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Trace Metals Load in Environment: Ecological Impact Assessment of Aluminum Smelting Activities in South West, Nigeria using Geochemical Methods

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ABSTRACT

The trace metals load burden in the environment is increasing continuously, particularly in the soil due to various anthropogenic activities. The quality impacts evaluation of Aluminum smelting processes, a main source of trace metals in the root zone of soil is investigated using geochemical methods. Thirty (30) top and sub composite soil samples, and ten (10) bark samples of *Magnifera indica* (Mango tree) and *Azadirachta indica* (Dogonyaro) plants were collected each from Agege, Lagos State, and Iseyin, Oyo State, South west, Nigeria and analyzed for trace metals employing standard method of United State Environmental Protection Agency (USEPA).Data obtained were analyzed using various multivariate geostatistical techniques including; Enrichment Factor (EF), Pollution Load Index (PLI), Pollution Classification (PC), Geoaccumulation Index (I_{geo}) and Potential Ecological Risk Index (RI) so as to reveal the environmental impact of the trace metals analyzed in the soil environment. Lead (Pb) has the highest mean concentration of 216 mg/kg and iron (186 mg/kg) in Agege and Iseyin respectively. Aluminum showed positive chemical association with iron in Agege and with zinc in Iseyin soil. The PLI reveals deteriorations of the soil thus implicating the smelting activities in the study areas. Hence, there is need for measures to avoid continuous build-up of trace metals in the environment, as well as regular monitoring to ensure the safety of lives and sustainable environment.

Keywords: Aluminum smelting, multivariate geostatistical techniques, soil, trace metals

INTRODUCTION

Increase in trace metals concentration in the biosphere remains an environmental concern due to its non-degradable nature and its involvement in the food chain, thereby constitute a health threat to man (Hashem *et al*., 2017). The metals are classified into two classes; nutritive and toxic metals. Their toxicity depends on several factors such as the dose, route of exposure, and chemical species (Mansourri and Madani, 2016), as well as the age, gender, genetics, and nutritional status of exposed individuals. Based on their high degree of toxicity, elements such as arsenic, cadmium, chromium, lead, and mercury rank among the priority metals that are of public health significance (He *et al*., 2005).

Various anthropogenic activities including industrialization, mining, agriculture, solid wastes municipal disposal and smelting processes continue to build up trace heavy metals in the environment. The smelting industries are of immense economic importance globally with consequential environmental damages and pollution. Rybicka (2016) highlighted the damaging effects of mining and smelting activities on an environment to include: (i) Changes to hydro geological system (ii) Hydrological transformation of soil and surface water flow (iii) Contamination of soil surface and ground water resources and (iv) pollution of atmosphere.

Top soil (0 – 15 cm) is a root zone, where most of the vegetables and common plants derive their nutrients from and is severely exposed to deleterious impacts of various sources of heavy metals. Accumulation of heavy metals in crop plants is of great health concern and it often occurs through the soil root interface (Chibuike, and Obiora, 2014).Toxic elements from smelters have been implicated in birth defects, kidney and liver diseases, blue baby syndrome and gastrointestinal tract problems, as well as damage to the respiratory systems, nervous systems, and reproductive systems (Moretto *et al*., 2017). Aluminum toxicity is an important growth-limiting factor (Ding *et al* 2021), for plants in acidic soils, particularly in pH of 5.0 or below. Smelting activities operate at both industrial and local production levels. Pockets of Aluminum smelting activities are scattered in southwestern Nigeria particularly Oyo and Lagos States, with direct ecological impacts on air, soil, plants, surface and groundwater. These undoubtedly progressively raise the levels of trace heavy metals in the environment. The aim of this study was to investigate the level of heavy metals in environmental media; soil and tree barks in Aluminum smelting areas of Iseyin town, Oyo

State and Agege, Lagos State and to compare the data generated with the allowable range, and define the ecological status of the study areas.

MATERIALS AND METHODS

Study areas

This study was carried out in Agege, Lagos State and Iseyin, Oyo State, Southwest Nigeria. Agege is a residential area, and the headquarters of Agege Local Government Council, a suburb in Ikeja division of Lagos State, Nigeria. It lies on Longitude 3^{o}32'and Latitude 60^o.\61'6".Agege Local Government Council has a total population of 459,939 (UN-HABITAT, 2006). Iseyin town is located 100 km north of Ibadan. Iseyin occupies area of 1,419kmwith population of 236,000 per a United Nations 2005 estimate. Iseyin isin Longitude 3^{o}35'59" and Latitude 7^{o}51'59", 26^{o}C, Wind SW at 6Km/h, 79% humidity.

