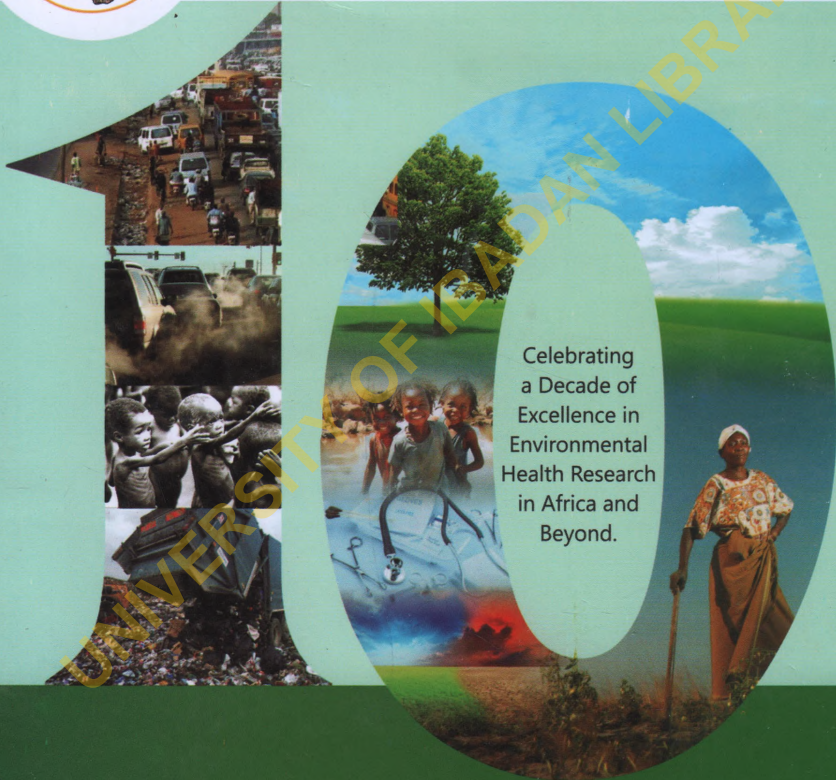


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# Health Risk Assessment of Heavy Metals in Soils within the Vicinity of a Metal Recycling Factory in Southwestern Nigeria

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## Abstract

Industrial emissions from scrap metal recycling plants have been implicated as a major source of heavy metal (HM) contamination to soil and threatens the wellbeing of humans, and our terrestrial environment. This study evaluated the seasonal variations of surface soil concentration of Al, Cd, Cu, Mn, Pb and Zn within the vicinity of a metal recycling factory in Ile-Ife, Nigeria. Sixty-six surface soil samples were systematically collected at 0-15 cm depth across three consecutive months during dry and rainy seasons from the factory premises vicinity. Samples determination of heavy metals contamination were conducted using Atomic Absorption Spectroscopy. Public health risks were evaluated using Geo-accumulation Indices (Igeo), Average daily intake, health quotient (HQ) and health index (HI) standards not exceeding average shale limits and between acceptable range  $1 \times 10^{-4}$  and  $1 \times 10^{-6}$ . Total concentration (mg/kg) of heavy metals in soil samples ranged from 0.50 Al to 2,219.10  $\mu\text{g/g}$  Cu during wet season, while the range was from 0.59 Al to 3,019.10  $\mu\text{g/g}$  Cu in dry season. Results of non-carcinogenic risks of HMs for HQ (0.038) and HI (0.06) values were generally lower than one ( $<1$ ) indicating no health risk. However, the HI values for children were higher than those of the adults. An exception to this is the high HI value for Cu at 1.23 and 1.11 for children and adult, respectively. The study concluded that the study area soil was heavily polluted with Cu and Cd, and the HI values for children indicated that children could suffer higher potential health risk than adults.

## Une Évaluation des risques sanitaires liés aux métaux lourds dans les sols à proximité d'une usine de recyclage de métaux dans le sud-ouest du Nigéria

### Résumé

Les émissions industrielles des usines de recyclage de ferraille sont considérées comme une source majeure de contamination des sols par les métaux lourds (MH) et cela pose de problème au bien-être humain et l'environnement. Cette étude a évalué les variations saisonnières des concentrations en Al, Cd, Cu, Mn, Pb et Zn dans les sols de surface à proximité d'une usine de recyclage de métaux à Ile-Ife, au Nigéria. Soixante-six échantillons de sol de surface ont été systématiquement

prélevés à une profondeur de 0 à 15 cm pendant trois mois consécutifs, en saison sèche et en saison des pluies, à proximité des locaux de l'usine. La détermination de la contamination par les métaux lourds a été réalisée par spectroscopie d'absorption atomique. Les risques pour la santé publique ont été évalués à l'aide des indices de géoaccumulation (Igeo), de la dose journalière moyenne, du quotient santé (QS) et de l'indice santé (IS), des normes ne dépassant pas les limites moyennes des schistes et se situant entre  $1 \times 10^{-4}$  et  $1 \times 10^{-6}$ . La concentration totale (mg/kg) de métaux lourds dans les échantillons de sol variait de 0,50 Al à 2 219,10  $\mu\text{g/g}$  Cu pendant la saison humide, et de 0,59 Al à 3 019,10  $\mu\text{g/g}$  Cu pendant la saison sèche. Les résultats des risques non cancérogènes des HM pour les valeurs HQ (0,038) et HI (0,06) étaient généralement inférieurs à 1 ( $< 1$ ), indiquant l'absence de risque pour la santé. Cependant, les valeurs HI pour les enfants étaient supérieures à celles des adultes. Une exception à cette règle est la valeur HI élevée pour le Cu, de 1,23 et 1,11 respectivement pour les enfants et les adultes. L'étude a conclu que le sol de la zone d'étude était fortement pollué par le Cu et le Cd, et que les valeurs HI pour les enfants indiquaient que ces derniers pourraient être exposés à un risque potentiel plus élevé pour la santé que les adultes.

## Introduction

Soil is a vital resource for sustaining the human needs of quality food supply and quality environment. Environmental pollution by heavy metals from a metal recycling industry can become a very important source of contamination of soils, air and water within the vicinity of an industry (Aswal *et al.*, 2023). Excessive accumulation of such metals in agricultural soils causes soil contamination and bring about detrimental effect on food safety (Jomova *et al.*, 2025) and medicinal plant grown within the same vicinity. Urban environments are affected by a wide range of contaminants which vary appreciably within and among cities. Extremely high levels of pollutants in soils can be found in many industrial sites and waste disposal dumps, which result from very localized additions or accidental spillages of highly concentrated pollutant materials.

Heavy metals have important positive and negative roles in human life (Mitra *et al.*, 2022; Aswal *et al.*, 2023). Some heavy metals, such as Cu, Zn, Mn, Co and Mo act as micronutrients for the growth of animals and human beings just as trivalent chromium is beneficial to health (Jomova *et al.*, 2025) when present in trace quantities, whereas others, such as Cd, As, and Hg act as

carcinogens (Acheampong, 2023). Jomova *et al.*, (2025) reported that heavy metals, such as As, Pb, Hg and Cd are cumulative poisons, which cause environmental hazards and are exceptionally toxic. On the other hand, metals like Fe, Cu, Zn and Mn are essential metals for humans, since they play an important role in biological systems, but such essential heavy metals can produce toxic effects when their intake is excessively elevated (Mitra *et al.*, 2022). In fact, chronic health complications associated with long-term heavy metal exposures are metal lapse caused by Pb exposure while Cd has been implicated as having effects on the kidney, liver and gastrointestinal tract (Li *et al.*, 2022). Mileti'c *et al.*, (2023) identified ingestion through food chain contamination as one of the important pathways for the entry of these toxic pollutants into the human body and USEPA (1993) clearly stated the threshold of reference dose (RfD) indicating whether there is likely an adverse health effect during a life time. For instance, if an average daily dose value is lower than the reference dose, it is indicated that there would not be any adverse health effect; while in cases where average daily dose (ADD) values are higher than the RfD, it is likely that the exposure pathway will cause adverse human health effect (USEPA 1993, Aliyu *et al.*, 2022).

