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Assessment of Concentrations and Ecological Risk of Heavy Metals at Resident and Remediated Soils of Uncontrolled Mining Site at Dareta Village, Zamfara, Nigeria

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ABSTRACT: This study determined the levels of some heavy metals at resident and remediated soils of uncontrolled gold mining activities with a view to providing information on the extent of contamination and ecological risk to the resident area. The soil samples were collected from two site at the resident and one remediated soil, and analyzed for metals (Cr, Ni, Pb, Fe, Cu, Cd and Mn) using Atomic Absorption spectrophotometer (AAS). The concentrations of heavy metals (mg/kg) in residents samples ranged from 1.500-13.30 (Cr), 0.0001-0.05 (Ni), 0.18-3.754 (Pb), 0.0003-0.10 (Fe), 0.0005-0.88 (Cu), 0.0009-0.27 (Cd) and 0.0003-0.0035 (Mn) and for the remediated sample are 12.3000, 0.0001, 1.1989, 0.0002, 0.0006, 0.0003, and 0.0003 for Cr, Ni, Pb, Fe, Cu, Cd and Mn respectively. The calculated geo-accumulation index (I_{geo}) shows that the soil samples fall under unpolluted to moderately pollute for all the studied metals with respect to all studied sites. Pollution Load Index values (PLI>1) were all less than 1 for each metals in all studied sites, thus indicating perfection. The contamination factor (C_f) and degrees of contamination (C_d) of the soil samples were very slightly contaminated to slightly contaminated with Cr and Cd; The ecological risk results revealed that site A, B and Remediated samples were fall under low ecological risk index with values of 0.28, 10.28 and 0.33 respectively. The contaminations of these studied metals may not add ecological risk to the local environment.

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Environmental pollution by heavy metals has been studied to cause severe illness and sudden death in human beings for many centuries. It can be from air, water or soil and can result from automobile exhaust, agriculture, industries and mining activities among others (Galadima and Garba, 2012). Environmental pollution from mining activities has continued to cause unpleasant implications to human health and economic development all over the globe (Adamu *et al.*, 2014). Galadima and Garba (2012), reported that Zamfara lead poisoning is the worst and most recent heavy metals incidence in the Nigeria records that claimed the lives in 2010 due to the resident gold mining activities. Many deaths are being recorded which necessitated an immediate remediation of the affected villages. Dareta village was remediated between June and July, 2010 (Udiba *et al.*, 2013). There is tendency for the crude process to contaminate the environment with other types of heavy metals apart from the lead which is already detected as major hazard for human health. Likewise, there is no evidence that the villagers have stop their illegal activities because of the huge amount of money realize from it. There is need to assess the level of other heavy metals in the residential soils and the remediated one in order to ascertain the human safety and to avoid future occurrence of what happened in 2010. The risk assessment of heavy metals would provide a certain theory support for risk management. Methods used to evaluate the ecological risk posed by heavy metals in soil include calculation of the enrichment factor, geo-accumulation (Reimann and Caritat, 2005; Pekey, 2006; Zhu *et al.*, 2011; Sulaiman *et al.*, 2018b) and potential ecological risk index (Hakanson, 1980). This study was aimed to determine the levels and ecological risks of some heavy metals at Resident and Remediated Soils of Uncontrolled Mining Site at Dareta Village, Zamfara, Nigeria.

MATERIALS AND METHODS

Study Area: The study area is Dareta village, Anka LGA of Zamfara, located at latitude 12°06′30″N and longitude 5°56′00″E, with coverage area of 2,746 km² and population of 142,280 (FRN, 2007). The climate is tropical with two distinct seasons; rainy (May-October) and dry (November-April) seasons and with

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temperature recorded average annual of about 21 ºC and average rainfall of about 579 mm (Figure 1), with the average of 76% humidity (Sulaiman *et al.*, 2016).