Samples and Sampling Technique

A total number of Thirty(30) top and sub composite soil samples in line with United State Environmental Protection Agency (USEPA, 2020)and a total of ten (10) tree bark samples comprising of *Magnifera indica* (Mango tree) and *Azadirachta indica* (Dogonyaro plant) were collected. Composite tree bark samples were collected at a height of 3m above the ground level (Majolagbe *et al*., 2013). The tree barks samples were placed in clean acid washed polyethylene bags. All soils and plant barks samples were air dried at room temperature and kept until analysis.

Sample Chemical Analyses

i. Soil samples pre analyses preparation

Soils samples were collected at depth of 1- 15 cm (top soil) and 15- 30 cm (sub soil) with the aid of stainless soil auger. The soil samples were air dried and pulverized using pre cleaned laboratory mill (ceramic mortar and pestle), sieved through 2 mm aperture. The mill was cleaned in between each sieving to prevent cross contamination.

ii. Metal content of the soil samples.

2 g of pulverized soil sample was taken in a 250cm^2 beaker and moistened with few drops of deionized water to prevent loss by spattering during digestion. The sample was digested with 10ml of concentrated HNO_3 on a low heat hotplate in a fume cupboard to volume of about 3 ml. The residues obtained were further digested with a mixture of concentrated acids containing 5 ml each of concentrated HCl, HNO_3 and $HClO_4$ for 10 minutes until the solution was brought to a final volume of about 5ml on a hot plate in fume cupboard. The digest was filtered using Whatmann No.1 filter paper, made up to mark in 100 ml standard volumetric flask with deionized water. The control samples were also treated with the same procedure for test sample.

iii. Metal content of the Tree bark samples

2 g each of the powdered tree bark samples were weighed into 250 ml beaker, a mixture of 20 ml HNO_3 and 8 ml $HC1O_4$ was used to digest the samples on a low heat using hot plate to a final volume of 5 ml. The digest was cooled, drops of deionized water were added and the solution filtered using Whatman No.1 filter paper, and made up to the 100 ml mark in standard volumetric flask with deionized water. All digests were analyzed for heavy metals using Flame Atomic Absorption Spectrophotometer (Buck 210 VGP). All analyses were duplicated to test for reliability of the method and instrument. The control samples were also treated with the same procedure for test samples.

Data Analyses

Statistical analyses: mean, standard deviation and other descriptive statistical analyses were performed employing Pearson correlation. Various multivariate geostatistical indices were also used to assess potential ecological risks. These indices include Enrichment factor (EF), Contamination factor (CF), Geo accumulation index (I_{geo}) and Pollution load index (PLI). Cluster analysis was also performed using the statistical package for Social Sciences Software (SPSS) statistic 20.0.

i. Enrichment Factor (*EF*): The Enrichment Factor is a concept based on standardization of element of interest against a reference element or normalizer. It helps in identifying metal concentrations of environmental concern. Common normalizer reported in past studies include: Fe, Al, Mn, Rb, soil organic carbon and soil particle size (Feng *et al*., 2010). The EF of heavy metals in the soil can be calculated using equation 1;

$$EF = \frac{Cmetal\ /Cnor\ maliser\ ]sample}{Cmetal\ /Cnormaliser\ ]control} \quad (1)$$

Where, C_{metal}, $C_{normalizer}$ are concentrations of heavy metals and normalizer in soil and control. Sutherland and Tolosa (2000) listed five categories of contamination: EF < 2,2-5,5-20,20-40 and > 40 as deficient, moderate, significant, very high and extremely high mineral enrichment respectively.

ii. Contamination Factor (CF): This expresses the contamination of soil and is calculated using equation 2;

$$CF = \frac{Cmetal\ Sample\pi}{Cmetal\ Control} \quad (2)$$

Where, $C_{metal\ sample}$, $C_{metal\ control}$ is the concentration of the heavy metal in the study sample and control sample. Contamination categories known are as follows: CF <1, 1< = CF < 3, 3 < = CF < 6 and CF > 6 means low, moderate, considerable, and very high contamination respectively.

