Unilag Journal of Medicine, Science and Technology (UJMST) Vol. 7, No 2, 2019

PRELIMINARY STUDIES ON THE DISTRIBUTION CHARACTERISTICS OF POTENTIALLY TOXIC METALS IN SOILS AROUND A GOLD MINING SITE IN IJERO, EKITI STATE, NIGERIA

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ABSTRACT

Metal pollution in soils arising from mining activities has become a growing concern especially in developing countries like Nigeria. Illegal mining of solid minerals pervades the entire country leaving behind their deleterious effects on the environment. This research focused on the preliminary studies on the distribution characteristics of nine potentially toxic metals in soils around a mining site in Ekiti State, Nigeria. Thirteen (13) soil samples were randomly collected in and around the vicinity of the mining site and a control sample at a farther distance from the mining site. The soil samples were air dried, sieved through a 63 mm mesh sieve and 1g of each of the samples was digested using a microwave digester for two hours. The potentially toxic metal concentration was determined using an Agilent 7700s Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The concentration of the metals analysed in the samples were within the following ranges; As (0.20 to 83.49 mg/kg), Cd (0.03 to 0.39mg/kg), Cr (0.65 to 38.16 mg/kg), Cu (3.11 to 11.46 mg/kg), Fe (2.46 to 137.63 mg/kg), Mn (45.88 to 557.20 mg/kg), Ni (0.30 to 10.84 mg/kg), Pb (2.83 to 20.28 mg/kg) and Zn (5.68 to 24.16 mg/kg). Concentrations of As and Cd were above the permissible levels in the environment. The calculated pollution index (Pi) values for As (location 2) and Cd (location 5) under the study exceeded 1 confirming that the soils are highly polluted particularly with As and Cd. Therefore, it is recommended that farmers should not grow agricultural foods such as edible vegetables, rice and potato in these soils unless the soils have been treated and remediated. In addition, mining activities had impacted negatively on the surrounding environment and the results of this analysis suggests that the metal concentrations of the sites resulted from mining activities are expected to be higher in the nearest future due to bioaccumulation and as such, the activities should be regulated and arrested.

Keywords: *Mining, Potentially Toxic Metals, Soil, Environmental Pollution Index*

1.0 INTRODUCTION

Potentially toxic metals contamination of soils has become a topical issue around the world as a result of anthropogenic activities (Soriano *et al*., 2012; Zhao *et al*., 2012). Potentially toxic metals are the most dangerous anthropogenic environmental pollutants due to their toxicity and persistence in the environment (Guo*et al*., 2012; Koz*et al*., 2012). The most harmful and dangerous of these potentially toxic metals are lead, arsenic, cadmium and mercury (used in the extraction of gold in most mining areas around the worldwide) due to their harmful effects on human health(ATSDR, 2015). Past studies have revealed that human exposure to high concentrations of potentially toxic metals would lead to their accumulation in the human body. Human exposure to potentially toxic metals occurs through three primary routes namely inhalation, ingestion and skin absorption. The threat that potentially toxic metals poses to human and animal health is aggravated by their low environmental mobility, even under high precipitations, and their long term persistence in the environment (Adelekan and Abegunde, 2011;Liu *et al.*, 2011).

Artisanal mining is a mining operation with intense labour activities that is carried out in remote and isolated sites with the use of rudimentary techniques low technical knowledge, low degree of mechanization and low or no health and safety awareness. The people involved in these practices are low income rural dwellers who complement their income with agricultural practices (Veiga, 2013). Some of the potential adverse impacts of mining include displacement of local people from ancestral lands, marginalization and oppression of people belonging to lower economic classes and discharge of mine tailings which are dispersed through erosion and wind action thereby polluting arable land, vegetation, waters bodies, destroying aquatic habitats) and causing health problems to humans (Makinde*et al.*, 2013).

Essaghah*et al*. (2013) investigated environmental and socio-economic effects of lead and zinc ores mining in Ishaiagu Community in Ivo Local Government Area of Ebonyi State, South Eastern Nigeria. The results obtained revealed serious environmental pollution and degradation, threatening farming activities in the area.

Ako *et al*. (2014) in another study evaluated environmental hazards associated with artisanal gold mining in Luku, Minna, North Central Nigeria. It was revealed that mining activity resulted in a lot of physical environmental impacts such as land degradation, destruction of vegetation, erosion of soils and degradation of water quality Odukoya et al., (2017, 2018), determined the health risk of potentially toxic elements (PTEs) in soils of gold mining area in Ilesha, Southwestern Nigeria. Results of this study showed that the ingestion route was the major contributor to excess lifetime cancer risk followed by the dermal pathway for all the metals analysed.