When hazard quotient (HQ)  $\leq 1$ , it indicates no adverse health effects, whereas HQ  $< 1$  indicates likely adverse health effects (Panqing, *et al.*, 2023). Other exposure pathway such as inhalation and dermal contact are also taken into consideration and in that case, hazard index (HI) is used to assess human health risk of metal exposure.

Numerous studies have been performed on heavy metal contamination of soils around Ile-Ife and other southwestern cities (Oyekunle *et al.*, 2014; Akpan, *et al.*, 2022, Tovide *et al.*, 2025) with major focus on concentration, distribution, source identification of heavy metals in roadside and surface dusts (Ogundele *et al.*, 2020).

However, there is still no explicit model and standard to assess the health risk of heavy metal pollution in soil of the study area. With the health risk assessment system by Environmental Protection Agency of United States (USEPA 2001), this study attempted to evaluate non-cancer health risk which represents a broad category of chronic toxicity including mutagenicity, developmental toxicity and neurotoxicity based on the

concentrations of six metals (Al, Cd, Cu, Mn, Pb and Zn) in surface soil through three different exposure pathways on both children and adults. The baseline results of the health risks assessment of heavy metals within the vicinity of the metal recycling factory are useful to the residents around the place for the purpose of taking protective measures.

### Materials and methods

#### Study area

The metal recycling factory (Figure 1) is located along the Ife-Ibadan expressway adjacent to Fashina community, Ile-Ife, Southwest Nigeria. It lies between latitudes 07°29.521'N and 07°29.670' N and longitudes 004°28.605' E and 004°28.627' E. The factory occupies a total area of 15 hectares and is about 5 km away from the core of the Obafemi Awolowo University, Ile-Ife campus in the northeast direction (Owoade *et al.*, 2013, Oyekunle *et al.*, 2014).

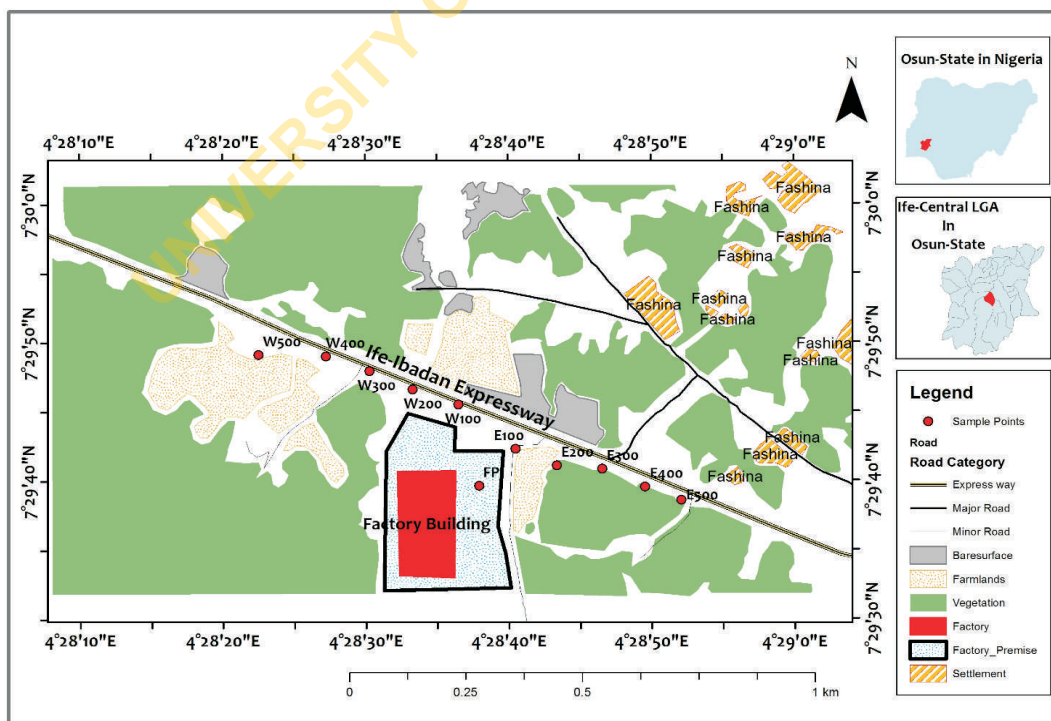


Figure 1: Map of the sampling area showing the sampling sites within the vicinity of the metal recycling factory

### Sample collection

Top soil samples at 0-15 cm depth were collected during the rainy season in the months of June, July and August, and in the dry season in the months of January, February and March, using a clean stainless soil Auger at three close spots from eleven selected locations as shown in Figure 1. The collected soil samples from the three spots within the same equidistant sites were homogenized and made into a composite sample placed in well labelled clean and sealed polyethylene (Nylon) bags. The samples were collected at 0-15 cm depth because the higher concentrations of anthropogenic metals are usually present in the top soil, and thereafter decrease with depth (Omonona *et al.*, 2020). A soil control sample was collected for each season from an unpolluted sample location.

### Apparatus and reagents

All the apparatus used (propylene bottles, teflon tubes, conical flask, and stirrer) were first washed with liquid detergent, rinsed with tap water and distilled water, and then soaked in 10% HNO<sub>3</sub> (v/v) for 48 h. They were then re-washed with liquid detergent and rinsed thoroughly with doubly distilled water. Thereafter, the apparatus was oven-dried for 12 h at a temperature of 105°C (Ogunfowokan *et al.*, 2013). All the reagents used, namely: HNO<sub>3</sub> (Riedel-deHaën, Germany), HCl (Sigma-Aldrich, Germany) and HF (British Drug House (BDH) Chemicals Ltd, Poole, England), were of analytical grade. The distilled water was redistilled to obtain doubly distilled water.

### Sample preparation and analysis

Wet (acid) digestion was employed to secure the release of bound or free metals from the environmental matrix in their highest oxidation states. Accurately weighed 0.25-0.50 g of the selected soil sample of approximately 0.5 mm in diameter was weighed into a Teflon beaker, 5 mL of 70% HNO<sub>3</sub> was added and the beaker was covered with a watch glass. This was placed on a thermostatically controlled hot plate maintained at 120°C for about 2 hours. Replenishing of the

acid content was done at intervals to avoid bringing the content to total dryness. The beaker was allowed to cool and 5 mL concentrated HNO<sub>3</sub>, 2 mL 60% HClO<sub>4</sub> and 5 mL 40% HF were added. The beaker was replaced on the hot plate with a digestion temperature of 180-200°C.

When the solution became clear, the digestion was considered complete. The watch glass was slid sideways to volatilize most of the acid content at about 100°C. The beaker was removed from the hot plate and cooled down after which 5 mL of 6 M HNO<sub>3</sub> was added. Further boiling and gentle simmering for about 5 minutes was done. The watch glass was rinsed with doubly distilled water into the Teflon beaker. The content of the beaker was quantitatively transferred into a 50 mL volumetric flask and made up with doubly distilled water to the mark (Ogunfowokan *et al.*, 2013). A blank determination was carried out to establish blank levels for the metal analysis.