iii. Pollution Classification (P_c): This helps to establish the distinction between soil contamination and pollution range. P_c> 1.0 and < depicts the pollution. Pollution index helps compute P_c of an area using the Dutch formula (Longe *et al.*, 2017) as in equation 3;

$$P_c = \frac{Cin - Cib}{Pi} \quad (3)$$

Where, $C_{in,}C_{ib}$ means concentrations of the soil, control sample or background value pollutant in mg/kg respectively and P_i is pollution index.

iv. Geo accumulation Index (I_{geo}): The I_{geo} of heavy metals in the soil can be calculated through equation 4;

$$I_{geo} = \quad Log2\, \frac{Cmetal\ \ Sample}{1.5\ x\ Cmetal\ \ Control} \quad (4)$$

Where, $C_{metal\ sample}$, $C_{metal\ control}$ are the concentrations of the heavy metals in the soil and control samples respectively. The factor 1.5 is introduced to minimize the effect of variations in the background value, attributed to lithogenic variations in the soil (Akoto *et al*., 2008).

The degree of metal pollution is assessed by seven contaminant categories based as follow: I_{geo}= 0,0 < = I_{geo}<1, 1< = I_{geo}<2,2 < = I_{geo}<3,3< = I_{geo}<4,4< = I_{geo}<5 and I_{geo}>=5 which means unpolluted, unpolluted to moderate, moderate, moderate to strong, strong to very strong and very strong polluted respectively.

v. Pollution Load Index (PLI): The PLI helps to evaluate the extent to which a site is polluted by metals load .It is calculated using equation 5;

$$PLI = (CF_1\ x\ CF_2\ xCF_3\ x\ldots CF_n)^{1/n} \quad (5)$$

Where, n is the number of metals studied and CF is the contamination factor. The degree of site deterioration is categorized as: PLI <1 means perfect site; PLI =1 means base line pollution; PLI >1 means deterioration.

vi. Potential Ecological Risk Index (RI): It has been successfully used for quality assessment of heavy metals in soil and sediment (Weiping *et al.*, 2015). Ecological Risk Index could evaluate risks caused by toxic metals comprehensively, and RI is the potential ecological risk caused by the overall contamination.

$$F_i = C^i_n / C^i_o E_{ir} = T^i_r\ x\ F_i RI = \Sigma^{n}_{1=}\ {}^{i}_{r}$$

where F_i is the single metal pollution index; C^i_n is the concentration of metal in the samples; C^i_o is the reference value for the metal; E^i_r is the monomial potential ecological risk factor; T^i_r is the metal toxic response factor according to Awokunmi *et al.* (2020). The values for each element are in the order; Zn = 1 <Cr = 2 < Cu = Ni = Pb = 5 < As = 10 < Cd = 30 < Hg = 40. There are four categories of RI and five categories of E^i_r as shown in Table 1.

RESULTS AND DISCUSSION

The descriptive analyses results of the trace metals of the soils samples from Agege and Iseyin study areas are presented in Table 1. The concentration of metals ranges from 193-259 (97.1-247),109 – 279 (101-235), 39.9 – 860 (39.4 - 78.2), and 19.2-46.2 (13.4- 31.7) mg/kg for Al, Fe, Pb and Zn respectively for top and (sub) soils at Agege, while the concentration ranges from 108-342 (33.2–216),361-1130 (31.4 – 175), 399-782(16.2 -84.9) and 1.43-48.3(4.7-29.6) mg/kg for Al, Fe, Pb and Zn respectively for Iseyin top and (sub) soils. The levels of metals in Agege were observed to be higher than that of Iseyin probably due to other possible sources of metals in Agege environ including industrial activities, urban runoff, municipal solid wastes disposal and vehicular emission (Majolagbe *et al*., 2010). The concentration of metals present in the top soils were also found higher than the subsoil in the two study areas except Pb in Agege which could be a reflection of the geological composition of the soil. The order of metals in top(sub) soil was Al > Fe > Pb > Zn (Pb > Fe > Al > Zn) for the Agege site, while the order of Fe > Al > Pb > Zn was for both top and sub soils in Iseyin study site. Aluminum is a major constrain to plant growth particularly in a low pH area. The aluminum toxicity affects inhibition of cell elongation and results in stunt root system (Liu *et al*., 2020).

