fe	1.00	1.33	NA
Pb	1.27	1.70	8.50
Mn	0.99	1.32	NA
Ni	NA	NA	NA
Zn	0.83	1.01	1.01
PLI	**0.53**		
PERI	**59.26**		

NA = Not Available, EF = Enrichment Factor, CF = Contamination Factor, PLI = Pollution Load Index, ERI = Ecological Risk Index, PERI = Potential Ecological Risk Index

6.1 Concentrations of metals in soils

Cadmium is toxic and, when present in soils at elevated levels, could be environmentally hazardous. The mean concentration of cadmium from the study area was 9.38±2.98 mg/kg (Table 1). This value is on the high side and could be attributed to the mining activities in the area, and this is even revealed by the fact that it is higher than the mean value of 6.40±1.99 mg/kg obtained for the control site. The mean value of cadmium from this study is higher than the mean value of 6.13 mg/kg for cadmium in soils from a typical Pb – Zn mining area in Hunan Province, China, reported by Huang *et al.* [13]. But it is lower than the mean value of 0.99 mg/kg for cadmium in soils from an abandoned Pb - mine in Zaidia (Morocco) which was reported by Laghlimi *et al.* [14]. This mean value of cadmium in soil from the study area is far high than the value of 3.00mg/kg recommended as the maximum permissible limit [12]. This suggests the contamination of the soils from the study area with cadmium which could probably be due to mining. This could get into the food chain through uptake by plants, bioaccumulation and translocation.

The mean concentration of cobalt in soil from the Onda tantalite mining site was 18.25±5.32mg/kg (Table 1). This value is moderate; however, elevated levels of cobalt in the soil could be attributed to mining as a case in point and as well as the wide application of fertilisers and agrochemicals to soil [15]. This explains the reason why the value for the mean concentration of cobalt in soil from the control site, 21.00±3.68 mg/kg, is higher than that for soils from the mining site. The mean concentration of cobalt from the study area is far lower than the mean values of 397.60±0.1 – 902.70±0.14 mg/kg from three sites but higher than the mean value of 0.03±0.00 mg/kg for one site for cobalt in soils from vegetable farms in Dorowa mining area of Barikin Ladi, Plateau State as reported by Shibdawa *et al.* [16]. The value of the mean concentration of cobalt from the study area is higher than the values of 2.80 – 16.50 mg/kg for cobalt in soils from all studied sites around artisanal gold mining in Dar – Mali locality, North of Atbara, River Nile State, Sudan reported Ali *et al.* [17]. This value from the study area is lower than the value of 50.00mg/kg recommended as the permissible limit for cobalt in soils [12]. Therefore, the level of cobalt at the moment portends no danger but overtime with continuous mining activity could lead to soil contamination with the metal.

The average chromium concentration in soils from tantalite mining sites in Onda, Nasarawa Local Government Area, was 40.29±8.47 mg/kg (Table 1) and its content in soils from the control site was below detection limits. The difference in the contents of chromium in soils of mining site and control site could be attributed to the anthropogenic activity (mining operations) taking place on the mining site. The mean value of chromium from the study area is far above the values of chromium in soils, 0.140 – 0148 mg/kg at different

depths in a gold mining site in south-western Nigeria reported Abiya *et al.* [5]. This value of 40.29±8.47 mg/kg from the study is higher than 36.38 mg/kg, which was the mean value of chromium in soil from soils in the abandoned Pb – mine of Zaida (Morocco), which was recorded Laghlimi *et al.* [14]. The mean values of chromium in soils used for the cultivation of vegetables in Dorowa mining areas of Barkin Ladi, Plateau State, Nigeria, which ranged from 3.30±0.62 – 33.90±0.15 mg/kg [16], are, however, lower than the mean values from the present study area and could be attributed to the extent of association of chromium with the different mines. The value from the study area is lower than the value of 100.00 mg/kg for chromium in soils recommended as the maximum permissible limit [12]. This has no implication in terms of soil contamination at the moment but could be overtime with bioaccumulation.

