



Speciation, Bioavailability and Human Health Risk of Heavy Metals in Soil and Spinach (*Amaranthus spp.*) in Kano Metropolis, Northwestern-Nigeria

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ABSTRACT

The rapid population growth and industrialization affected the environment momentarily and one of the most noteworthy impacts is the toxicological effect of toxic chemical pollutants. The noxiousness of toxic heavy metals to ecosystem rests on their biochemical form therefore, measuring their chemical status gives more information than the determination of the concentration. This research aimed at assessing the chemical forms of heavy metals and ecological effects. Eight soil and spinach samples were collected using point composite sampling method. The soil was analyzed using five stages of sequential extraction methods. The results were subjected to statistical analysis to carry out a descriptive and inferential statistic. The results revealed that significant fraction of the heavy metals exist in carbonate bond form (63.57%) which is accessible to plant, then residual (11.46%), Fe – Mn oxide (9.39%), organically bond (8.12%) and, exchangeable form (7.53%), furthermore, Ni (100.02 mg kg⁻¹) and, Pb (29.02 mg kg⁻¹) have the highest concentration in the spinach. The bioavailability of chemical pollutants ranked in this direction as: Ni > Cd > Pb > Zn & Cu > Cr. The high potential of non-carcinogenic effect by Ni and the carcinogenic effect in the area due to elevated values of risk proportion and risk guide. The available form of heavy metals is present in substantial proportion and consequently, there is serious threat with regard to the carcinogenic effect.

Keywords: Bioaccumulation, Health risk, Heavy metals, Sequential extraction, Toxicity

INTRODUCTION

Heavy metals are tenacious in soil ecosystem, contaminate various tropics level in the food chain and consequently causes some ecological problems due to their toxicity (Ali *et al.*, 2019). Extensive heavy metal pollution of soil within and around metropolis implies that water bodies (surface and groundwater) within the environment may correspondingly be polluted due to continuous interactions between soil and water, and high spreading rate by leaching and runoff (Virukyte and Sillanpaa, 2006). Some of the major sources of increasing heavy metal concentration into the ecosystems in Nigeria include industrial and domestic waste generation and, auto mechanic activities (Adewole and Uchegbu, 2010). However, soil is the medium of plant growth, the habitat of various forms and types of living organisms and almost all living organisms on the earth depend either directly or indirectly on the resources provided by the soil (Hall, 2008; Mohammed, 2017). Therefore, alteration of soil quality by contaminants may affect the capability and capacity of soil to provide ecological services to the environment (Mohammed *et al.*, 2015). The ecological effect of heavy metal is not only concerned with total concentration in soil, but also in the distribution of its chemical speciation that

exist in soils (Wei *et al.*, 2019). Various form of heavy metals exert a serious forms of ecotoxicological effect which directly affect the natural cycling and heavy metals migration. The speciation of heavy metals identified five forms as: exchangeable fraction, bound to carbonate, bound to oxides, bound to organics and residual fraction (Kanat *et al.*, 2018). The soil's ability to immobilize heavy metals increases with rising pH, organic carbon (OC), clay and cation exchange capacity (CEC), and peaks under mildly alkaline conditions (Brady and Weill, 2014).

The bio-accumulated heavy metals transferred from one tropic level to another in the food chain, thereby the magnitude of accumulation depend on the rate of accrual and elimination from vegetables (Ali *et al.*, 2019). The quantity of heavy metals accumulated in the vegetables hinge on the chemical form in which heavy metals exist in soil and the advancement of physiological mechanisms of the vegetable for purification, homeostasis and regulation of heavy metals (Ali and Khan, 2018). Heavy metals contained in the vegetables can be superbly perilous to the human body system even at low level due to their gradual accumulation in to body system (Ghosh, 2012). The toxic heavy metals causes of human health risk which include cancer, mutilation to renal system, hepatic and,

mental retardation, thus avoiding uses of vegetable cultivated in contaminated environment may reduce the potential risk transmitted by toxic heavy metals (Latif *et al.*, 2018). Determination and evaluation of heavy metals and bioaccumulation is very pertinent because sustainable management strategies can be proposed to remediate and mitigate the ecotoxicological effect of heavy metals in the area.