### Quality control work

#### Recovery experiment

Two 0.5 g portions each of properly dried and pulverized soil sample from the selected samples were used for recovery analysis. One portion was spiked with 10 mL of 1000 mg/L standard mixture of the heavy metal solutions while the other (control) portion was left unspiked. The resulting solutions after digestion were subjected to FAAS analysis.

The analytical results of the seasonal variations of the total concentration of the heavy metals in the soil samples are presented tables and compared with the "average shale" concentration, which is considered as a "geogenic background" adopted as background concentration for soil (Ogbeide and Henry, 2024).

Calculation of percentage recovery (% R) was done based on:

$$\% R = \frac{A - A'}{B} \times 100$$

where A = heavy metal concentration in spiked soil sample, A' = heavy metal concentration in

Table 1: Calibration Curve and Percentage Recovery (% R) for the heavy metals.

Heavy metal	Amount spiked (µg/g)	Amount recovered (µg/g)	% R
	10	9.615	96.15 ±3.96
Cd	10	8.923	89.23±0.93
Cu	10	9.825	98.25±3.45
Mn	10	7.961	79.61±7.73
Pb	10	8.653	86.53±2.84
Zn	10	9.351	93.51±2.10

unspiked soil sample and B = concentration increase achieved by spiking (the amount of heavy metal used for spiking).

The reliability of the analytical procedure adopted in this study was tested in terms of recovery, precision and accuracy. Table 1 gives the result of the recovery analysis of the soil. Under the experimental conditions used, the standard calibration curves obtained showed high linearity level with  $r^2$  values between 0.9356 and 0.9895. Recoveries of heavy metals ranged from 79.61 ± 7.73% for Mn to 98.25±3.45 % for Cu. These values were adjudged acceptable because the recovery values were generally above 75%. The percentage relative standard deviation (% RSD) values obtained (0.93 to 7.73 % RSD) showed that precision was better than 10 % RSD level and were in good agreement with the values (Oyekunle *et al.*, 2011).

**Health risk assessment**

*Exposure dose*

According to the Exposure Factors Handbook (USEPA 1997; Onanuga *et al.*, 2023), the average daily intake (ADI) (mg/Kg/day) of a pollutant via ingestion, dermal contact and inhalation as exposure pathways can be estimated using equations (1), (2) and (3).

$$ADI_{ing} = \frac{C \times R_{ing} \times CF \times EF \times ED}{BW \times AT} \times 10^{-6} \quad (\text{Eqn. 1})$$

$$ADI_{inh} = \frac{C \times R_{inh} \times EF \times ED}{PEF \times BW \times AT} \quad (\text{Eqn. 1})$$

$$ADI_{derm} = \frac{C \times SA \times CF \times SL \times ABS \times EF \times ED}{BW \times AT} \quad (\text{Eqn. 3})$$

where:  $ADI_{ing}$  is daily exposure amount of metals through ingestion (mg/kg/day);  $ADI_{inh}$  is daily exposure amount of metals through inhalation (mg/kg/day);  $ADI_{derm}$  is daily exposure amount of metals through dermal contact (mg/kg/day). The exposure factors for these models are shown in Table 2 with the reference of USEPA and environmental site assessment guideline (2009). The values of these factors are combined between the standards from USEPA and real actual data for Chinese. The calculated values of ADI are calculated and shown in Table 2.

After the calculation of the Average Daily Intake for the three exposure pathways, the Hazard Quotient (HQ) for non-cancer toxic risk are often calculated using the relationship:

$$HQ = \frac{ADI}{RfD} \quad (\text{Eqn. 4})$$

where: the reference dose (RfD) is an estimation of maximum permissible risk on human population through daily exposure taking into consideration of sensitive group during a lifetime, the hazard index (HI) can be generated by adding the HQs together to estimate the risk of mix metal contaminates, such that:

Table 2: Exposure factors for dose models

Factor	Definition	Unit	Value		Reference
			Children	Adult	
C	concentration of the contaminant in soil	mg/kg			This study
Ring	ingestion rate of soil	mg/day	200	100	USEPA 1989
EF	exposure frequency	days/year	350	350	
ED	exposure duration	Years	6	24	USEPA 1989
BW	average body weight	Kg	15	55.9	
AT	average time	days/year	365xED	365xED	USEPA 1989
CF	conversion factor	kg/mg	1x10 <sup>-6</sup>	1x10 <sup>-6</sup>	Du <i>et al.</i> , 2013
Rinh	inhalation rate	m <sup>3</sup> /day	5	20	Du <i>et al.</i> , 2013
PEF	particle emission factor	m <sup>3</sup> /kg	1.32x10 <sup>9</sup>	1.32x 10 <sup>9</sup>	Du <i>et al.</i> , 2013
SA	surface area of the skin that contacts the soil	cm <sup>2</sup>	1800	5000	Du <i>et al.</i> , 2013
SL	skin adherence factor for soil	mg/cm <sup>2</sup>	1	1	Du <i>et al.</i> , 2013
ABS	dermal absorption factor (chemical specific)		0.001	0.001	Du <i>et al.</i> 2013

$$HI = \sum_{i=1}^3 HQ_t \quad (\text{Eqn. 5})$$

HI refers to the "sum of more than one hazard quotient (HQ) for multiple substances and/or multiple exposure pathways" and it is calculated separately for chronic, subchronic and shorter-duration exposure if each exposure pathway contributing to exposure of the same individual or subpopulation (USEPA 1989).

## Results and Discussion

### Levels of heavy metals in the soil

The mean concentration of Al for surface soils in the wet season ranged from 0.41 ± 0.12 (mg/kg) eastern direction (400 m) to 0.69 ± 0.25 (mg/kg) (0 m) with an overall mean concentration of 0.56 ± 0.13 (mg/kg) which fell below both the normal crustal average of 8.0 mg/kg and 15.0 mg/kg for uncontaminated soil as well as the normal background value of 10 mg/kg reported by (Thiombane *et al.*, 2023).

In the dry season, Al concentration ranged from 0.59±0.31 (mg/kg) eastern direction (100 m) to 0.90±0.51 (mg/kg) (400 m) with an overall mean concentration of 0.73±0.11 (mg/kg) which also fell below the crustal average of 8 mg/kg for uncontaminated soil. The highest concentration (0.69±0.25 mg/kg) in the eastern direction (0 m)

was obtained at the location closest to the source of pollution, which is the factory premise (FP) and was higher than the Al concentration (0.52±0.07 mg/kg) in the preliminary study obtained by Oyekunle *et al.*, (2014), indicating appreciable increase in Al contamination despite being below normal background level. Also, the overall mean Al concentration (0.65±0.13 mg/kg) in soil for both seasons were far above the range of Al concentration (0.30±0.02 - 0.52±0.07 mg/kg) obtained in the soil from previous study within the vicinity of the metal recycling factory at Fashina, Ile-Ife, Southwestern, Nigeria (Oyekunle *et al.*, 2014). However, Al concentrations reported in the present study were much lower than the values (9320-27500 mg/kg) reported for soils at the Aluminium smelting industrial area of Ikot Abasi Southeastern, Nigeria (Ipeaiyeda *et al.*, 2012) which is the second largest producer of primary aluminum in the world (World Bank, 2009). Generally, Al concentration decreased with increased distance from the factory premise (FP) particularly along the west axis of the study area (FP > W100 > W200 > W300) suggesting aerial-metal dispersion of contaminant from the point source except for sites E200, E400 and W400. One of the reasons that could be responsible for higher Al contaminations obtained at preceding sites E100, E300 and W300, respectively is higher pH values (8.2, 6.8 and 7.6) which were also higher than the pH value (6.7) of the soil within the

factory premise in the wet season. The slightly alkaline pH values observed at the extreme ends of both the east and west axes to the factory premise during the wet season is common to reduced aerobic soils and presumably accounted for increased absorption/desorption of metal contaminants in the soil. The high buffering capacity resulting from high soil organic matter content (9.4-55.50%) probably influenced the soil pH to be slightly alkaline. Also, the relatively high concentrations of Al observed at sites E400 (wet season) and W400 (dry season) might be connected with local agricultural practice, such as evidences of past and fresh mechanical soil clearing and burrowing, applications of fertilizer, animal manures and pesticides on farm produce while this study was in progress. These anthropogenic activities are capable of introducing trace metals to the soil, since the Al load in soil of the study area was lower than the average background levels of 8  $\mu\text{g/g}$  in polluted soil thus, negative health effects associated with excess Al in soil environments were not expected.

