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Ecological and Health Risk Assessment of Heavy Metals and Metalloid Levels in Soil around Metal Works Wukari

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Abstract

Metal works process is one of the most important anthropogenic sources of heavy metal emissions into environment, consequently posing a risk to human health through inhalations, ingestion and dermal contact. This study assessed the total levels of Al, Si, Zn, Fe, Pb and Cd in soils around metal works, their potential risk to the environment and health. The study provides baseline of the determine analytes in the under review as well as the potential risk associated with them. Soil quality parameters reveals the soil pH 8.78 ± 0.30 as strongly alkaline (8.50 – 9.00), organic matter content ($2.15 \pm 0.42\%$) and effective cation exchange capacity (ECEC) (18.56 cmol/kg) been moderate. The heavy metals and metalloid levels were in the order: Fe (20647 mg/kg) > Al (3940.90 mg/kg) > Zn (373.03 mg/kg) > Pb (120.2 mg/kg) > Si (45.54 mg/kg) > Cd (6.37 mg/kg) respectively where the geo-accumulation indices of Zn (1.73), Pb (2.52) and Cd (5.27) showed moderate contamination with respect to zinc; moderate to strong contamination with respect to lead and strong to extreme contamination with respect to cadmium. Similarly, contamination factor of Zn (4.97) reveals considerable contamination with zinc likewise the contamination factors of Pb (8.58) and Cd (57.9) implied very high contamination by Pb and Cd. Cancer Risk (CR) of Pb and Cd in adults were all greater than the value found for children in all respect either via ingestion, inhalation or dermal route of exposures. The CR_{derm} of both Cd and Pb exceeded the carcinogenic risk limit of 1.0×10^{-4} hence indicates a lifetime cancer risk to both children and adults. Hence, the soil is recommended for cleanup in order to guaranty sound health and ecological sustainability with respect to the contaminants.

Keywords : Metal works, heavy metals, contamination, environment, potential health risk

Introduction

Over the years, rapid and uncontrolled urbanization alongside industrialization, mining, smelting, manufacturing, e-waste production among others have been causing immense pressure on the global environment [1,2]. Likewise, population explosion and the quest to have a better life has led to continuous industrial revolutions as well as an increase in the used of metals with industrial values such as iron, steel, aluminum, zinc among others. For instance, steel, aluminum and zinc have proven degree of resistance to corrosion giving them vast application in fabrications of some installations. Mild steel is an essential metal in most industries because it is ductile and malleable. It has been proven experimentally that metals are not free from corrosion as long as they have contact with aggressive medium, like acid, base, salt, gaseous materials such as formaldehyde, acid vapour, and sulphur containing gases. Reported cases of severe corrosion attacks in some industries such as rice milling plant, fertilizer plant, oil exploration/refinery companies, metallurgical industries and other, have been evidently linked

to some operational processes such as acid wash, pickling, moisture, varying temperatures etc. usually carried out using the metallic facilities thereby leaving behind debris of metallic that does contaminate the environment [3-5].

Metal works process is one of the most important anthropogenic sources of heavy metal emissions into environment, thereby degrades environmental quality, consequently posing a high risk to human health through inhalations, ingestion and dermal contact [6]. A number of researchers have found an increased Cd, Cu, and Pb content in soil as well as increased bio-accumulation on consumption of crops grown around the metal smelting with most pronounce intake in children [7,8]. This study assessed the level of heavy metals in soils around metal works, their potential risk to the environment and health. The study provides baseline of the determine analytes in the under review as well as the potential risk associated with them.

Materials and Methods

Study Area

The study area was the Wukari Local Government area located in Taraba state, Nigeria, at 7.89°N and longitude 9.78°E of the equator with a topography of 189 m above sea level; covering an area of 4,308Km² [9,10]. The primary occupation of the inhabitants is agriculture. Major cash crops produced include yam, maize, millet, rice, sorghum, cassava and other tree crops like mango, cashew, oranges and also rearing of animals which include cattle, sheep, goats, pigs and poultry with a land mass area of 4,308km² and a population of 241,546 people with a projected growth rate of 3.8% per annum based on the 2006 census. Over the years like most cities in Nigeria, the town has undergone massive infrastructural transformations and have to contend with issues of environmental contaminations associated with urbanization [11-13].