Some studies like Haruna *et al.* (2019) determine the concentration of some heavy metals in irrigation water, therefore the partitioning of heavy metals in soil, bioaccumulation and ecotoxicological effect were not considered. However, it is generally recognized that the unique behavior of heavy metals in soil is determined by their specific chemical form rather than their total concentration. This is because concentration of heavy metals in soil gives a limited information about their potential behavior, bioavailability and, heavy metal of geological origin may not be detected (Ogunbanjo *et al.*, 2016). To prevent the environmental health risk posed by heavy metals, the exploration of heavy metals through chemical speciation, bioaccumulation status and, health hazard are very important for environmental

sustainability and harmony. The objectives of the paper is to evaluate the chemical speciation of heavy metals, bioavailability and human health hazard in the area.

MATERIALS AND METHODS

Study Area

The study was conducted in irrigated land around mechanical village located within Kano Metropolis where waste water emanates from mechanical workshop, city abattoir and other domestic sources. The area lies between Latitude $12^{\circ}1'11''\text{N}$ to $12^{\circ}1'23''\text{N}$ and longitudes $8^{\circ}31'25''\text{E}$ to $8^{\circ}31'35''\text{E}$ (Fig. 1). The area fall within the basement complex and is about 500m above mean sea level with little granite, few literate outcrops and relatively plain (Olofin, 1987).

Materials

The materials used include soil auger and spade for collecting the soil samples, pH meter, Global Position System (GPS), polyethylene bags, marker for labeling the samples, measuring tape to measure the distance and Atomic Absorption Spectrophotometer (AAS) for heavy metals determination.

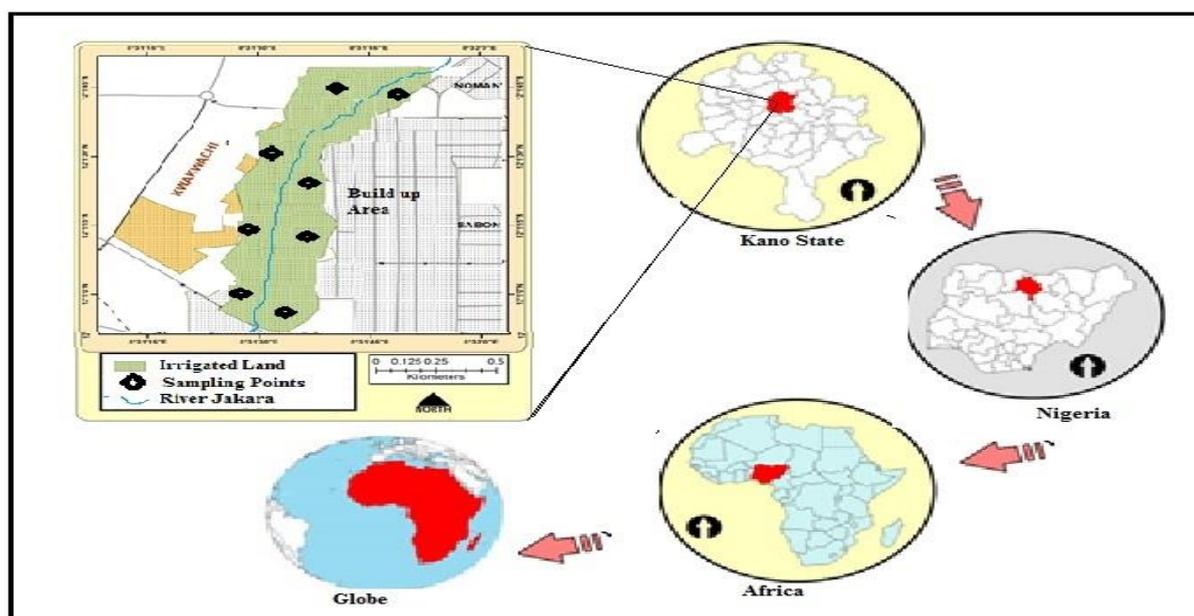


Fig. 1. Study Area Showing Sampling Points

Soil and Spinach Sampling

Free traverse soil sampling method was adopted because of the morphology of the sampling area. The traverse lines were drawn along the irrigated land and sampling points were established along the traverse line of about 500 m interval. Point composite sampling methods was used whereby five different samples were collected from 0 – 15 cm depth within a sampling point (Fig. 2), the samples collected were mixed vigorously, homogenized to form a bulk samples and, then about 1 kg (composite sample) sample was collected out of the bulk sample. The samples