In the case of Cd, its levels ranged from  $1.68\pm 0.41$  mg/kg at W400 (near farmland) to  $2.94\pm 3.84$  mg/kg at W100 (near the metal recycling factory) in the wet season, while the dry season levels ranged from  $2.20\pm 0.45$  mg/kg at E100 (near the metal recycling factory) to  $3.84\pm 0.32$  mg/kg at W300 (near Fashina forested area) indicating greater contamination occurring during the dry season. The overall mean value of  $2.64\pm 0.54$  mg/kg for both seasons and even the lowest Cd concentration  $1.68\pm 0.41$  mg/kg obtained at site W400 near a farmland highlighted in Table

2 were all higher than the 1.0 mg/kg background levels stated for unpolluted soils (Pais and Jones, 1997). Soil Cd levels around the factory were generally higher than the background levels  $0.58\pm 0.24$  and  $0.45\pm 0.80$  of control samples collected 5km away at control sites CS1 and CS2, respectively (Owoade *et al.*, 2013). Evidently, these clearly showed that Cd levels of the study area far exceeded the average Shale level of 0.3 mg/kg for uncontaminated soils or 0.6 mg/kg from Environmental Quality Standard set by State Environmental Protection Administration (SEPA 1995) for soils in China and 3.0 mg/kg international standard tolerable limit (EC 2001). The high and fluctuating distribution pattern of Cd concentrations (Table 3) in the surrounding soils could be due to anthropogenic activities such as the smelting process from recycling factory, open waste dump and from agricultural practices observed during the investigation. For example, Cd levels at E400 were much higher than the values reported for soils at site E300 probably because fresh mechanical soil clearing and burrowing was carried out alongside the applications of fertilizer and pesticides on the adjoining farmlands. Thus, the metal recycling and local activities pose a threat to human health because of the carcinogenic effect of Cd. Onweremadu and Duruigbo (2007) regarded Cadmium as a biotoxic heavy metal and as an important pollutant in agricultural soils. It has been observed that foodstuffs obtained from soils heavily polluted with Cd could greatly increase its concentration in human bodies and possibly damage the filtering mechanisms of the kidney (Oyekunle *et al.*, 2011).

Table 3: Heavy metal concentration of soil in Fashina area, Ile-Ife (mg/kg<sup>-1</sup>)

Season	Sampling Site	Concentration (mg/kg)					
		Al	Cd	Cu	Mn	Pb	Zn
East							
Wet Season	E100	0.50±0.12	2.12±0.31	1620.90±78.87	408.73±0.51	18.30±0.43	39.73±0.41
	E200	0.62±0.31	2.55±0.54	1960.50±303.42	491.13±0.81	19.14±0.62	45.76±0.53
	E300	0.50±0.24	2.09±0.18	1601.00±69.98	408.75±0.91	18.25±0.21	36.31±0.62
	E400	0.68±0.26	2.79±0.25	2219.10±32.45	558.28±0.32	18.79±0.71	49.19±0.21
	E500	0.50±0.24	2.18±0.14	1711.80±67.56	430.20±0.53	17.52±0.71	35.60±0.41
	FP	0.69±0.25	2.63±0.31	2101.00±45.96	525.25±0.91	16.50±0.87	43.77±0.78
West							
	W100	0.60±0.31	2.94±0.49	1880.40±91.63	470.35±0.51	18.93±0.31	41.03±0.18
	W200	0.50±0.14	2.05±0.50	1609.80±34.61	404.70±0.81	19.26±0.21	36.39±0.17
	W300	0.53±0.42	2.15±0.53	1711.50±56.63	429.38±0.34	19.51±0.05	38.53±0.21
	W400	0.41±0.12	1.68±0.41	1359.10±31.53	330.53±0.21	17.54±0.24	30.38±0.20
	W500	0.66±0.31	2.68±0.52	2145.10±95.81	535.28±0.64	19.57±0.19	48.36±0.45
	<b>Mean±s.d.</b>	<b>0.56±0.09</b>	<b>2.35±0.39</b>	<b>1810.93±270.94</b>	<b>453.87±68.66</b>	<b>18.48±0.97</b>	<b>40.46±5.84</b>
East							
Dry Season	E100	0.59±0.31	2.20±0.45	1765.60±26.54	443.90±0.81	17.66±0.32	36.74±0.45
	E200	0.72±0.46	2.90±0.29	2327.70±78.65	585.93±0.86	19.06±0.24	48.41±0.72
	E300	0.66±0.42	2.62±1.23	2121.60±59.64	525.90±0.72	20.50±0.34	43.74±0.36
	E400	0.76±0.47	3.03±0.26	2429.00±60.69	608.00±0.87	21.30±0.24	50.42±0.53
	E500	0.61±0.01	2.35±0.28	1880.80±27.05	470.45±0.83	18.94±0.16	39.12±0.75
	FP	0.78±0.51	3.11±0.31	2490.10±28.64	622.53±0.88	19.48±0.14	51.88±0.58
West							
	W100	0.68±0.61	2.75±0.21	2174.90±22.38	545.98±0.45	19.68±0.31	55.25±0.45
	W200	0.62±0.30	2.41±0.24	1915.50±20.35	480.88±0.41	19.03±0.29	42.82±0.41
	W300	0.86±0.62	3.84±0.32	3019.10±29.42	758.03±0.51	20.79±0.24	66.84±0.23
	W400	0.90±0.51	3.59±0.32	2835.10±61.41	709.53±0.49	21.33±0.45	60.96±0.23
	W500	0.86±0.81	3.38±0.34	2668.60±73.43	670.40±0.56	22.91±0.24	57.53±0.31
	<b>Mean±s.d.</b>	<b>0.73±0.11</b>	<b>2.93±0.53</b>	<b>2329.81±404.93</b>	<b>583.78±101.76</b>	<b>20.06±1.47</b>	<b>50.34±9.37</b>
<b>Overall Range</b>		<b>0.41-0.90</b>	<b>1.68-3.84</b>	<b>1359.10-3019.10</b>	<b>330.53-758.03</b>	<b>16.50-22.91</b>	<b>30.38-66.84</b>
<b>“n”</b>		<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>	<b>3</b>
<b>Overall Mean±S.D</b>		<b>0.65±0.13</b>	<b>3.19±0.54</b>	<b>2070.37±428.43</b>	<b>518.82±107.68</b>	<b>19.27±1.46</b>	<b>45.40±9.14</b>
<b>CS1</b>		<b>0.63±1.02</b>	<b>0.58±0.24</b>	<b>73.48±11.24</b>	<b>362.23±1.21</b>	<b>1.75±0.04</b>	<b>176.3±0.89</b>
<b>CS2</b>		<b>0.58±2.01</b>	<b>0.45±0.80</b>	<b>60.60±24.4</b>	<b>211.23±2.93</b>	<b>1.79±0.41</b>	<b>161.3±1.23</b>
<b>*Average Shale</b>		<b>8</b>	<b>0.3</b>	<b>45</b>	<b>850</b>	<b>20</b>	<b>95</b>