In 2010, more than 400 children died in Zamfara, Nigeria from acute lead poisoning caused by unsafe mining and processing lead-containing gold ore. People grinding the ore, often in and around their homes, contaminated at least 180 villages over a wide area. Health Ministry figures stated the discovery of 355 cases, with 46 percent proving fatal. In May 12, 2015, sixty-eight (68) cases of lead poisoning resulting in the death of twenty-eight (28) children were reported in Kawo and Magiro villages of Rafi local government area of Niger State, Nigeria (Greig*et al.*, 2014).

However, mining activities in the study area have been reported to be carried out by illegal, inexperienced and unconcerned miners which consequently resulted in the pollution of the environments while the miners smile to the bank. These activities constituted environmental degradation to the local environment and the people in and around the vicinity of the mining areas. This is one of the reasons for the selection of the study area. Therefore, this study is aimed at assessing the level of some potentially toxic metals in and around the vicinity of the mining site in Ijero, Ekiti State Nigeria.

2.0 MATERIALS AND METHODS

2.1 Brief description of study area

The study area, Ijero (7^{o}49’5’’N and 5^{o}05’0” E)is bordered by Moba Local Government in the North, Ido-Osi Local Government in the East, Ekiti West in the south and Ila Orangun in Osun State. With a population of about 220,000 people, it is the second largest town in Ekiti State. It is also the seat of mineral resources such as tourmaline, columbite feldspar, tantalite, rubilite, sodonite, tin, and kaolin.

2.2 Sample collection

Soil samples of the sampling areas were collected in May 2015. The soil samples were collected with an improvised soil auger to a depth of 30 cm from areas approximately 1 m^2 chosen to be representative of the land cross-section at the site. Twelve (12) samples were randomly collected from different spots around the mining area and a control sample was collected about 250 m away from the mining site. The sampling locations and distances away from the site of mining activities are as shown in fig 1. The soil samples were placed in dust-free polythene bags,zipped and properly labeled. All the samples were transported to Chemistry laboratory, University of Lagos for the determination of nine (9) potentially toxic metals which are arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu),iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn).

Table 1: Sample ID, GPS locations and distances of sampling points from the mining site

Location and sample ID	Latitude	Longitude	Approximate distance (in meters) from mining site
1	N07°49’05”	E05°5’10”	10
2	N07°49’11”	E05°5’19”	200
3	N07°49’25”	E05°6’26”	25
4	N07°50’20”	E05°6’43”	30
5	N07°52’15”	E05°7’28”	40
6	N07°51’43”	E05°6’36”	36
7	N07°52’55”	E05°7’50”	50
8	N07°53’58”	E05°8’22”	60
9	N07°53’30”	E05°9’39”	80
10	N07°54’13”	E05°9’50”	100
11	N07°54’42”	E05°10’17”	110
12	N07°55’48”	E05°10’46”	140
13	N07°56’24”	E05°11’33”	150
Control	N07°58’38”	E05°13’03”	>250

2.3 Sample Preparation

The collected soil samples were air dried at ambient temperature (25°C) in the laboratory and passed through a stainless-steel sieve to remove large and gravel-size materials. The dried samples were then homogenized and sieved through a 63 mm mesh sieve. Accurately one (1g) of each of the samples was weighed and transferred into microwave digestion tube, 8 mL of concentrated nitric acid was added and the mixture put in the microwave digester and digested for two hours. The digest was filtered into a 50-mLstandard flask and made up to the mark with distilled water and potentially toxic metal contents were determined using an Agilent 7700s Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

3.0 RESULTS AND DISCUSSION

The total concentrations and mean concentrations of potentially toxic metals (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the soil samples analysed are shown in Table 2. Arsenic ranged from 0.20 to 83.49 mg/kg with mean value of 8.21±22.66 mg/kg, Cd ranged from 0.03 to 0.39 mg/kg with a mean value of 0.10±0.11 mg/kg, Cr contents ranged from 0.65 to 38.16 mg/kg with a mean value of 16.01±13.21 mg/kg, Cu contents varied from 3.11 to 11.46 mg/kg with a mean value of 6.74±2.71 mg/kg, the concentrations of Fe ranged from 2.46 to 137.63 mg/kg with a mean value of 50.34±44.28 mg/kg, Mn concentrations ranged from 45.88 to 557.20 mg/kg with a mean value of 210.02±197.67 mg/kg, Ni contents ranged from 0.302 to 10.84 mg/kg with a mean value of 4.93±3.49 mg/kg, Pb contents varied from 2.83 to 20.28 mg/kg with mean value of 9.68±5.11 mg/kg, while Zn concentrations ranged from 5.68 to 24.16 mg/kg with mean value of 14.89±6.58 mg/kg.

