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ENRICHMENT AND GEOACCUMULATION OF Pb, Zn, As, Cd, Mn and Cr IN FARM SOILS AROUND TIN MINE AREAS IN PLATEAU STATE, NIGERIA

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ABSTRACT: *Enrichment factor (EF), contamination factor (CF), geo-accumulation index (Igeo), and pollution load indexes (PLI) were employed to evaluate Pb, Zn, As, Cd and Cr in farm soils around tin mine areas in Plateau State, Nigeria. Arsenic and Cd were graded as unpolluted to moderately polluted while Pb, Zn and Cr indicated moderate contamination (Igeo > 1) in the soil. EF values for Pb, Zn, Mn, As and Cr where attributed to natural processes with evidence of anthropogenic activities. Meanwhile, Cd showed significant contamination in soil at B_4 with CF > 6.13 and a mean value of 3.79. The PLI values for 95 % of the sample sites were ≥ 1.88, which is an indication of soil quality deterioration.*

KEYWORDS: Geo-Accumulation Index, Enrichment Factor, Contamination Factor, Pollution Load Indexes

INTRODUCTION

Mining which involves the extraction of naturally occurring minerals from the earth's crust is considered as the world's second oldest and most important industry after agriculture (Amponsah-Tawiah, 2011). The mining industry being important to human development becomes evident when one considers the naming of the pre-historic period after mined products "Stone" age, "Bronze" age and "Iron" age (Jennings, 1999). In Nigeria, mining started as far back as the eighteenth century. Over five hundred (500) occurrences and deposits of different minerals are known so far to exist within the country with the exploration of some of them being on a small scale (Adegbulugbe, 2007).

Tin is said to be one of the oldest mineral resources known to man as its strategic importance was recognized as far back as some 300 years ago when its hardening effects on copper was discovered (Adegbulugbe, 2007). Tin ore has been mined in several parts of Nigeria including Zaria, Kano, Bauchi, Ilesha and Jos provinces, with over 80 % of the production coming from the Jos Plateau (Ajaegbu *et al.*, 1992).

Mining operations can be environmentally disruptive if proper setting, design, construction, operation and follow-up monitoring are not provided (Abua and Eyo, 2013). The operations are known to have various negative effects on our environment such as alteration of landscape, deterioration of vast land areas and extinction of wild life (Vincent *et al.*, 2012). Mining activities are also associated with dust particles which constitute one of the most invasive and potentially irritating air pollutants (Larger, 2014). Mining is an important source of toxic metals into the environment and mine tailing disposal may result in acid mine drainage and the release of metals of toxic levels that impact negatively on human health and the environment (Davies and Rice, 2001).

Tin mining gives rise to large number of excavated overburdens dumped on the surface (mine spoil); this may contain various heavy metals, some of which are toxic in nature and affect the environment when their concentration exceeds the permissible limit (Mafuyai *et al.,* 2019). Surface runoff and wind erosion from mining sites could cause increase in concentration of the heavy metals in local biota and have more significant effect on the ecosystem that may lead to geo-accumulation, subsequently bio-accumulation and bio-magnifications in the food chain (Koushik *et al.*, 2012).

Studies have shown that metals are extremely persistent in the environment, non-biodegradable and readily accumulate to toxic levels (Forstner, 1985, Giller *et al*., 1988, Kozak, 1991 and Grzebisz *et al*., 2002). Contamination of soil is a reoccurring danger due to pollution by toxic metals resulting in the infertility and unsuitability of the soil for plant growth and affecting the food web (Marques *et al*., 2011). These metals can accumulate to phytotoxic levels, especially in low pH soils and subsequently reduce plant growth and enter the food chain (Chaney, 1993).

Moreover, the tailings dump is not covered by vegetation and susceptible to water and wind erosion which may consequently enrich the surrounding environment with toxic metals (IMWA, 2017). These heavy metals get accumulated through time in soils and plants and would have a negative influence on physiological functions in plants causing undesirable changes on their growth patterns, dry matter accumulation and yield (Ojekunle, 2014). This study focused on metal (Mn Cu, Pb, As, Cd and Cr) contamination in the vicinity of tin mine dump. The assessment of soil contamination based on Geo-accumulation index (Igeo), enrichment factor (EF), contamination factor (CF) and pollution load indexes (PLI).