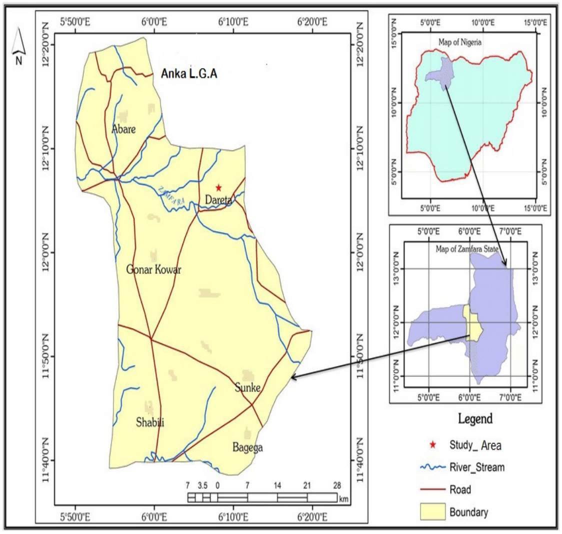

Fig.1: Map of Zamfara State showing the study area

Sample collection: Soil samples was collected from residential soil at two different sites labeled A and B, and remediated soil at 0-15 cm, at each sampling locations, subsamples were randomly collected to make a composite sample. Each (500 g) sample was placed inside polyethylene bag and covered with aluminum foil. The samples were taken to the laboratory and stored under room temperature until analysis.

Treatment and analysis: One gram each air dried soil sample was weighed into a 125 mL beaker and digested with a mixture of 4 mL, 25 mL and 2 mL each of concentrated $HClO_4$, HNO_3 and H_2SO_4 respectively, on a hot plate in a fume cupboard. On completion of digestion, the samples were cooled and 50 mL of distilled water was added and then the samples were filtered. The samples were made up to 100 mL with distilled water and concentrations of the elements determined using atomic absorption spectrophotometer (AAS Model SP 9 Unicam 1984) Chiroma *et al.* (2014).

Pollution indices: Pollution index are tools used for processing and conveying raw environmental information to decision makers and to the public (Caeiro *et al.*, 2005; Sulaiman *et al.*, 2018b). The following indices; geo-accumulation index, degree of Contamination and pollution load Index were used to measure the extent of pollution.

Geo-accumulation Index: Geo-accumulation Index was calculated using the method proposed by Muller (1969).

$$I_{geo} = \mathrm{Log}_2\left[\frac{C_n}{1.5B_n}\right] \qquad \text{Eq. (1)}$$

Where C_n is the metal content in the soil sample and B_n is the geochemical background concentration or reference value. The factor 1.5 is introduced to minimize the effect of possible variations in the background or control values in the soil. The average elemental concentration reported by Turekian and Wedepohl (1961), in the earth's were used as a reference for study. The contamination was classified as follows; $I_{geo} < 0$ means unpolluted; $0 \leq I_{geo} < 1$ means unpolluted to moderately polluted; $1 \leq I_{geo} < 2$ means moderately polluted; $2 \leq I_{geo} < 3$ means moderately to strongly polluted; $3 \leq I_{geo} < 4$ means strongly polluted; $4 \leq I_{geo} < 5$ means strongly to very strongly polluted; $I_{geo} > 5$ means very strongly polluted (Huu *et al.*, 2010).

Degree of Contamination (C_d): The contamination factor was derived by employing the model by Lacatusu (2000). The following equation 2 and 3 below was used to define as a contamination factor (C_f) and degree of contamination (C_d) respectively;

$$C_f = \frac{C_n}{C_o} \qquad \text{Eq. (2)}$$

$$C_d = \sum Cf \qquad \text{Eq. (3)}$$

Where C_d is degree of contamination, C_f is a contamination factor, C_n is the metal content in the soil sample and C_o is the geochemical background concentration or reference value the uncontaminated soil (Khairy *et al.*, 2011). The DPR (2002), reference (background) value were used as a reference value to the study. The terminology used was according to Sulaiman *et al.* (2018a).