Table 1: Concentration of Trace Metals in Top and Sub Soils (mg/kg) in Agege and Iseyin

Metals	Depth	Maximum n= 30		Minimum n= 30		Mean± SD		Control	USEPA	EPA	Common Range in soil mg/kg
		Agege	Iseyin	Agege	Iseyin	Agege	Iseyin				
Al	I	259	242	193	108	210±29	195±42				10,000-300,000
	II	247	216	97.9	33.2	173±46	101±50				
Fe	I	279	1130	109	36.1	206±50	257±310	81.6			7,000-550,000
	II	231	175	101	31.4	183±42	116±39	83.2			
Pb	I	860	78.2	39.9	39.4	159±250	60.9±16	125	400	200	2-200
	II	1290	84.9	16.7	16.2	273±370	50.8±23	125			
Zn	I	46.2	48.3	19.2	14.3	32±9.1	31.2±9.8	22.8	300 – 600	1100	10-300
	II	31.7	29.6	13.4	4.7	24±5.1	16.8±9.2	26.8			

I = top soil =1- 15 cm, II = sub soil = 15- 30 cm

The aluminum toxicity affects inhibition of cell elongation and results in stunt root system (Liu *et al*., 2020). Aluminum tends to bond with phosphorus (P) in a less available and insoluble form in soils and plant roots, thereby creating a P deficiency for plant growth to overall stunting, small, dark green leaves and late maturity, purpling of stems, leaves, and leaf veins, yellowing and death of leaf tips. There is no established beneficial; effect of Al, perhaps the initial stimulating effect on early stage plant a in a very low concentration of the element. The toxic effect of the Al depends on the total concentration, pH, chemical environment (Kisnieriené and Lapeikaité, 2015) its speciation of the metal. Its toxicity diminishes in the following order: Al, $Al(OH)^{2+}$, $Al(OH)_2{}^+$, $Al(OH)_4{}^-$with trivalent aluminum (Al^{3+}) being the most abundant form and has the greatest impact on plant growth (Bojórquez-Quintal, 2017).
Zinc is an essential element at low concentration and serves as a source of plant nutrients (Sharma *et al*., 2013; Roohani *et al.*, 2013). Zinc is also a cofactor for several enzymes such as anhydrases, dehydrogenases, oxidases and peroxidases and plays an important role as metalloenzyme (Castillo-González *et al*., 2018), regulation of nitrogen metabolism, cell multiplication, photosynthesis and auxin synthesis inplants (Zhao, 2014). It also plays an important role in the synthesis of nucleic acid and proteins and helps in the utilization of phosphorous and nitrogen during seed formation. Hyper accumulation of zinc has been observed in many plant (Out and Das 2003). Zinc toxicity depends on pH, and consequently the concentration of zinc in solution. The toxic effects include stunting of shoot, chlorosis and death of leaf tips (Out and Das, 2003). The level of some of the metals observed in this study is higher compared with Ogulana *et al*. (2020) (Al, 9 - 27; Pb, 11-68 mg/kg). Iron (Fe) is an important element required for plant growth and development through primary processes: photosynthesis, respiration and Nitrogen metabolism (Krohling *et al*., 2016). Fe helps in electron transport chain in photosynthesis. Iron can also act as catalyst through Fenton reaction to generate hydroxyl radicals that influence lipids, protein and DNA (Phaniendra *et al*., 2015).Iron (Fe) is an important element required for plant growth and development through primary processes: photosynthesis, respiration and Nitrogen metabolism (Krohling *et al*., 2016). Fe helps in electron transport chain in photosynthesis. Iron can also act as catalyst through Fenton reaction to generate hydroxyl radicals that influence lipids, protein and DNA (Phaniendra *et al*., 2015).Hence, plants respond to iron stress either as a result of deficiency or overload. Other beneficial elements include Co, Mo, Cu and Zn. They are useful to plants at low level, but become toxic when the concentrations of metals become higher. The mean concentration of Al, Fe, and Zn investigated are within the common range in soil (Table 1).

These results were also found to be within the range given on soils around smelting activities generate hydroxyl radicals that influence lipids, protein and DNA (Phaniendra *et al*. 2015). Hence, plants respond to iron stress either as a result of deficiency or overload. Other beneficial elements include Co, Mo, Cu and Zn. They are useful to plants at low level, but become toxic when the concentrations of metals become higher. The mean concentration of Al, Fe, and Zn investigated are within the common range in soil (Table 1), but lower than results in Ikot, Nigeria (Ipayeda *et al*., 2012). The level of Pb in some sampling locations in both study areas were above the allowable limits of 200 mg/kg of Pb in soil by Environmental Protection Agency (EPA). This portends health risk to plants and animals in the areas. Pb forms various complexes with soil components; though some of these complexes are not phytoavailable. The absorption of lead by plants is often through apoplastic pathway and Ca^{2+}permeable channel. Excess Pb accumulation impair morphological and biochemical functions which can induce some deleterious effect.