MATERIALS AND METHODS

Study Area

The study was carried out in Barkin – Ladi Local Government Area of Plateau State as presented in Figure 1. The geographical coordinates are: latitude 9°24’N to 9°28’N and longitude 8°54’E to 8°56’E. The study areas played host to a lot of mining activities by foreign companies’ such British Mines Corporation Limited, Bisichi Jenta Limited, Gold and Base Corporation, Exland and Kaduna Prospectors (Jiya and Musa, 2012). These companies rendered the area derelict with numerous waste dumps and ponds. The impact of the past mining activities on the landscape is devastating as several tin mined- dumps were left with various hazardous effects that pose serious threat to human and animal lives (Adiukwu and Ogezi, 2000). The people of these areas are predominantly farmers and most of the vegetables grown in the area include tomato, pepper, cabbage, carrot, spinach, garden egg and many other varieties of vegetables.

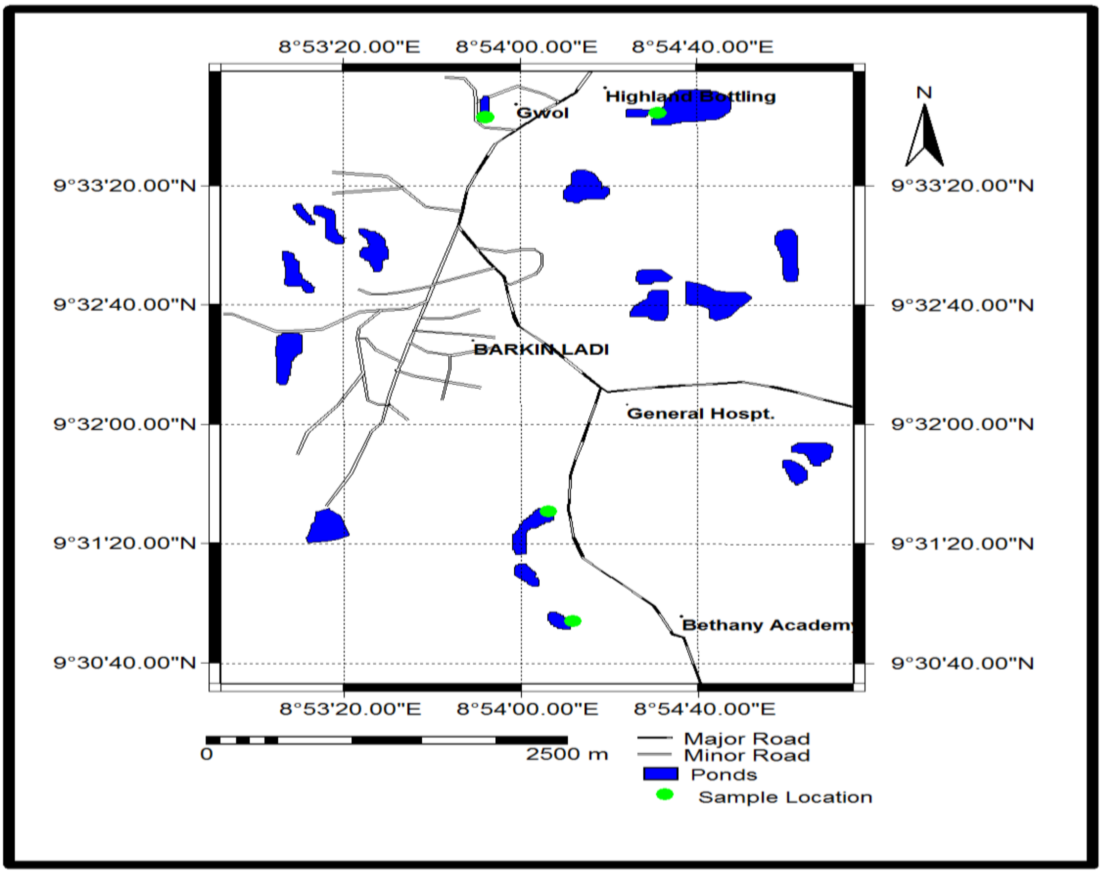

Figure 1: Map of Barkin – Ladi Showing the Sampling Sites

Sampling of Soil

Soil samples were obtained from two farms closed to the piled tin mine dump. The soil samples were at the depth of 0 - 20 cm using a steel soil auger and transferred into tagged polythene bags and transported to the laboratory, air-dried and sieved (< 0.25 mm) then stored in desiccators prior to digestion for analysis of heavy metals.