Pollution load index (PLI): Pollution Load Index (PLI) is obtained as Contamination Factors (C_f) and was developed by Thomilson *et al.* (1980). The PLI was calculated by obtaining the n-root from the nC_fs that were obtained for all the metals as follows:

$$PLI = \sqrt[n]{(Cf_1 \times Cf_2 \times Cf_3 \times Cf_4 \times Cf_n)} \qquad \text{Eq. (4)}$$

Where n is the number of metals studied and Cf is the contamination factor calculated as described in Equation 2. The PLI gives an estimate of the metal concentration status. The rank of values of PLI < 1 donate perfection: PLI = 1 present that only baseline levels of pollutant are present and PLI > 1 would indicate deterioration of site quality (Thomilson *et al.*, 1980).

Ecological Risk Assessment: The ecological risk index (R_i) was introduced to assess the degree of heavy metal pollution in surface sediment or soil, according equation proposed by Hakanson (1980).

$$R_i = \sum E_r^i \quad \text{Eq. (5)}$$

$$E_r = \left(\frac{C_n}{C_o}\right) \quad \text{Eq. (6)}$$

Where R_i is calculated as the sum of potential ecological risk factor for heavy metals in sediments, E_i is the monomial potential ecological risk factor, T_i is the toxic-response factor of a certain metal, C_n is the metal content in the sediments and C_o is a background values (reference value of metals in soil). The terminology used to describe the ecological risk index as classified by Hakanson, (1980).

RESULTS AND DISCUSSION

Heavy metal content in the soil samples: The mean concentrations of heavy metals in resident and remediated soils from Dareta village are presented in Figure 2.

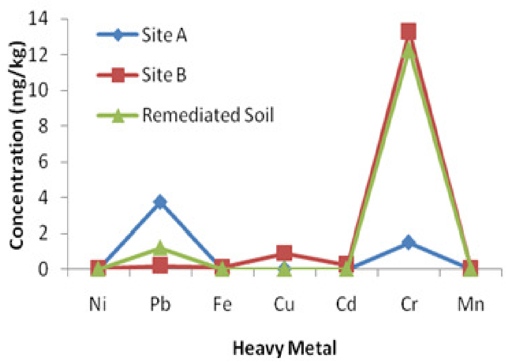

Fig. 2: Mean Concentration (mg/kg) of Heavy Metal in Site A, Site B and Remedial soil from Dareta

The results shows that there is high concentration of Cr in one of the resident soil (site B) and the remediated soil, while the level of Pb is higher in site A when compared to site B and the remediated soil. In the remediated soil, it was shown that the concentration of Pb and Cr are the only elevated elements while Ni, Fe, Cu Cd and Mn are low as in site A which was 50 meters away from site B, the latter is closer to their farm lands and located almost at the out sketch of the town. The different in concentration of site A and B might be due to long time leaching of the heavy metals from Site A to site B when the whole area was polluted, but now there is no much leaching from the compounds and within the community to site A since the polluted soils have been scraped and replaced with safer one as indicated in the analysis of the remediated soils and this can be the genesis of low concentration in most metals in site A.

Geo-accumulation Index: The results of the geo-accumulation index of the soil samples from the site A, B and remediated soil are presented in Fig. 3. The geo-accumulation index of the metals from all the studied sites with respect to all studied metals fall under class 0 - unpolluted except Cd in site B soil sample which fall under class 1 - from unpolluted to moderately polluted.