Geostatistical Analyses

The inter elemental association was established among the metals investigated using Pearson Correlation Coefficient. Table 2 shows the results of correlation of metals in Agege and Iseyin.

Table 2: Correlation coefficient of metals in soils in Agege and Iseyin

	Agege				Iseyin			
	Al	Fe	Pb	Zn	Al	Fe	Pb	Zn
Al	0				0			
Fe	0.40	0			-0.38	0		
Pb	-0.02	-0.66	0		-0.23	-0.03	0	
Zn	0.14	0.09	-0.10	0	0.56	-0.24	-0.42	0

Elemental pair Al/Fe had a fairly strong correlation and Pb/Fe also had strong association, though negative in Agege while Zn/Al had a fairly strong positive association (0.56) in Iseyin. This suggests that Zn, Fe, and Al are the core metals in this study and are introduced through same source, smelting activities. The Enrichment factors in metals and Geo accumulation Index are indicators suggesting anthropogenic contaminant deposition on surface soil (Barbieri, 2016).

Table 3: Geostatistical of Trace Metals in Top and Sub Soils Iseyin and Agege

Metals	Sample Mean(mg/kg)	Control Mean(mg/Kg)	Ef	CF	I_{geo}	Pollution classification	Pollution Load Index (PLI)
Al	(148)192	(76.3)76.3	(1.00)1.00	(1.94)2.51	(0.41)0.51	(36.9)115.7	(1.17)1.67
Fe	(187)195	(82.3)82.3	(1.27)0.94	(2.24)2.34	(0.46)0.47	(46.7)111.6	
Pb	(55.9)171	(125)125	(0.18)0.54	(0.45)1.37	(0.09)0.28	(-154)33.6	
Zn	(24)28	(24.8)24.8	(0.49)0.44	(0.97)1.13	(0.19)0.19	(-0.82)0.82	

The geochemical factors, Table 3 reveals the index value of unpolluted to moderately polluted for study areas (0< $=I_{geo}<1.0$). This indicates a low negative impact. This is further corroborated by the contamination factor (CF) values: The pollution classification (P_c) of both sites is pollution in respect of Fe, Pb and Al but contamination in respect of Zn. The pollution load index (PLI) is severely polluted with Agege (1.67) and Iseyin (1.17). The grades of ecological potential risk and nominal potential risk of heavy metals investigated are shown in Tables 4 and 5.

Table 4: Grades of single and overall Ecological Potential Risks

Eir value	Grades of ecological risk of metals	RI value	Grades of the environment
Eir< 40	Low ecological potential risk	RI < 110	Low ecological potential risk
40 ≤ Eir< 80	Moderate ecological potential risk	110 ≤ RI < 200	Moderate ecological potential risk
80 ≤ Eir< 160	Considerable ecological potential risk	200 ≤ RI < 400	strong ecological potential risk
160 ≤ Eir< 320	High ecological potential risk	400≤RI	Very strong ecological potential risk
320 ≤ Eir	Significant very ecological potential risk		