Heavy Metals Determination in Soil Irrigated with Tin Mine Pond Water

Procedure: About 5 g of dried and sieved subsoil sample was taken into 100 mL of conical flask. 20 mL of 1:1 HNO_3 was added to the conical flask and covered with a watch glass, then, evaporated to 5 mL on a hot plate. After cooling, 5 mL of $HClO_4$ and 20 mL of distilled water was added and further evaporated to 10 mL on the hot plate. The sample solution was cooled, filtered through Whatman No. 42 filter paper and the filtrate transferred to a 100 mL volumetric flask and make up to mark with distilled water (Hseu *et al.*, 2002). The concentrations of Pb, Cr, Cu, Cd, Mn, and As were be determined by Atomic Absorption Spectrophotometer The quality control of the analytical procedure was carried out by analyzing the standard reference material (SRM-CC141) bought from Sigma Chemical Laboratory in Lagos, a representative of Sigma-Aldrich, USA. The SRM were analyzed (in triplicate) in the same way as treated actual samples.

$$\text{Concentration of metal (mg/Kg)} = \frac{[(C_1 - C_2) \text{ x V x D.F}]}{\text{D.W}} \quad (1)$$

where;

C_1 = concentration of metal in the sample obtained from calibration curve (mg/L)

C_2 = concentration of metal in the blank obtained from calibration curve (mg/L)

V = total volume of digested sample (mL)

D.F = dilution factor of digested sample and

D.W = dry weight of sample (kg)

Contamination Assessment Methods

Enrichment factor (EF) and Geoaccumulation index (Igeo) defined by Muller (1969) were used for assessment of soil contamination in the vicinity of the tailings dump.

Enrichment Factor (EF)

Enrichment factor (EF) is used to differentiate between the metals originating from anthropogenic activities and those from natural sources. Enrichment factor of the metals was calculated as the ratio of elemental concentration of sediment normalized to a reference Fe. Using the following equation (Ridgway and Shimmield, 2002).

$$EF = \frac{[Me/Fe]_{\text{sample contaminated site}}}{[Me/Fe]_{\text{background uncontaminated site}}} \quad (2)$$

where

(Me/Fe) is the metal to Fe ratio in the sample of interest

(Me/Fe) is the background value of metal to Fe ratio.

Iron was chosen as the element of normalization because natural sources (1.5 %) vastly dominate its input. A crucial step in evaluating the impact of soil pollution is to establish a reference background or baseline sample of known metal composition. In this study, the local baseline value was established by analyzing comparable local soil unaffected by anthropogenic activity. The EF categories for describing the contamination levels is summarized as: < 2 = deficiency to minimal enrichment; 2-5 = moderate enrichment; 5- 20 = significant enrichment; 20-40 = very high enrichment; > 40 = extremely high enrichment.

Geoaccumulation Index (Igeo): The index of geoaccumulation (Igeo) is widely used in the assessment of contamination by comparing the levels of heavy metals obtained to background levels originally used with bottom sediments (Atiemo *et al.*, 2011; Muller, 1969). It is calculated using the equation:

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$$\text{Igeo} = \log_2 \frac{Ci}{1.5B} \quad (3)$$

where, Ci represents the measured concentration of the elements studied and B is the geochemical background value of the element in fossil argillaceous sediment (average shale).

The following classification is given for geoaccumulation index: < 0 = practically unpolluted, 0 – 1 = unpolluted to moderately polluted; 1 – 2 = moderately polluted; 2 – 3 = moderately to strongly polluted; 3 – 4 = strongly polluted; 4 – 5 = strongly to extremely polluted and > 5 = extremely polluted (Lu *et al*., 2009).