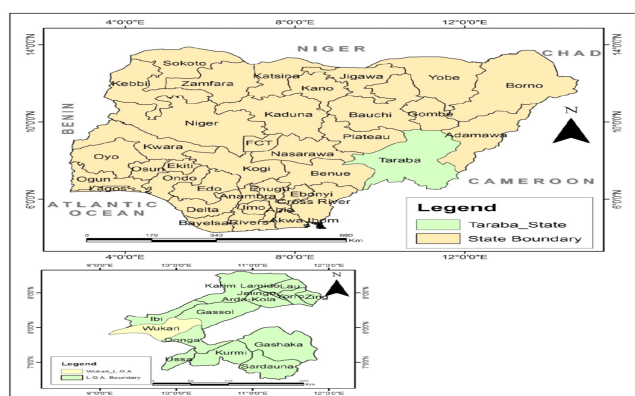


Figure 1: Map of Nigeria and Taraba State showing Wukari local Government Area.

Source: Ministry of Land and Survey, Jalingo, Taraba State (Oyatayo et al., 2015;) [10].

Sampling and sample pre-treatment

Stratified sampling technique was applied for soil sample collection around the geographical coordinates 7o52'40.602"N, 9o46'50.724"E and 7o51'11.802"N, 9o47'44.802"E [11]. Under this sampling technique, each sampling site was broken into three (3). Each stratum was further subdivided into four quadrants of equal size before five (5) samples were taken randomly by grab method within the depth of 0 – 15 cm in the individual quadrant (smaller area) making a total of twenty (20) samples per strata (small area) and a total of sixty (60) samples from the three to enable detailed representation of variability within the study area.

The 60 sample units of approximately equal size were pooled together to form the composite and a representative sample Metal works Wukari. The soil samples were pooled together to form their composite and representative samples of Metal works Wukari.

The control soil sample was collected in a farmland within 1.8 km radius from the industrial layout. The control sampling site was remote to possible sources of contamination associated with the industry.

Determination of Total Heavy Metal Concentration

Sample Digestion

Digestion of soils samples was carried out by adding, 10.0 mL of 1:1 HNO₃ to 1.00 g of the air-dried sieved sample in a 25 x 150 mm glass digestion tube. The samples were then heated to 95 ± 10°C for about 15 minutes by means of microwave digestion system. When cool, 5.00 mL of the HNO₃ was added and heat was applied for another 30 minutes. The digests were again allowed to cool, before 2 mL of deionized water and 3.00 mL of 30 % H₂O₂ was added and heated to 95 ± 5 °C. After the digests were cooled again, another 1.00 mL of 30% H₂O₂ was added while heating continued until the sample volumes reduced to approximately 5.00 mL.

The digests were then allowed to cool and filtered before being diluted again to 50.0 mL with deionized water prior to the determination of total Al, Si, Zn, Fe, Pb and Cd content in the soil samples using MP-AES [12].

MP-AES Conditioning

The Agilent Microwave Plasma Atomic Emission Spectrophotometer (4210 MP-AES) technologies generates microwave plasma (MP) of about 5000 K temperature using nitrogen gas from the atmosphere for the atomic emission. Sample introduction to the MP is pneumatic using a concentric nebulizer and cyclonic spray chamber. Emission line isolation and detection is sequential using a monochromator and charge-coupled device detector. This MP-AES is condition for 3 replicate parameter value, 15 rpm pump rate, 25 seconds sample uptake delay, 25 times rinse time, 5 seconds stabilization time. Fast pump during uptake and rinse time during fast pump were set on at 80 rpm while the auto sampler was Agilent SPS 4.

Ecological Risk Assessment

Geo-accumulation Factor (Igeo): Igeo proposed by the German scientist Muller in 1969 was also used to evaluate the pollution status of heavy metals in soil around the metal works with respect to the background (control) values. The Geo-accumulation index was calculated using equation (1)

$$I_{geo} = \log_2[C_n/1.5B_n] \quad (1)$$

where C_n is the heavy metals and metalloids levels in soil around the metal works and B_n is the geochemical or background (control) value adopted by Sharma *et al.* (2016) [14]. The constant value, 1.5, is back-ground matrix correction factor due to the lithological variations.

Levels of contamination described by Muller in 1969 was adopted where the geo-accumulation value of (0) is considered, uncontaminated; (0 - 1) uncontaminated to moderately, contaminated; (1 - 2) moderately contaminated; (2 - 3), moderately to strongly contaminated; (3 - 4) strongly contaminated; (4 - 5) strongly to extremely strongly contaminated while (>5) extremely contaminated [12,15].