\*NA: Not applicable; FP: Factory Premise, E400: Farmland

Thus, the soil should be used cautiously for food crop production. The highest concentration of Cd (3.84±0.32 mg/kg) at site W300 in the dry season was far higher than 2.94±0.49 mg/kg at W100 in the wet season and is comparable to corresponding levels in smelting waste contaminated soil from Sierra Almagrera in Spain (Navarro *et al.*, 2008; Ipeaiyeda *et al.*, 2012). On the other hand, the mean values of Cd (3.19±0.54 mg/kg) were 7

times higher than 0.44± 0.08 mg/kg obtained in previous investigation by Oyekunle *et al.*, (2014), 13 times higher than the 0.21±0.21 mg/kg reported for Abakaliki (Chukwuma, 1996), about 6 times higher than 0.55±0.49 mg/kg reported by Oniawa (2001) for Ibadan and about 10 times higher than the average background levels of 0.3 µg/g in polluted soils. It was noted that Cd had a worrisome heavily polluted status in all the

investigated sites, and being known as a metal notorious for its toxicity may lead to cadmium induced pollution problems, such as diarrhea, reproductive failure, DNA damage and cancer development (Oyekunle *et al.*, 2011; Ogunfowokan *et al.*, 2013; Panqing, *et al.*, 2023).

The highest degree of contamination in this study was obtained in Cu, and there was a clear difference in the levels of contamination between the wet and dry seasons. The maximum Cu concentration ( $3019.10 \pm 29.42$  mg/kg) was obtained at site W300 west direction of the study area during the dry season, while the least concentration ( $1601.00 \pm 69.98$  mg/kg) occurred during the wet season with an overall average value of  $2329.81 \pm 104.93$  mg/kg as contained in Table 2. The bedrock geology of the area is primarily igneous rock with four sub-surface layers of lateritic clay, clayey sand/sand, weathered/fractured bedrock and fresh bedrock (Adepelumi *et al.*, 2001). Thus, soil weathering is slow and mineralization of Cu from the rock material is minimal and could not have been responsible for Cu concentration. However, elevated levels of Cu at the sites might be as a result of combination of aerial metal particulate deposition from the nearby metal recycling factory and the fairly extensive pesticides applications in farmlands that have been identified in agriculture and horticulture to contain substantial concentrations of metals. For instance, in the recent past, about 10% of the chemicals approved for use as insecticides and fungicides in the UK were based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as Bordeaux mixture (copper sulphate) and copper oxychloride (Wuana and Okiemen, 2011).

Generally, copper concentrations were not only enhanced above background level of 45 mg/kg but far above control site values of  $73.48 \pm 11.24$  mg/kg (site CS1) and  $60.60 \pm 24.4$  mg/kg (site CS2), as well as all sample locations indicating a significant level of pollution of the factory vicinity with Cu. With respect to seasonal mean values of  $1810.93 \pm 270.94$  mg/kg and  $2329.81 \pm 404.93$  mg/kg for wet and dry seasons, all measured values exceeded the range 5-20 mg/kg being the background level

of Cu in an unpolluted soil (Pais and Jones, 1997) and far above 80 mg/kg set as international standard tolerable limits (European Communities, 2001), as well as the range of Cu concentrations (2.7-92.5 mg/kg) reported at Ibadan, Nigeria (Onianwa, 2001). Hence, negative health effects associated with excess Cu in soil and soil environment are expected.

The levels of Mn determined in this study ranged between  $330.53 \pm 0.21$  mg/kg and  $558.28 \pm 0.32$  mg/kg for wet season and from  $433.90 \pm 0.81$  -  $758.03 \pm 0.51$  mg/kg for dry season. The values of Mn in the soil fell within the range 20-3000 mg/kg stated as its background levels in an unpolluted soil (Krauskopf, 1972), but lower than average shale value of 850 mg/kg, but much higher than those reported for Ile-Ife roadside soil ( $35.93 \pm 0.15$  -  $83.76 \pm 0.006$  mg/kg). Hence, the effect of severe exposure is not expected. Manganese was reported by Oyekunle *et al.*, (2011) as an essential element required for the regulation of reproduction, carbohydrates and lipid metabolism and normal brain function, yet the normal human dietary intake is estimated to be approximately 2-5 mg/day for sound health.

At elevated levels, lead can cause serious health problems, especially for infants, children and pregnant women (Oyekunle *et al.*, 2011; Panqing, *et al.*, 2023), and as such, UNEP and BMFT (1983) have placed standard limit of Pb in soil for developing countries with respect to health of vegetation, livestock and man at 0.1-2 mg/kg, >1 mg/kg to 135 mg/kg for agricultural soils (Holmgren *et al.*, 1993), while the content in an unpolluted soil has been stated to range between 2 to 200 mg/kg (Pais and Jones, 1997). In the present study, measured seasonal mean values of Pb ranged from  $16.50 \pm 0.87$  -  $19.57 \pm 0.19$  mg/kg in wet season to  $17.66 \pm 0.32$  -  $22.91 \pm 0.24$  mg/kg in the dry season. Although, the values were in close range with shale value of 20 mg/kg and fell within the range of agricultural and unpolluted soil values (Pais and Jones 1997; Holmgren *et al.*, 1993), they were nonetheless higher than the values stated by UNEP and BMFT (1983) and 0.9-26 mg/kg reported as Pb concentrations by Reimann *et al.*, (1997). Thus, farmers cultivating edible

and medicinal plants such as vegetables, tubers and other root crops within the vicinity of the metal recycling factory should be mindful of the crop species grown having the tendency of bioconcentrating Pb in their tissues, which can predispose consumers to undue health risks (Oketola and Akpotu, 2015).

Zinc, as a micronutrient, is an essential element for plants, microorganisms, animals, and humans (Wuana et al., 2011), but at elevated levels it can become toxic and interrupt the activity in soils, as it negatively influences the activity of microorganisms and earthworms, thus retarding the breakdown of organic matter (Greany 2005). However, in the present study, Zn concentration in soil samples ranged from  $30.38 \pm 0.20$ – $48.36 \pm 0.45$  mg/kg in wet season, while dry season values varied from  $36.74 \pm 0.45$ – $66.84 \pm 0.23$  mg/kg, with an overall range and mean value of  $30.38$ – $66.84$  mg/kg,  $45.40 \pm 9.14$  mg/kg and  $45.40 \pm 9.14$  mg/kg, respectively. Notably, soil Zn levels around the metal recycling factory were generally lower than the average shale level of 95 mg/kg, but greatly exceeded 1.10 mg/kg recommended permissible limit (WHO 2006). Thus, using the soil for cultivating edible plants should be done with caution.

The mean levels of Cu from this study were significantly (at  $P \leq 0.05$ ) higher than those reported for previous studies both within Nigeria and other industrialized countries as shown in Table 3. Generally, the mean levels of Al, Cd, Mn and Pb were significantly higher (at  $P \leq 0.05$ ) than the values obtained in the previous study carried out some two years earlier. Thus, the rate at which the surface soil of the study area is becoming anthropogenically enriched with heavy metals should be controlled to forestall negative impacts on the biota and humans as a whole.