Contamination Factor (CF)

The contamination factor was determined to express the level of metal contamination in surface soil and vegetables. The contaminant factor is calculated using the following formula:

$$CF = \frac{C_{metal}}{C_{background}} \quad (4)$$

C_{Metal} is the concentration of a given metal in the sediment and $C_{background}$ is a metal concentration of a control sample. The CF value for describing the contamination levels is summarized as < 1 = no contamination; 1 - 2 = suspected contamination; 2 – 3.5 = slight contamination; 3.5 – 8 = moderate contamination; 8.0 – 27 = severe contamination and > 27 = extreme contamination.

Pollution Load Index

Pollution load index (PLI) for each site was evaluated using the procedure of Tomlinson *et al.* (2008).

$$\text{PLI} = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots\ CFn\ )^{1/n}$$

where:

n = number of metals and

CF = contamination factor.

PLI is a potent tool in heavy metal pollution evaluation. According to Chakravarty and Patgiri (2009), the PLI value higher than 1 indicates the samples have been polluted while the PLI value less than 1 indicates no pollution occurred.

RESULTS AND DISCUSSION

Metal Concentrations

The minimum, maximum, mean, standard deviation and standard error of Pb, Cd, Zn, Cr, Mn and As in soil samples collected around tin mine dump in Barkin – Ladi Plateau State is presented in Table 1. The heavy metal concentration was in the range Pb (59.2 – 80.6), Cd

(0.28 – 1.17), Zn (54.3 – 94.8), Cr (11.1 – 14.5), Mn (16.3 – 19.8) and As (114 – 174) mg/kg. The elements' dominance was in the order: As > Zn > Pb > Mn > Cr > Cd. The minimum and maximum Arsenic levels recorded in this work are higher than the WHO (2001) threshold of 20 mg/kg. Similarly, the minimum and maximum levels of Pb are above the WHO (2001) limit of 50 mg/kg. The global estimated scale of 25 mg/kg Pb levels suggests anthropogenic influences (Kabata-Pedias, 2001). The concentrations of Zn, Mn and Cr (94.8, 19.8 and 14.5 mg/kg) recorded were below the threshold limit of WHO, (2001), 300, 437and 54 mg/kg, respectively. The mean concentration of Cd (0.94 mg/kg) was higher than the global mean for surface soil (0.53 mg/kg) apparently higher and may reflect anthropogenic influences. Since the contents of metals in soils are specific and depend on the lithology producing soil and the conditions of soil formation for determination of pollution level.

Table 1: Distribution of Heavy Metals in Soil Around Tin Mine Dump (mg/kg)

Soil variables	Pb	Cd	Zn	Cr	Mn	As
B_1	59.2	1.17	55.2	14.5	16.3	114
B_2	80.6	0.87	94.8	11.1	17.4	141
B_3	61.4	1.10	54.3	12.8	18.8	174
B_4	70.1	0.28	71.2	11.6	19.8	155
Mean	67.8	0.94	68.9	12.5	18.1	146
Standard Error	8.23	0.07	11.6	2.83	0.88	15.1
Minimum	47.7	0.78	48.4	6.99	16.3	114
Maximum	80.6	1.2	94.8	12.5	19.8	174
SD	17.9	0.35	18.4	4.14	1.33	22.7

Enrichment Factor and Pollution Index of Soil Around Tin Mine Dump

The results of the EF obtained for the metals studied are presented in Table 2. The control sampling point was considered to be the unpolluted or background point. The EF values for Pb, Cr and Zn observed in the present study were found not exceeding the level of moderately enriched with the EF values < 5. In general, it was found that the surface soils were negligibly enriched with these metals. However, Cd indicated significant enrichment with EF of 6.13 soils sampled at site B4 with mean Cd value of 3.79

Based on the contamination categories as proposed by Sutherland (2000) it is found that the soils around tin mine dump show moderate enrichment for Cr, Pb, and Zn. The rest of the metals exhibit the minimal deficiency of mineral enrichment in all sites and a very significant enrichment was observed in Cd in all the sites. High Cd levels in sediments are detrimental to plants and can be transmitted through the food chain to higher organisms such as humans.

Contamination Factor and Pollution Load Indexes

The Pollution Load Index (PLI) calculated from CF indicated that the soils were moderately to heavily contaminated by investigated metals. The values ranged from 0.56 to 1.88 indicating that some of the studied metals exceeded the background metal concentration. The overall contamination of soils at the sites assessed based on CF indicated more contamination by Cd and moderately contamination by Pb, Zn, Cr As but showed no contamination by Mn.