Contamination Factor (CF): The contamination factor (CF) ratio was estimated by dividing the concentration of each metal in the soil by the background/control value as shown in equation

(2); where the different levels of degree of contamination include: low contamination for C_f value < 1 ; moderate contamination for $C_f \geq 1$ to < 3 ; considerable contamination for C_f value ≥ 3 to < 6 and very high contamination for C_f value ≥ 6 as describe by Rahman *et al.* (2012) [16].

$$CF = \frac{C_{\text{heavy metals}}}{C_{\text{background}}} \quad (2)$$

Human Health Risk Assessment

The carcinogenic and non-carcinogenic risks were evaluated using the human health risk assessment model for dermal contact, ingestion and inhalation exposure pathways. The health risk assessment is centered on the exposure factors and guidelines handbook of United States Environmental Protection Agency (USEPA, 2003). The average daily dose (ADD) via ingestion (D_{ing}), inhalation (D_{inh}) and dermal contact (D_{derm}) for both children and adults were evaluated using equations (3) - (5) as adopted from Qing *et al.* (2015) [17].

$$\text{Ingestion dose } (D_{\text{ing}}) = \frac{CS \times \text{IngR} \times EF \times ED \times CF}{BW \times AT} \quad (3)$$

$$\text{Inhalation dose } (D_{\text{inh}}) = \frac{CS \times \text{InhR} \times EF \times ED}{BW \times AT \times PEF} \quad (4)$$

$$\text{Dermal dose } (D_{\text{derm}}) = \frac{CS \times SA \times SL \times EF \times ED \times CF}{BW \times AT} \quad (5)$$

where CS is the concentration of the analytes in the soil from the exposure point (mg/kg), IngR - tailing ingestion rate for the receptor (mg/d), InhR - soil inhalation rate for the receptor (m^3/d), EF - exposure frequency (days/year), ED - exposure duration (years), PEF - soil-to-air particulate emission factor (m^3/kg), SA - skin surface area available for exposure (cm^2), SL - soil-to-skin adherence factor ($\text{mg}/\text{cm}^2/\text{event}$), BW - time-averaged body weight (kg), AT - average time of non-carcinogenic and carcinogenic risks (days) and ABS - dermal absorption factor (dimensionless). The hazard quotient (HQ), hazard index (HI) and cancer risk (CR) were evaluated using equations (6) – (8) as adopted from Bwede *et al.* (2021) [18].

$$HQ = \frac{D}{\text{RfD}} \quad (6)$$

$$HI = HQ_{\text{ing}} + HQ_{\text{inh}} + HQ_{\text{derms}} \quad (7)$$

$$CR = D \times SF \quad (8)$$

Where D = Dose (ingestion, inhalation or dermal), RfD = Reference dose and SF = Slope factor.

Risk characterization was considered separately for carcinogenic and non-carcinogenic effects [18-21]. Health risks were obtained by comparing the calculated HQ, HI and CR values with recommended maximum values presented on Table 1

Heavy metal/ RfD	Zinc	Lead	Cadmium	Iron	Silicon	Aluminium
RfD _{ing} ($\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$)	3×10^{-1}	3.5×10^{-3}	1×10^{-3}	7×10^{-3}	NA	1
RfD _{inh} ($\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$)	3×10^{-1}	3.5×10^{-3}	1×10^{-3}	7×10^{-3}	NA	2.7×10^{-1}
RfD _{der} ($\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$)	3×10^{-1}	5.25×10^{-5}	1×10^{-3}	7×10^{-3}	NA	1.0×10^{-3}
SF _{ing}	NA	8.5×10^{-3}	5.0×10^{-1}	NA	NA	NA
SF _{inh}	NA	NA	6.3	NA	NA	NA
SF _{derm}	NA	4.25×10^{-1}	NA	NA	NA	NA

RfD_{ing} = Reference dose for ingestion, RfD_{inh} = Reference dose for inhalation, RfD_{der} = Reference dose for dermal contact, SF_{ing} = Slope factor ingestion SF_{inh} = Slope factor inhalation SF_{derm} = Slope factor dermal NA=Not Available.

Table 1: USEPA Reference Doses for Non carcinogens and Slope Factor for Carcinogens

Data Analysis

Data obtained were subjected to statistical tests of significance using the one-way analysis of variance (ANOVA) to assess significant variation in the concentration levels of the trace metals in the soils sample across the sampling points locations. Probability less than 0.05 ($p < 0.05$) was considered statistically significant. All statistical analyses were carried out using SPSS 20.0 windows.