Table 2: Concentration of potentially toxic metals (mg/kg) in the analysed soil samples

Code	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	2.36	0.05	15.42	9.80	80.79	363.36	8.62	8.71	16.10
2	83.49	0.25	0.78	4.43	2.46	88.89	0.33	9.56	12.78
3	2.30	0.03	13.38	8.25	73.43	584.03	6.26	6.03	15.82
4	0.20	0.03	29.12	7.58	22.67	46.81	4.00	2.83	13.27
5	0.80	0.39	1.20	3.57	6.11	354.33	0.49	20.28	8.89
6	1.38	0.04	7.35	4.61	25.43	45.88	2.92	10.83	7.24
7	1.89	0.11	4.85	4.09	21.36	256.10	3.15	5.21	17.34
8	3.33	0.04	29.20	11.46	111.03	557.20	10.84	14.92	24.16
9	4.27	0.03	27.10	6.89	137.63	43.15	8.16	9.71	20.13
10	3.92	0.03	30.48	8.20	93.01	126.78	8.22	8.82	18.55
11	0.23	0.03	38.16	9.99	34.57	65.39	6.80	3.73	21.57
12	1.98	0.04	10.44	5.69	41.91	17.07	4.02	17.01	12.06
13	0.61	0.20	0.65	3.11	3.96	181.24	0.30	8.26	5.68
Mean	7.63	0.09	14.87	6.64	50.19	198.62	4.59	8.99	14.07
SD	3.88	0.01	13.39	2.64	42.55	194.64	3.58	5.56	6.19
Control	ND	ND	ND	5.28	48.33	80.47	0.21	ND	3.37
WHO	10.00	0.30	100.00	36.00	300.00	50.00	35.00	85.00	50.00

ND = Not Detected; SD = Standard Deviation

Table 2 shows the results of the potentially toxic metals determined. Zn was detected in all the samples because it is a more abundant anthropogenic pollutant. The high concentration of Mn in the analysed samples could be attributed to the background manganese in soil around the study area as this was also observed in the control soil sample collected in an unpolluted area.

The concentration of cadmium obtained in location 5 (0.39 mg/kg) was higher than the allowable limit of environmental safety as described by World Health Organization (1996) Standard for soil environmental quality of potentially toxic metals (0.3 mg/kg) while the results obtained in locations 2 and 13 (0.25mg/kg and 0.20mg/kg respectively) were very closed to the allowable limit for cadmium i.e 0.3 mg/kg. The concentration of arsenic obtained in all the analysed samples were lower than the minimum permissible limit except the result obtained in location 2 (83.49 mg/kg) where the result obtained was higher than the allowable limit for arsenic. The concentration of chromium obtained in the analysed soil samples ranged from 0.65 to 38.16 mg/kg and the concentration obtained were below the permissible limit for chromium (100 mg/kg) while the concentrations of zinc ranged from 5.6 to 24.16 mg/kg with the highest value (24.16 mg/kg) obtained in soil sample found in location 8 while the lowest value was found in location 13. The values of zinc obtained were found to be below the World Health Organization permissible limit 50 mg/kg. The highest concentration of manganese (584.03 mg/kg) was found in location 3 while the lowest concentration of manganese (17.07 mg/kg) was obtained in location 12. The permissible limit for manganese was not stipulated. The concentrations of nickel and copper were found to be below the permissible limit stipulated by WHO (1996) for uncontaminated soil. The hill slope location of the mine site has led to significantly different spatial distribution of heavy metals in the surface soil. Topographic conditions influenced redistribution and accumulation of water and products of mineral weathering, leading to different accumulation of organic matter and thence different concentrations of potentially toxic metals in the same type of soil at the same location (Wang *et al*., 2012).

The high concentrations of some of the potentially toxic metals determined suggest that these soils are not suitable for agricultural uses. The suitability of soils for agricultural uses could be further assessed by using pollution index which describes the environmental risk caused by the contaminated soils (Sheng et al., 2012, Odukoya *et al.*,2018). Many indexes have been used for the assessmentof soil heavy metal pollution, such as total concentration of heavymetals, the proportion of bioavailable fractionsand heavy metal cytotoxicity (Miao et al., 2012). Total content ofheavy metals has been used to assess the risk of soil pollution by comparingit with background or guideline values of heavy metals, andcomputing a pollution index (Liu et al., 2011; Sheng et al., 2012).Pollution index (Pi) value greater than 1 indicates that the soil sample is classed to be polluted while pollution index (Pi) less than or equal to 1 suggests that the soil is unpolluted. The estimated values of environmental quality index (Pi) assessed using single index methods are presented in Table 3. The calculated Pi values for As (location 2) and Cd (location 5) under study exceeded 1 confirming that the soils are highly polluted particularly with As and Cd. Therefore, it is recommended that farmers should not grow agricultural foods such as edible vegetables, rice and potato in these soils unless the soils have been treated and remediated.