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On the basis of the mean values of CF, soils were enriched with metals in the following order: Cd >As > Pb > Cr >Zn. This clearly explained why soils near tin mine dump have been largely polluted by Cd and moderate with Pb, Zn, Cr, As which is attributed directly or indirectly from the nearby mine dump. The highly contaminated sites with PLI > 1.5 is mostly due to the mining activities where the metal occurs as a vital component of the ores present in the tin mine area (Gan and van Reenen, 1995 and Billay *et al.,* 2008)

Table 2: Enrichment Factor and Pollution Load Indexes

Site	B1	B2	B3	B4	Mean (EF)	PLI
Pb	1.54	2.09	1.59	1.82	1.76	1.32
Cd	2.60	4.00	2.44	6.13	3.79	1.88
Zn	1.52	2.62	1.50	1.96	1.90	1.36
Cr	2.00	1.53	1.77	1.61	1.73	1.31
Mn	0.29	0.31	0.33	0.35	0.32	0.56
As	1.10	1.36	1.68	1.50	1.41	1.18

Contamination Evaluation Based on Geo-Accumulation Index of Soil Around Tin Mine Dump Sites

The results of Igeo of metal contamination level in the soils are presented in Table 3. The mean Igeo values for all metals ranged from -2.69 – 1.48 suggesting that some soils were not contaminated while others were moderately contaminated. The Igeo values for As and Mn showed that all the soil samples are in uncontaminated class (≤ 0). Pb, Zn and Cr indicated in the sample locations as uncontaminated to moderately contaminated (classes 1 and 2 respectively). Igeo values for Cd indicated 95% of the samples being uncontaminated to moderately contaminated (classes 1 and 2). However, there was no definable Igeo trends with distances ranging from 100 to 500 m from the tailings dump. This may be attributed to differences in the soil matrix such organic matter, changes in pH and redox potential and anthropogenic activities.

Table 3: Geo-Accumulation Index of Soil Around Tin Mine Dump Sites

	Geo-accumulation Index				
	B1	B2	B3	B4	Mean
Pb	0.01	0.14	0.03	0.08	0.26
Cd	1.44	1.47	1.35	1.67	1.48
Zn	0.01	0.24	0.00	0.12	0.36
Cr	0.13	0.01	0.07	0.03	0.24
Mn	-0.72	-0.69	-0.66	-0.63	-2.69
As	-0.13	-0.04	0.05	0.00	-0.13

CONCLUSION

Anthropogenically and geogenically impacted soils in Barkin – Ladi Tin Mine dump sites were assessed using enrichment factor, contamination factor, geoaccumulation index and pollution load indexes. The mean concentrations of metals in in the vicinity of the mine decreased in the following order As > Zn > Pb > Mn > Cr > Cd. The EF values for Pb, Zn and Cr showed that these metals were derived mainly from natural processes or geogenic sources and were related to the exposure of the Earth's crust material with evidence of the tailings dump impacts. However, Cd indicated significant enrichment with a maximum EF values of 6.13 and a mean of 3.79. Cd also showed significant contamination in soil and made contribution to contamination of the soil expressed by contamination factor. Based on the Igeo, the soil was graded as unpolluted to moderately polluted with As and Mn and being free from contamination by Pb, Zn and Cr (Igeo > 0), while Cd was moderately polluted with Igeo value (>1). Although the nature of calculating geoaccumulation indices (Igeo) is somewhat different from pollution calculation methods discussed in this study, the Igeo obtained from the studied metals are generally comparable to results reported for EFs and CFs. The PLI values for metals at all the sites were ≥ 1.88, which indicated deterioration of soil quality except for Mn. Since induced pollution can pose serious threats to water, soil, fauna, flora and undoubtedly human health of the area nearest to the mine site, calculating the CF and PLI from the pollution source and wind direction can provide more reasonable results. This study recommended an immediate plan for analysis of the quality of drinking water and some staple crops grown in the area to determine the levels of these noxious metals and uptake by plants, to be followed by a comprehensive mitigation or remediation plan.

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