It was observed that the mean concentrations (and range) of total Cu  $2070.37 \pm 428.43$  mg/kg ( $1359.10 \pm 31.53$  -  $3019.10 \pm 29.42$  mg/kg) and Mn  $518.82 \pm 107.68$  mg/kg ( $330.53 \pm 0.21$  -  $758.03 \pm 0.51$  mg/kg) in the soil were significantly higher at  $p \leq 0.05$ , than levels (mg/kg) of Cu ( $21.4 \pm 2.0$ – $102 \pm 10.0$ ) and Mn ( $123 \pm 11.0$ – $259 \pm 12.0$ ) while the levels of Zn ( $45.40 \pm 9.14$ ) were lower than those reported for the industrial soils (Olajire et al., 2003) and background level of 95 mg/kg as shown in Table 2.

#### ***Metal composition of soil in study area between the present and previous study***

Table 4 provides information on the metal composition of the soil within the same study area as compared to earlier study by Oyekunle et al., (2014). The seasonal survey of the present study further revealed an astronomical rise of Cu from  $39.29 \pm 13.98$  mg/kg to  $2104.94 \pm 50.51$  mg/kg Cu eastward of the factory during the present study and from  $48.66 \pm 8.99$  mg/kg to  $2522.64 \pm 24.37$  mg/kg west ward of the study area. Based on comparison by mass concentration, Table 4 showed that except for Zn, which was higher in the previous study than the present, all other metal concentration were approximately 2 - 54 times higher in the present study than the previous study. Notably, Cu had the highest mass concentration in the present investigation while Mn had the peak value in the previous study. Comparing the seasonal mean values within the present study, it is evident that heavy metals in soil were generally higher in the dry season than in the rainy season due to evaporation of water in soil leading to concentration of metals in soil (Table 5).

Table 4: Soil metal level ( $\mu\text{g g}^{-1}$ ) obtained from other cities, compared with the present study

Location	Season		Al	Cd	Cu	Mn	Pb	Zn	References	
Ife, Nigeria	Dry	Mean	0.67±0.07	2.62±0.35	East	2104.94±282.98	526.84±70.95	19.49±1.43	43.68±58.47	Present study
					West	2522.64±46.00	632.96±115.76	20.75±1.51	56.68±8.89	
	Wet	Mean	0.56±0.08	2.35±0.31	East	1822.66±263.77	459.42±64.75	18.40±0.61	41.32±5.96	
					West	1741.18±294.38	434.05±76.1	18.96±0.83	38.94±38.53	
	Both season	Range	0.41-0.90 0.65±0.13	1.68-3.11 3.19±0.54	1359.10-3019.10 2070.37±428.43	330.53-758.03 518.82±107.68	17.52-22.91 19.27±1.46	35.60-57.53 45.40±9.145		
	Ife, Nigeria	Mean	0.40±0.07	0.44±0.08	West	48.66±8.99	196.61±57.58	1.03±0.55	83.89±13.21	Oyekunle <i>et al.</i> , (2014)
					East	39.29±13.98	215.76±45.35	1.17±0.18	99.34±20.97	
					Range	0.30-0.50	0.31-0.58	22.01-60.96	136.48-266.60	
	Abakaliki, Nigeria	Mean	N.A.	0.21±0.21	28±14	N.A.	78±180	111±88	Chukwuma (1996)	
Range		N.A.	0-1.0	11.0-61.0	N.A.	12-882	27-319			
Ibadan, Nigeria	Mean	N.A.	0.55±0.49	17±17	N.A.	81±140	48±37	Onianwa (2001)		
	Range	N.A.	0.02-2.7	2.7-92.5	N.A.	15.0-650	2.9-278			
London, United Kingdom	Range	N.A.	NA	1.7-6.3	N.A.	261-2296	245-2133	Elis and Revitt (1982)		
Arctic Catchment N. Europe	Range	N.A.	0.24-0.31	4-22.70	N.A.	0.9-26	17-60	Reimann <i>et al.</i> ,(1997)		
Hong Kong Spain	Mean	N.A.	0.9±0.3	16±50	N.A.	90±53	59±5	Chen <i>et al.</i> ,(1997)		
	Range	N.A.	N.A.	N.A.	366-1815	46-95	N.A.		Garcia and Millan (1998)	
Ikot Abasi City, Nigeria	Mean	17700±6600	2.17±0.55	N.A	1.64±1.30	27.00±3.90	127±170	Ipeaiyeda <i>etal.</i> , (2012)		
	Range	9320-27500	0.06-3.20	N.A	8.94-311	20.80-184.0	8.50-319.00			

Table 5: Comparison of mean values of investigated heavy metals (mg/kg) in soil during the dry season of present study and rainy season

Metal	Axis	Present study		Values for previous study		
		Mean values for dry season (I)	Mean values for wet season (II)	Ratio III (I:II)	IV	Ratio III:IV
		Al	East	0.67	0.56	0.84
	West	0.78	0.54	0.69	0.40	1.95
Cd	East	2.62	2.35	0.90	0.46	5.70
	West	3.19	2.30	0.72	0.44	7.25
Cu	East	2104.94	1822.66	0.87	39.29	53.57
	West	2522.64	1741.18	0.69	48.66	51.84
Mn	East	526.84	459.42	0.87	215.76	2.44
	West	632.96	434.05	0.69	196.61	3.22
Pb	East	19.49	18.40	0.94	1.17	16.66
	West	20.74	18.96	0.91	1.03	20.14
Zn	East	43.69	47.32	1.08	99.34	0.44
	West	56.68	38.94	0.69	83.89	0.68

**Geoaccumulation Index (I-geo)**

The geoaccumulation index for soil is shown in Table 6. Using the seasonal mean values of metals in the soil with the background levels of heavy metals in non-polluted soils (Huu *et al.*, 2010), the results of the calculated I-geo values for soil samples of the study area showed that the soil was unpolluted with respect to Al, Mn, Pb and Zn. On the other hand, the pollution status of the soil ranged from moderately polluted (MP) to heavily polluted (HP) with respect to Cd, while in the case of Cu, the soil status was either heavily polluted (HP) or very heavily polluted (VHP) during both seasons.

These findings clearly indicated that there were high levels of Cu and Cd being anthropogenically added from the metal recycling factory onto the soils within the vicinity of the factory at Fashina. Hence, the high dependence of the inhabitants within the vicinity of Fashina soil as their main source of crop cultivation and grazing of ruminant animals, such as cow, sheep and goat as well as harvesting of medicinal plants may lead to serious copper and cadmium while the generated ADI values are shown in Table 7.