The mean copper concentration in soils from the study area was 34.40±8.47 mg/kg (Table 1). This mean value of copper in the soil is lower than the mean value of 36.36±5.26 mg/kg from the control site. This could be attributed to the difference in the compositional and mineralogical characteristics of the parent/source geological materials between the mining site and the control site [18]. The mean copper contents in soil from this present study are lower than the mean value of 57.33 mg/kg for copper in soils from around Enyigba Pb – Zn Mines District, south-eastern Nigeria [3] as well as the values of 54.30±0.23 – 65.70±0.08 mg/kg for copper in soil reported [16]. Soils with copper concentrations of more than 20.00 mg/kg are considered to be contaminated with copper [19, 20]. However, in this present study, its concentration is lower than 100.00 mg/kg for copper in soils recommended as maximum permissible limits [12]. Therefore, there is no implication of metal pollution of the soil with copper metal.

Iron had a mean concentration of 1590.57±403.46 mg/kg in soil from the study area (Table 1). This value is relatively high because iron is the second most abundant metal in the earth's crusts. The value from the study area is higher than the mean iron concentration in soils from the control site, which was 1195±314.52 mg/kg. This could be due to the mining activity on the mining site. The value from the study area is lower than the mean value of 60,924.50 mg/kg for iron soils from around Itakpe iron – ore mining area reported [9],and the range values of 6,355 – 14,635 mg/kg for iron in soils from a gold mining area in Dar – Mali locality, North of Atbara, River Nile State, Sudan [17]. The difference in the contents of iron in soils from the study area and other studies considered could be attributed to the degree of association of iron with the different ore. The value of 1590.57±403.46 mg/kg from the study area is lower than that of 50,000 mg/kg for iron in soils recommended as maximum permissible limits [12]. Therefore, the soils have no implication of metal pollution with iron at the moment.

The lead had a mean concentration of 53.10±11.65 mg/kg in soils from the mining sites used as the study area. Lead is a major environmental contaminant in mining-impacted soils. Due to the mining activities, the mean value of lead from the mining site is higher than the mean value of lead in soils from the control site, 31.24±6.95 mg/kg. The mean value of lead from the mining site falls within the range concentrations for lead in soils from coal mines in various cities/countries globally, 0.50 – 110 mg/kg [21]. Nevertheless, it is higher than the concentrations of 0.216 – 0.278 mg/kg at different depths for lead in soils from a gold mining site in southwestern Nigeria [5]. The mean value of lead in soils from the mining site in the study area is below the value of 100.00 mg/kg recommended as the maximum permissible limit [12]. Therefore, no implication of lead polluted soils in the area of study.

The mean manganese concentration in soils from the mining site was 188.57±41.3 mg/kg. Manganese is a frequently abundant constituent of soil; however, its low solubility at neutral and alkaline pH prevents its excessive uptake by plants. Therefore, manganese toxicity is nearly always associated with acidic soils [16]. The mean value of manganese in soils from the control site, 143.23±28.26 mg/kg, is lower than its values from the mining site, and the difference could be attributed to the mining activities. The mean concentration of manganese from the mining site, 188.57±41.13 mg/kg, is slightly higher than its mean value of 183.82 mg/kg in soils from around Enyigba Pb – Zn, Mines District, south-eastern Nigeria [3], but lower than the range values 549.6±49.4 – 1411.7±144.2 mg/kg for manganese in soils from a near coal mining area in Gujarat, India [22]. Meanwhile, the manganese mean value from this present study is within the range values of 40.00 – 564 mg/kg for manganese in soils of the Kette Batouri Region, Eastern Cameroon [23]. The concentration from the study area is far lower than the concentration of 2000.00 mg/kg for manganese in soils recommended as the maximum permissible limits [12]. Manganese, therefore, is not much of a problem concerning the metal pollution of soils.

Nickel is a poisonous heavy metal. In the studies on nickel the metal, nickel contaminates the soils when its concentration is higher than 40.00mg/kg [20]. Nickel in soils from the mining site and the control site was below the detection limits of the instrument used.