Results and Discussion

Parameter	Sample	Mean \pm standard deviation	Minimum	Maximum	Variance
pH	Test	8.78 \pm 0.30	8.75	8.81	0.06
	Control	7.80 \pm 0.16	7.64	7.98	0.34
Organic Carbon (%)	Test	1.25 \pm 0.24	1.18	1.25	0.07
	Control	0.71 \pm 0.07	0.700	0.80	0.11
Organic Matter Content (%)	Test	2.15 \pm 0.42	1.85	2.45	0.60
	Control	1.23 \pm 0.01	1.22	1.28	0.06
Acidity (H ⁺ and Al ³⁺) Content (cmol/kg)	Test	1.00 \pm 0.54	1.00	1.50	0.50
	Control	1.40 \pm 0.84	1.19	1.74	0.55
ECEC (cmol/kg)	Test	18.56 \pm 0.61	17.49	19.65	2.16
	Control	18.45 \pm 1.87	17.12	19.23	2.13

Table 2: Physiochemical properties of the test and control soil

Soil Quality Parameters

The mean soil pH of the soils obtained from Metal Works Wukari 8.78 ± 0.30 as shown in Table 2. The soils pH around the metal works was strongly alkaline (8.50 – 9.00) based on USDA classification [22]. The high soil pH value impedes heavy metals availability for plant uptake in soil.

The mean percentage organic matter content of the $2.15 \pm 0.42\%$ as displayed in Table 2 was moderate. While the mean effective cation exchange capacity (ECEC) of soils obtained from Metal Works Wukari was 18.56 ± 0.61 cmol/kg. The (18.56 cmol/kg) falls within the moderate capacity base on USDA classification (12.0-25.0 cmol/kg). The CEC measures the quantity of negatively charged sites on soil surfaces capable of retaining

cat-ions especially. CEC is usually high when the soil has higher proportion of clay and organic matter at pH near neutral [23]. Elevated CEC and organic matter content decreases heavy metals availability in soil by immobilizing them.

Results obtained from particles size analysis revealed that the mean percentage clay content of the soils obtained from Metal Works Wukari was 9.00 ± 1.73 % while the percentage silt content was 31.2 ± 7.19 %. The percentage sand content was: 59.8 ± 8.87 % respectively for the soil obtained Metal works Wukari the textural property is within sandy loam classification [24,25]. Implying that the soil under review have its silt and clay content in moderation that would relatively retain heavy metals.

Heavy metal/Sample	Zinc	Silicon	Lead	Cadmium	Iron	Aluminium
Test sample (mg/kg)	373.03 ± 1.55	45.54 ± 1.71	120.20 ± 1.87	6.37 ± 0.04	20647 ± 129.90	3940.90 ± 25.61
Control sample (mg/kg)	223.62 ± 0.35	31.15 ± 0.31	7.26 ± 0.09	0.34 ± 0.01	13135 ± 57.22	2491.40 ± 5.27
Background level (mg/kg)	75	277100	14	0.11	41000	82000

Background level [12,14].

Table 3: Heavy Metal Concentration in mg/kg in Metal works soil

Metals and Metalloid Content

Silicon Content

The mean content of total silicon in soils obtained from Metal Works Wukari was 45.54 ± 1.71 mg/kg while the corresponding content of the control sample was 31.15 mg/kg. Both the silicon content of the test and control soil samples were much less than the 277100 mg/kg background concentration [12,14].

Silicon is the second richest element in the soil and surface of earth crust. It decreases the bioavailability of heavy metals in soil and their accumulation in plant roots by competing for uptake with heavy metals such as arsenic, aluminum, and cadmium [26].

Zinc Content

The mean content of total zinc in soils obtained around Metal works Wukari 373.03 ± 1.55 mg/kg supersedes the 223.62 mg/kg of the control sample. Han *et al.* (2021) found a lower mean value of 200 mg/kg in farmland soil around non-ferrous metal smelting industry in North China [27]. The high concentration of zinc content in soil around the metal works Wukari is likely due to the utilization of zinc compound in galvanization to prevent iron corrosion [12].

Lead Content

The mean content of total lead in soils obtained from Metal Works Wukari was 120.2 ± 1.87 mg/kg, the mean Pb content was greater than the 7.6 mg/kg content of the control soil. And less than 146 mg/kg Pb content in farmland soil around non-ferrous metal smelting, North China, as well as the 86.29 mg/kg Pb content reported in mechanic village Wukari, Nigeria [12,27]. The high level of lead content in soil around the metal works Wukari may be traceable to the use of lead compound such as lead oxide, a very stable and suitable ingredient in corrosion-resistance coating for iron and steel.