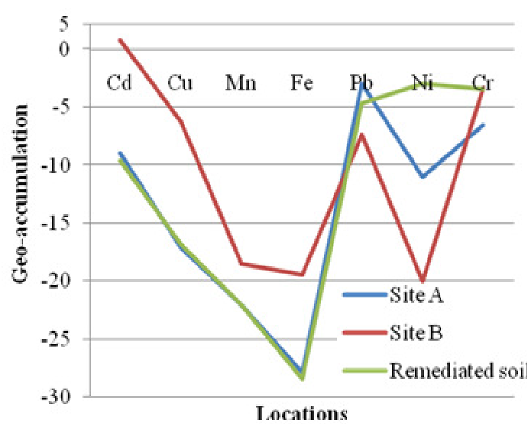

Fig. 3: Geo-accumulation index of the soil

Contamination Factor (C_f) and Degree of Contamination (C_d): The contamination factor (C_f) values were shown in Table 3. The values of contamination factor at site A, B and Remediated site were < 1. Thus, all the studied sites can be categorized as uncontaminated to low contamination. This indicated that contamination of soil at site A, B and Remediated soil are all having low contamination in respect to all studied metals. Degree of contamination of site A, B and Remediated soil also indicate low degree of contamination with C_d values of 0.060, 0.487 and 0.137 respectively. The studied samples are therefore, categorized to have low degree of contamination, this indicates very low anthropogenic pollution at these sites.

Table 3: Contamination factor (C_f) and degrees of contamination (C_d) values

Sample/Elements	C_f						
	Cd	Mn	Fe	Pb	Ni	Cr	C_d
Site A	1.12E-03	6.30E-07	6.0E-08	0.044	2.85E-06	0.015	0.060
Site B	0.33	7.35E-06	2.0E-05	2.1E-03	1.43E-03	0.133	0.487
Remediated Soil	3.75E-04	6.30E-07	4.0E-08	0.014	2.85E-06	0.123	0.137

Pollution load index (PLI): The values obtained for Pollution Load Index values (PLI>1, Fig. 4) were all less than 1 for each metals in all the studied sites, thus indicating perfection.

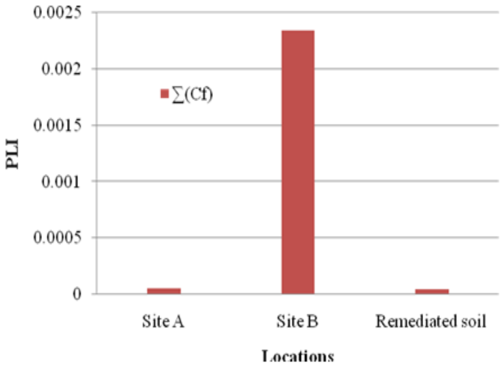

Fig. 4: Pollution Load Index values

The contamination of studied sites has not been to the level where immediate intervention would be needed ameliorate pollution.

Ecological Risk ($E^i r$) and Potential Ecological Risk Index (R_i): Potential ecological risk factor is summarizes in Table 4. Site A, B and Remediated soil were found to have low potential ecological risk factor in respect to all studied metals such as Cr, Ni, Pb, Fe, Cu, Cd, Mn which were all below (E_i < 40). The Ecological risk index (R_i) was calculated as sum of all risk factor (Table 4). Ecological risk index (R_i) characterized sensitivity of local ecosystem to the toxic metals and represent ecological risk resulted from the overall contamination. The Ecological risk index result revealed that in all the studied sites the R_i < 150 this indicate low ecological risk.

Table 4: Potential ecological risk factor (E_r) and ecological risk index (R_i) values

Sample/Elements			**E_r**			
	Cd	Cu	Pb	Ni	Cr	**R_i**
Site A	0.034	6.8E-05	0.22	1.43E-05	0.03	0.284
Site B	9.90	0.10	0.01	7.15E-03	0.27	10.28
Remediated Soil	0.011	8.2E-05	0.07	1.43E-05	0.25	0.331

Conclusion: The results of heavy metals concentrations in the soil samples revealed that the soil contains substantially amount of metals determined (Pb, Cu, Cd, and Cr) due to illegal mining activities taking place in the area. The Geo-accumulation index (I_{geo}) examined in this study revealed that the soil samples to be unpolluted to moderately pollute of all studied metals while the contamination factor (C_f) and degrees of contamination (C_d) of the soil as very slightly contaminated to slightly contaminate by Cr, and Cd. The pollution load index (PLI>1), were all less than 1 for each metals in all the studied sites, thus indicating perfection and Ecological risk assessment showed low ecological risk index with values less than R_i <150.

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