The mean zinc concentration in the soils from the mining site was 620.44±91.47 mg/kg, which is higher than its mean concentration of 564.15±120.82 mg/kg for the control site. The difference could be due to the mining activities. The high zinc concentration could result from the oxidation of organic matter and sulfides in the soil in the presence of abundant oxygen [20]. The mean concentration of zinc, 620.44±91.47 mg/kg, is higher than the range concentrations of zinc 7.00 – 222.00 mg/kg in soils from an active mining site (tantalum – niobium mining site) in Iludun – Oro and its environs, south-western Nigeria reported Oyebamiji *et al.* [1]. The

mean range concentration of zinc in soils from the Draa Lasfar mining area in Marrakech (Morocco) 648.0±174.3 – 2847.8±460.3 mg/kg [24] is higher than the mean zinc concentration from the present study. The mean zinc concentration in soils from the study area is far higher than the concentration of 200.00 mg/kg for zinc in soil recommended [12] as the maximum permissible limits for zinc. This degree of concentration implies that the soils from the mining site are polluted with zinc metal.

The coefficient of variation is a measure of relative variability which compares the degree of variation in the concentration of one metal to the other across the study area [1]. The coefficient of variation (CV%) for the heavy metals studied was Cd (31.77), Co (29.15), Cr (21.02), Cu (25.49), Fe (23.37), Pb (21.94), Mn (21.81) Ni (ND) and Zn (14.47) (Table 1). The highest coefficient of variation was observed with cadmium, and zinc had the lowest coefficient of variation. The coefficient of variation of all the metals is CV < 90%, indicating that anthropogenic sources dominate the heavy metals. However, several other factors are for the coefficient of metal variation across the study area, including sampling method, sample preparation methods, and analytical techniques employed [1].

6.2 Pollution indices

The pollution indices include enrichment factor, contamination factor, pollution load index, ecological risk index and potential ecological risk index. The values obtained for the enrichment factor (FF), contamination factor (CF), pollution load index (PLI), ecological risk index (ERI) and potential ecological risk index (PERI) are shown in Table 2.

The enrichment factor calculated for the heavy metals analysed in soils from the study area showed that Cd (1.09), Fe (1.00), and Pb (1.27) had EF that are between 1.00 – 2.00, which signifies depletion to minimal enrichment in soil [25]. On the other hand, EF was not available for Cr and Ni, Co (0.65), Cu (0.73), Mn (0.99) and Zn (0.83) had EF that was less than 1.00 and are, therefore, said to have background concentrations as was observed in a research work carried out [25].

The contamination factor for Co (0.87) and Cu (0.95) indicated a low contamination factor. Cd (1.50), Fe (1.33), Pb (1.70), Mn (1.32) and Za (1.01) showed $1 \leq CF \leq 3$ which were indications of moderate contamination factor [25]. CF was not available for Cr and Ni.

The Pollution Load Index (PLI) calculated for the heavy metals analysed in soils from the mining site, which is the study was 0.53, which is PLI < 1, and it reveals that the soils from the mining site are not polluted with the heavy metals [1].

The ERI calculated for the heavy metals studied in soils from the study area were Cu (4.75) and Zn (1.01), where ERI < 30 implies low risk. ERI were not available for Co, Cr, Fe, Mn and Ni. ERI for Cd (45.00) revealed an indication of moderate-risk [10].

The Potential Ecological Risk Index (PERI) for the heavy metals in soils from the mining site studied was 59.26, which is shown to be PERI <110, which is an indication of a low potential ecological risk index for the mining site [11].

7.   Conclusion

Heavy metals determined in soil samples were present, except for chromium in the control site and nickel in mining and control sites that were not within detection limits. Concentrations of all heavy metals in soils from the study site were higher than those of the soils from the control site due to mining activities, except for Co and Cu, which had concentrations lower than those of the control, which could be attributed to the difference in the compositional and mineralogical characteristics of the parent/source geological materials between the mining and control sites. For all the metals in the soil samples, only Cd and Zn had concentrations higher than the recommended values by WHO, and therefore, the soils stand the risk of metal pollution by Cd and Zn. However, there is no sign of significant pollution from the pollution indices as EF ranges from depletion and background value to minimal enrichment. Furthermore, CF range from low to moderate contamination, PLI indicates no pollution, and ERI shows moderate risk. Finally, PERI indicates low potential risks for the metals determined in the soil samples.

8.   Conflict of Interest

The authors declared that there is no conflict of interest.

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