Table 6: The Geoaccumulation Index (I-geo) Values in Soil at Various Sites

Element	Site	Cn		Bn	I-geo		Class		Pollution Intensity (PI)	
		Wet Season	Dry season		Wet season	Dry season	Wet season	Dry Season	Wet Season	Dry Season
Al	E100	0.49	0.53	8	-4.63	-4.5	0	0	PU	PU
	E200	0.59	0.7	8	-4.35	-4.11	0	0	PU	PU
	E300	0.48	0.63	8	-4.64	-4.25	0	0	PU	PU
	E400	0.67	0.73	8	-4.17	-4.05	0	0	PU	PU
	E500	0.51	0.56	8	-4.55	-4.41	0	0	PU	PU
	FP	0.63	0.75	8	-4.25	-4.01	0	0	PU	PU
	W100	0.56	0.65	8	-4.42	-4.2	0	0	PU	PU
	W200	0.48	0.57	8	-4.64	-4.39	0	0	PU	PU
	W300	0.51	0.9	8	-4.55	-3.73	0	0	PU	PU
	W400	0.39	0.85	8	-4.93	-3.82	0	0	PU	PU
Cd	W500	0.64	0.8	8	-4.23	-3.91	0	0	PU	PU
	E100	2.02	2.2	0.3	2.17	2.29	3	3	MP-HP	MP-HP
	E200	2.45	2.9	0.3	2.44	2.69	3	3	MP-HP	MP-HP
	E300	2	2.62	0.3	2.15	2.54	3	3	MP-HP	MP-HP
	E400	2.77	3.03	0.3	2.62	2.75	3	3	MP-HP	MP-HP
	E500	2.14	2.35	0.3	2.25	2.38	3	3	MP-HP	MP-HP
	FP	2.63	3.11	0.3	2.55	2.79	3	3	MP-HP	MP-HP
	W100	2.34	2.71	0.3	2.38	2.59	3	3	MP-HP	MP-HP
	W200	2	2.39	0.3	2.15	2.41	3	3	MP-HP	MP-HP
	W300	2.13	3.77	0.3	2.24	3.07	3	4	MP-HP	HP
Cu	W400	1.64	3.54	0.3	1.87	2.97	2	3	MP	MP-HP
	W500	2.66	3.33	0.3	2.56	2.89	3	3	MP-HP	MP-HP
	E100	1618.9	1763.6	45	4.58	4.71	5	5	HP-VHP	HP-VHP
	E200	1956.5	2323.7	45	4.86	5.11	5	6	HP-VHP	VHP
	E300	1599	2099.6	45	4.57	4.96	5	5	HP-VHP	HP-VHP
	E400	2217.1	2420	45	5.04	5.16	6	6	VHP	VHP
	E500	1708.8	1877.8	45	4.66	4.8	5	5	HP-VHP	HP-VHP

Element	Site	Cn		Bn	I-geo		Class		Pollution Intensity (PI)	
		Wet Season	Dry season		Wet season	Dry season	Wet season	Dry Season	Wet Season	Dry Season
Cu	FP	2101	2490.1	45	4.96	5.21	5	6	HP-VHP	VHP
	W100	1873.4	2171.9	45	4.79	5.01	5	6	HP-VHP	VHP
	W200	1602.8	1911.5	45	4.57	4.82	5	5	HP-VHP	HP-VHP
	W300	1705.5	3016.1	45	4.66	5.48	5	6	HP-VHP	VHP
	W400	1314.1	2830.1	45	4.28	5.39	5	6	HP-VHP	VHP
	W500	2129.1	2665.6	45	4.98	5.3	5	6	HP-VHP	VHP
	E100	404.73	440.9	850	-1.66	-1.53	0	0	PU	PU
	E200	489.13	580.93	850	-1.38	-1.13	0	0	PU	PU
	E300	399.75	524.9	850	-1.67	-1.28	0	0	PU	PU
	E400	554.28	605	850	-1.2	-1.08	0	0	PU	PU
Mn	FP	525.25	622.53	850	-1.28	-1.03	0	0	PU	PU
	W100	468.35	542.98	850	-1.44	-1.23	0	0	PU	PU
	W200	400.7	477.88	850	-1.67	-1.42	0	0	PU	PU
	W300	426.38	754.03	850	-1.58	-0.76	0	0	PU	PU
	W400	328.53	707.53	850	-1.96	-0.85	0	0	PU	PU
	W500	532.28	666.4	850	-1.26	-0.94	0	0	PU	PU
	E100	15.3	15.66	20	-0.97	-0.94	0	0	PU	PU
	E200	16.14	17.06	20	-0.89	-0.81	0	0	PU	PU
	E300	15.25	16.5	20	-0.98	-0.86	0	0	PU	PU
	E400	16.79	17.3	20	-0.84	-0.79	0	0	PU	PU
Pb	FP	16.5	17.48	20	-0.86	-0.78	0	0	PU	PU
	W100	15.93	16.68	20	-0.91	-0.85	0	0	PU	PU
	W200	15.26	16.03	20	-0.98	-0.9	0	0	PU	PU
	W300	15.51	18.79	20	-0.95	-0.67	0	0	PU	PU
	W400	14.54	18.33	20	-1.05	-0.71	0	0	PU	PU
	W500	16.57	17.91	20	-0.86	-0.74	0	0	PU	PU
	E100	33.73	36.74	95	-2.08	-1.96	0	0	PU	PU
	E200	40.76	48.41	95	-1.81	-1.56	0	0	PU	PU
	E300	33.31	43.74	95	-2.1	-1.7	0	0	PU	PU
	E400	46.19	50.42	95	-1.63	-1.5	0	0	PU	PU
Zn	FP	43.77	51.88	95	-1.7	-1.46	0	0	PU	PU
	W100	39.03	45.25	95	-1.87	-1.66	0	0	PU	PU
	W200	33.39	39.82	95	-2.09	-1.84	0	0	PU	PU
	W300	35.53	62.84	95	-2	-1.18	0	0	PU	PU
	W400	27.38	58.96	95	-2.38	-1.27	0	0	PU	PU
	W500	44.36	55.53	95	-1.68	-1.36	0	0	PU	PU

PU = practically unpolluted HP = heavily polluted

MP = moderately polluted VHP = very heavily polluted

\* Negative values suggest sites with values < 0, i.e practically unpolluted my specific metal.

**Health Risk Assessment of Metal in the Soil.**

The values of HQ and HI are presented in Table 8. However, it was observed that the HQ and HI for both children and adults had the same trends while the children are more susceptible to metal exposure more than adult population. The HQ values for the three pathways decreased in the

order of ingestion > dermal contact > inhalation, where the contribution of  $HQ_{ing}$  to the total risk (HI) accounted for more than 70%. This indicated that the ingestion is the primary pathway of heavy metals that could be harmful to human health and the order is as shown in Figure 2.

Table 7: Daily dose in three models

		ADD <sub>ing</sub> mg/(kg·d)		ADD <sub>inh</sub> mg/(kg·d)		ADD <sub>derm</sub> mg/(kg·d)		
		Children	Adult	Children	Adult	Children	Adult	
Al	Min	0.41	5.24E-06	2.81E-06	9.93E-11	4.26E-10	4.72E-08	1.41E-07
	Max	0.9	1.15E-05	6.18E-06	2.18E-10	9.36E-10	1.04E-07	3.09E-07
	Mean	0.56	7.16E-06	3.84E-06	1.36E-10	5.82E-10	6.44E-08	1.92E-07
Cd	Min	1.68	2.15E-05	1.15E-05	4.07E-10	1.75E-09	1.93E-07	5.76E-07
	Max	3.84	4.91E-05	2.63E-05	9.30E-10	3.99E-09	4.42E-07	1.32E-06
	Mean	2.335	2.99E-05	1.60E-05	5.65E-10	2.43E-09	2.69E-07	8.01E-07
Cu	Min	1359.1	1.74E-02	9.33E-03	3.29E-07	1.41E-06	1.56E-04	4.66E-04
	Max	3019.1	3.86E-02	2.07E-02	7.31E-07	3.14E-06	3.47E-04	1.04E-03
	Mean	1790.7	2.29E-02	1.23E-02	4.34E-07	1.86E-06	2.06E-04	6.14E-04
Mn	Min	330.53	4.23E-03	2.27E-03	8.00E-08	3.44E-07	3.80E-05	1.13E-04
	Max	758.03	9.69E-03	5.20E-03	1.84E-07	7.88E-07	8.72E-05	2.60E-04
	Mean	449.93	5.75E-03	3.09E-03	1.09E-07	4.68E-07	5.18E-05	1.54E-04
Pb	Min	16.5	2.11E-04	1.13E-04	4.00E-09	1.72E-08	1.90E-06	5.66E-06
	Max	22.91	2.93E-04	1.57E-04	5.55E-09	2.38E-08	2.64E-06	7.86E-06
	Mean	18.72	2.39E-04	1.28E-04	4.53E-09	1.95E-08	2.15E-06	6.42E-06
Zn	Min	30.38	3.88E-04	2.08E-04	7.36E-09	3.16E-08	3.50E-06	1.04E-05
	Max	66.84	8.55E-04	4.59E-04	1.62E-08	6.95E-08	7.69E-06	2.29E-05
	Mean	42.73	5.46E-04	2.93E-04	1.03E-08	4.44E-08	4.92E-06	1.47E-05