Cadmium Content

The mean content of total cadmium in soils obtained 6.37 ± 0.04 mg/kg in the present study was generally higher than the 1.4 mg/kg reported for metal smelting soils, North China; but were generally less than the 9.05 mg/kg observed in dumpsite soil from Uyo, Nigeria [27,28]. Cadmium is frequently discharged from anthropogenic sources since the element is use as an anti-corrosion coating in electroplating and stabilizer in plastics. It is a component of nickel-cadmium batteries and alloying metal in solders [12].

Iron Content

The mean content of total iron (20647 ± 129.90 mg/kg) in soils obtained from Metal Works Wukari was much greater than the 13135 mg/kg recorded in the control soil as well as the 3180.22 mg/kg *Amaranthus hybridus* planted in soil around automobile workshops at Iworoko-Ekiti, Nigeria [29]. However, higher iron level of 20,723 mg/kg was reported in soils within the vicinity of mechanic village Wukari, Nigeria [12]. High iron content in metal works soils is similar to that of mechanic village due to iron composite materials in both industries [30].

Aluminium Content

The mean content of total aluminium 3940.9 ± 25.61 recorded in metal works soils was far greater than the 2491.40 mg/kg found in the control sample. Frankowski (2016) reported a lower Al level 1429 mg/kg around the polluted and environmentally protected area of Poland [31]. However, both the test and control soil samples aluminium levels were far less than the 9761. mg/kg concentrations of aluminium around the cement factory Qaddahia, Libya; as well as the 82,000 mg/kg geochemical background value of aluminium on the earth crust implying no contamination [14,32]. Aluminium is one of the most important components of soils which finds great application in metal works due to the ability of its oxide to withstand corrosion.

Ecological Risk Assessment

Geo-accumulation index

The geo-accumulation index of -13.15, -4.96 and -1.57 for Si, Al and Fe respectively were all less than zero thereby indicating un-contamination with respect to silicon. While the geo-accumulation indices of 1.73, 2.52 and 5.27 for Zn, Pb and Cd respectively falls within (1.00 to 2.00), (2.00 to 3.00), and (4.00 to < 6.00) implying moderate contamination with respect to zinc; moderate to strong contamination with respect to lead and strong to extreme contamination with respect to cadmium. Similar pattern of soil contamination by Zn, Pb and Cd have been reported in auto mechanic village Wukari, Nigeria [12]. Soil contamination by Zn, Pb and Cd is traceable to the utilization of these elements as composite materials in metal works.

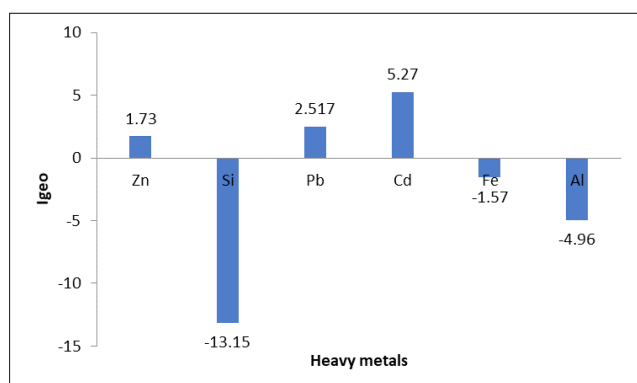


Figure 2: Index of geo-accumulation of heavy metals and metalloids in Metal works soil.

Contamination Factor

Likewise, the contamination factors of 1.64×10^{-4} , 0.048 and 0.503 for Si, Al and Fe respectively which were generally less than one, indicating low contamination with respect to Si, Al and Fe around the metal works. However, the contamination factor of Zn (4.97) was within (≥ 3 to < 6) classified as considerable contamination with respect to zinc.

The contamination factors of Pb (8.58) and Cd (57.9) were both greater than 6, implying very high contamination of the soil with respect to Pb and Cd respectively due to metal works. These metals are quite mobile in the environment and when accumulate in plants inhibits growth and photosynthetic activity [33].