Table 3: Environmental quality index *(Pi)* of heavy metals using single index method

Sample	T-As	T-Cd	T-Cr	T-Cu	T-Ni	T-Pb	T-Zn
1	0.24	0.17	0.15	0.27	0.25	0.1	0.32
2	8.35	0.83	0.01	0.12	0.01	0.11	0.26
3	0.23	0.1	0.13	0.23	0.18	0.07	0.32
4	0.02	0.1	0.29	0.21	0.11	0.03	0.27
5	0.08	1.3	0.01	0.1	0.01	0.24	0.18
6	0.14	0.13	0.07	0.13	0.08	0.13	0.15
7	0.19	0.37	0.05	0.11	0.09	0.06	0.35
8	0.33	0.13	0.29	0.32	0.31	0.18	0.48
9	0.43	0.1	0.27	0.19	0.23	0.11	0.4
10	0.39	0.1	0.31	0.23	0.24	0.1	0.37
11	0.02	0.1	0.38	0.28	0.19	0.04	0.43
12	0.19	0.13	0.1	0.16	0.12	0.2	0.24
13	0.06	0.67	0.01	0.09	0.01	0.1	0.11

Correlation of total concentrations of analysed metals

Data from this experiment were statistically analysed using SPSS program and correlation coefficients illustrating relationship among total concentration of heavy metals are shown in Table 4. The correlation matrix of the metals presented showed positive correlation and strong significant correlation. Zinc showed positive correlation with all the metals except lead, arsenic and cadmium, lead showed strong correlation with all the metals except chromium and Ni.

Table 4: Correlation Matrix of metals

	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
As									
Cd	.383								
Cr	-.331	-.679(*)							
Cu	-.236	-.650(*)	.822(**)						
Fe	-.275	-.593(*)	.609(*)	.674(*)					
Mn	-.172	.101	-.088	.353	.268				
Ni	-.358	-.723(**)	.785(**)	.907(**)	.895(**)	.321			
Pb	.004	.474	-.356	-.219	.035	.175	-.121		
Zn	-.082	-.524	.762(**)	.799(**)	.711(**)	.260	.838(**)	-.229	

* Correlation is significant at the 0.05 level (2-tailed).
**Correlation is significant at the 0.01 level (2-tailed).

The results showed that the concentrations of some of the analysed metals are within the maximum allowable limits for agricultural soils. However, bioaccumulation of these identified metals could be a major source of concern over time. According to the International Agency for Research on Cancer (IARC), inorganic As and Cd are classified as human carcinogens (IARC, 2016). Arsenic is related to cancer risk and skin damage, Cd is linked to kidney damage and cancer. Other effects such as heart diseases and blood cholesterol from Sb, Anemia from Pb, kidney and liver damage from Hg, and gastrointestinal disorder from Cu are also reported (ATSDR, 2015). Sub-chronic effects, such as the risk of still births, were increased by six fold in women who were exposed to As ≥ 200 μg/L during pregnancy (Fernandez-Luqueno*et al*., 2013). Pb was most investigated in the context of its public health effects as it affects the central nervous, renal, hematopoietic, cardiovascular, gastrointestinal, musculoskeletal, endocrinological, reproductive, neurological, developmental and immunological systems (ATSDR, 2015). Experiments on the exposure of animals to metals show that 50% of Cd absorbed in the lungs (Jaishankar*et al*., 2014).

CONCLUSION

The soil samples collected from within and around the mining sites showed that the soil samples were heavily contaminated by metals. Spatial distributions of heavy metals were found to be influenced by topographic condition. According to statistical analysis, it is obvious that Pb,Zn, Cu, Fe, Ni and Mn were positively correlated. The heavy metal environmental quality index (Pi) together with the World Health Organization Standards for Soil Environmental Quality of Heavy Metals suggests gross contamination of the area. The results presented in this work imply impending serious environmental or health challenges since some of the metals determined are above the maximum allowable limits for agricultural soils. Thus, this paper concludes that potentially toxic metal concentrations of the studied site pose impending contamination threat to the environment and that, the soil could be not be applied for agricultural purposes as a result of transportation of these metals.

ACKNOWLEDGEMENTS

The authors are grateful to the University of Lagos Central Research Committee (CRC) and Tertiary Education Trust fund (TETFUND) Institution Based Research (IBR) CRC/TETFUND/NO. 2018/014 for financial assistance to carry out this research.

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