Health risk assessment prediction by calculating ADI, HQ and HI indicated that Al, Cd, Mn, Pb, and Zn had lower values than the safe level indicating no risk from these metals, while Cu exhibited values higher than the safe level thus, generating the most concern based on the high HI value of 1.226 and 1.107 for children and adult, respectively. In addition, the HI calculation showed

results of less than 1 which indicated no risk exposure to Al in environmental media (FAO and WHO 1989). Therefore, farmers cultivating their crops and residents within the vicinity of the study area are considered safe from the dermal contact risk of excess Al, Cd, Mn, Pb, and Zn in the soil for the moment.

Table 8: Health risk from heavy metals in soil within studied area

		Conc.	RfD <sub>ing</sub>	RfD <sub>inh</sub>	RfD <sub>derm</sub>	HQ <sub>ing</sub>		HQ <sub>inh</sub>		HQ <sub>derm</sub>		HI	
		(mg/kg)		Mg/(kg·d)		Children	Adult	Children	Adult	Children	Adult	Children	Adult
Al	Min	0.41	0	0	0	7.49E-07	4.01E-07	0.00	0.00	0.00	0.00	7.49E-07	4.01E-07
	Max	0.90	7.00	N.A.	N.A.	1.64E-06	8.83E-07	0.00	0.00	0.00	0.00	1.64E-06	8.83E-07
	mean	0.56	0	0	0	1.02E-06	5.49E-07	0.00	0.00	0.00	0.00	1.02E-06	5.49E-07
Cd	min	1.68				0.022	0.012	4.07E-07	1.75E-06	0.004	0.012	0.025	0.023
	max	3.84	0.001	0.001	0.0001	0.049	0.026	9.3E-07	3.99E-06	0.009	0.026	0.058	0.053
	mean	2.335				0.030	0.016	5.65E-07	2.43E-06	0.005	0.016	0.035	0.032
Cu	min	1359.1				0.470	0.252	8.18E-06	3.51E-05	0.082	0.245	0.552	0.497
	max	3019.1	0.037	0.040	0.0019	1.043	0.559	1.82E-05	7.81E-05	0.183	0.547	1.226	1.107
	mean	1790.7				0.619	0.332	1.08E-05	4.63E-05	0.108	0.323	0.727	0.656
Mn	min	330.53				0.302	0.162	0.00	0.00	0.00	0.00	0.302	0.162
	max	758.03	0.014	N.A.	N.A.	0.692	0.371	0.00	0.00	0.00	0.00	0.692	0.371
	mean	449.93				0.411	0.221	0.00	0.00	0.00	0.00	0.411	0.221
Pb	min	16.50				0.060	0.032	1.14E-06	4.89E-06	0.004	0.011	0.064	0.044
	max	22.91	0.0035	0.004	0.0005	0.084	0.045	1.58E-06	6.76E-06	0.005	0.016	0.089	0.061
	mean	18.72				0.068	0.037	1.29E-06	5.54E-06	0.004	0.013	0.073	0.049
Zn	min	30.38				0.001	0.001	2.45E-08	1.05E-07	0.000	0.000	0.001	0.001
	max	66.84	0.30	0.30	0.06	0.003	0.002	5.4E-08	2.32E-07	0.000	0.000	0.003	0.002
	mean	42.73				0.002	0.001	3.43E-08	1.48E-07	0.000	0.000	0.002	0.001

\*FAO and WHO (1989) Al for RfD = 7 mg/kg/day, Conc. = concentration of metals, HQ = Hazard quotient, HI= Hazard Index

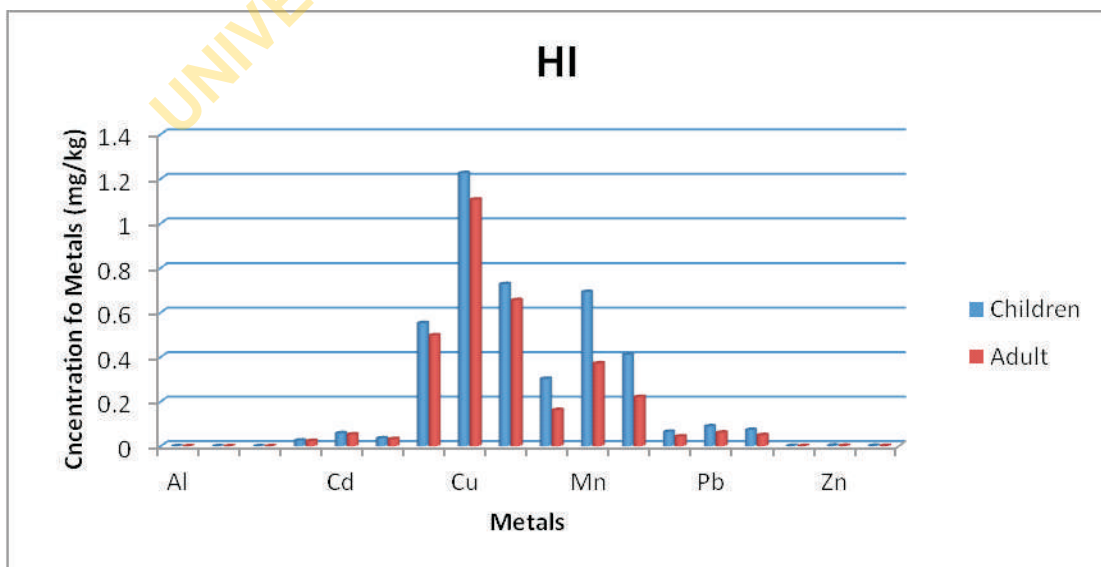


Figure 2: Health risk index for heavy metals

Although, people in the study area were generally exposed to pollutant via ingestion, dermal contact and inhalation, ingestion was the major exposure pathway of heavy metals to both children and adults, similar findings were reported in studies carried out by Panqing, *et al.* (2023). The HQ values for the pathways of this study increased in the order of inhalation < dermal contact < ingestion.

## Conclusion

The heavy metal concentrations of soil within the metal smelting industry vicinity were investigated in the present study. The overall mean concentrations (mg/kg) of Al, Cd, Cu, Mn, Pb and Zn were  $0.65 \pm 0.13$ ,  $2.64 \pm 0.54$ ,  $2070.37 \pm 428.43$ ,  $518.82 \pm 107.68$ ,  $19.27 \pm 1.46$ ,  $45.40 \pm 9.14$ , respectively. The seasonal heavy metal pollution status of surface soil samples of the study area with respect to Al, Cd, Cu, Mn, Pb and Zn, revealed that higher levels of metals were obtained in the dry season than in the wet season. The decreasing tendency with distance away indicated the enrichment of metals coming from the industrial operations. One of the worrisome facts is that the field under investigation was being used for food and medicinal crops cultivation. The pollution status of the soil under investigation had increased in 2 – 54 folds within the space of 2 years. However, the health risk values obtained were in the negligible range except for Cu concentration with associated consequences that could call for caution and concern.

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