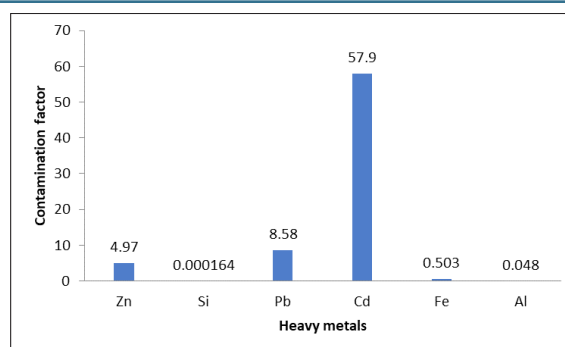


Figure 3: Contamination factor of heavy metals and metalloids in Metal works soil

Health Risk Assessment

Non-carcinogenic risk assessment of Zn, Fe, Al, Cd and Pb presented in Tables 4 on the basis of three human exposure routes: ingestion, inhalation and dermal exposure showed the HQ values for ingestion and inhalation for both children and adult were all less than 1. However, the HQ values for dermal contact of Fe, Al, Cd and Pb were greater than 1 for both children and adult. Likewise, the HI values of exposure to Fe, Al, Cd and Pb around the Metal works were all greater than 1 for both children and adult implying a potential non-carcinogenic health effect.

Cancer Risk (CR) of Pb and Cd in adults were all greater than the value found for children in all respect either via ingestion, inhalation or dermal route of exposures. The cancer risk of Pb via dermal exposure CR_{derm} (0.0169) is greater than CR_{ing} (1.33×10^{-13}) in children, this correlate with the CR_{derm} (0.0178) as against the CR_{ing} (1.42×10^{-13}) in adult. Likewise, the cancer risk of Cd via inhalation CR_{inh} (7.75×10^{-9}) is greater than the risk by means of oral ingestion CR_{ing} (4.07×10^{-12}) in children as well as CR_{inh} (8.32×10^{-9}) as against CR_{ing} (4.15×10^{-12}) in adult with respect to Cd exposure. International Agency for Cancer Research have considered both Pb and Cd as cancer agent classifying Pb (group 2B) and Cd (group 1) [34].

The CR_{derm} of both Cd and Pb exceeded the carcinogenic risk limit of 1.0×10^{-4} hence indicates a lifetime cancer risk to both children and adults [21]. High lead levels can affect the central nervous, renal, cardiovascular, gastrointestinal, musculoskeletal, reproductive, neurological, endocrine, hematopoietic, developmental and immunological systems [35,36]. Increases in tumor and various cancers risk such as lung, prostate, jugular, and pancreatic cancer due to Cd exposure through environmental and occupational means have been reported by a number researchers [37-39]. Early exposure of Cd to children is associated to low intelligent quotient in children even at low concentration [40].

Group	Metals	HQing	HQinh	HQderm	HI	CRing	CRinh	CRderm
Children	Zn	1.59×10^{-9}	2.54×10^{-7}	0.20	0.20	NC	NC	NC
	Pb	1.11×10^{-8}	6.07×10^{-7}	7.58	7.58	1.33×10^{-13}	NC	0.0169
	Cd	8.14×10^{-9}	1.23×10^{-6}	20.80	20.80	4.07×10^{-12}	7.75×10^{-9}	NC
	Fe	3.77×10^{-6}	5.71×10^{-4}	96.16	96.16	NC	NC	NC
	Al	5.04×10^{-9}	2.83×10^{-6}	128.5	128.5	NC	NC	NC
Adult	Zn	1.70×10^{-9}	2.58×10^{-7}	0.217	0.2172	NC	NC	NC
	Pb	1.19×10^{-8}	7.07×10^{-6}	80	80	1.42×10^{-13}	NC	0.0178
	Cd	8.73×10^{-9}	1.32×10^{-6}	22.30	22.30	4.15×10^{-12}	8.32×10^{-9}	NC
	Fe	4.04×10^{-6}	6.13×10^{-4}	103.03	103.03	NC	NC	NC
	Al	5.40×10^{-9}	3.03×10^{-6}	137.7	137.7	NC	NC	NC

HQ = Hazard quotient, HI = Hazard index and CR = Cancer risk, NC= Not calculated

Table 4: Human Risk Assessment of Carcinogenic and Non-carcinogenic Heavy metals

Conclusion

The study revealed that all heavy metals and metalloids determined in soils around Metal works Wukari were present in the order concentration: Fe > Al > Zn > Pb > Si > Cd and soil quality parameters such as pH being alkaline suggesting moderate availability of heavy metals. However, ecological and health risk assessment implied contamination of the by Zn, Pb and Cd and health risk by Al, Fe, Pb and Cd respectively. Hence, the soil is recommended for cleanup in order to guaranty sound health and ecological sustainability with respect to the contaminants. Further study could be carried out human and animal sample within the vicinity to find out if there is bioaccumulation of the determined analytes.

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