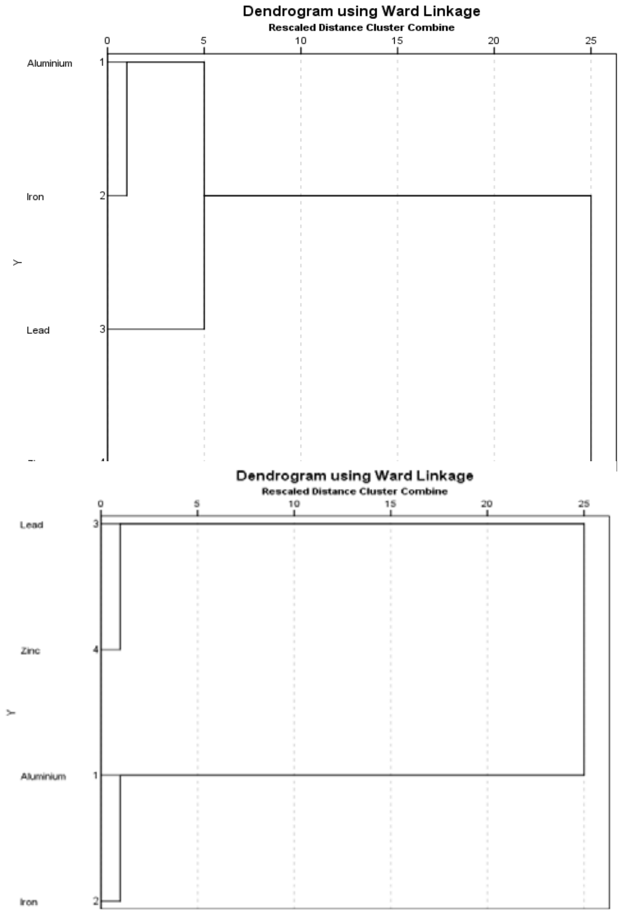
Table 5: Heavy Metal Ecological Potential Risk Indices in Soil of Agege and Iseyin

Study Area	**Monomial Ecological Risk For Single Metal E**				**RI**
	Zn	Fe	Al	Pb	
Agege	1.13			6.85	7.98
Iseyin	0.97			2.25	3.2

Table 5 shows a nominal potential risk of heavy for Zn and Pb as low risk (<40) and RI of the site under investigation as low potential risk (<110).

Cluster Analysis

The hierarchical clustering of the metals in this study reveals three (3) and two (2) clusters at 2.7 index of similarity for Agege and Iseyin respectively as shown in Figure 1(A and B).



A B

Figure 1: The dendogram of metals in soil in Agege(A) Iseyin (B)

The Agege study Cluster I comprises Al and Fe; Cluster II a lone metal of Pb and cluster III is also a lone metal cluster of Zinc. These elements are in the range of 206 – 210 mg/kg for top soil. The concentrations observed were lower than the control (Table 1). Pb is the only element with higher value in sub soil region than the top soil. The Iseyin study, Cluster I comprises Pb and Zn. Both metals have the lowest concentration. Cluster II comprises Al and Fe the metals with highest mean concentration ranging 31– 61(101-116) mg/kg for top (sub) soil region.

Plant Analysis

The results of zinc and aluminum in the plants investigated in both study areas are shown on Table 6. *Magnifera indica* (Mango tree) and *Azadirachta indica* (Dogonyaro plant) were used in the research and were from ten (10) different locations from each site.

Table 6: Concentration of Aluminum and Zinc in tree barks (mg/kg) Agege and Iseyin

	Al		Zn	
	Agege	**Iseyin**	**Agege**	**Iseyin**
Mean± SD	42.1 ±5.8	6.71±1.6	20.1±1.2	3.90±0.7
CV%	13.7	23.8	44.4	17.9

Kumar *et al*. (2013) has demonstrated *Azadirachta indica* as a good air pollutants indicator. Wide spread and easily adaptable favor its choice as indicator (Majolagbe *et al*., 2014; Zaghloul *et al*., 2020).The concentration of metals observed in samples from Agege were higher than that of metals in samples from Iseyin (Table 1), probably due to activities associated with trace metals pollution: vehicular emission and industrial activities. Agege is more densely populated compared with that of Iseyin; hence more metal load in the air. The use of tree plants as herbs are well-established practice, particularly, Africa. This portends health risk to man (Majolagbe *et al*., 2014).

CONCLUSION

This study investigated the quality impact of smelting activities on plants and soils in the environment; Agege (Lagos State) and Iseyin (Oyo State), South west, Nigeria, using geochemical multivariate indices: Enrichment factor (EF), Contamination factor (CF,) Pollution Load Index (PLI), and Geo accumulation factor (I_{geo}). Potential ecological risk (RI) was also employed which reveal deleterious impact of the smelting activity as well as building up of trace metals in the study areas. The order of metals in top and sub soil in Agege were Al > Fe > Pb > Zn and Pb > Fe > Al > Zn respectively. Fe > Al > Pb > Zn was the order for both top ad sub in Iseyin. The PLI put both sites investigated as polluted with PLI index value of 1.67 for Agege and 1.17 for Iseyin. However, the Potential ecological risk revealed low potential status for both sites. A continuous environmental monitoring is necessary by relevant agencies to ensure sustainable environment.

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