collected were kept into polyethylene bags, leveled appropriately and then taken to the laboratory for further analysis. The edible parts of spinach were collected as samples using hand-picked at each sampling point and then kept in polyethylene bags for the laboratory analysis.

The selected heavy metals Cadmium (Cd), Copper (Cu), Zinc (Zn), Lead (Pb), Chromium (Cr) and Nickel (Ni) were extracted using the five forms of sequential extraction as described by Tessier *et al.* (1979). Exchangeable fraction: 1g of soil was extracted at room temperature for 1 hour with 16 cm³ of magnesium chloride solution (1 M) at pH of

7.0. Soil and extracted solution was thoroughly agitated throughout the extraction. Metals extracted in the exchangeable fraction include weakly

adsorbed metals that can be released by ion-exchange process.

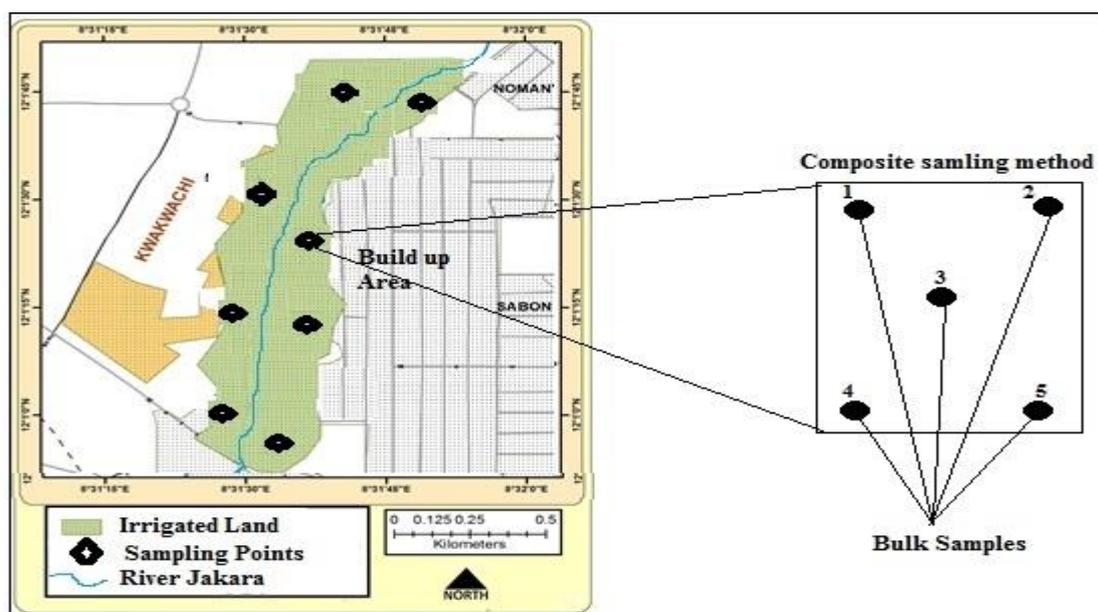


Fig. 2: Study Area Showing Composite Sampling Procedure

Experimental Procedure for Heavy Metals Determination

Bound to Carbonates: The residues of exchangeable fraction were extracted with 16ml of 1 M sodium acetate/acetic acid buffer at pH 5.0 for 5 hour at room temperature. The residual soils were used for the next extraction.

Bound to Oxides: 13.9 g of hydroxyl amine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) was dissolved in 500ml of distilled water to prepare 0.4M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) acetic acid with agitation at 96 °C in a water bath for 6 hour.

Bound to Organics: The residues from bound to oxides were oxidized as follows: 3cm³ of 0.02M HNO_3 and 5cm³ of 30% (v/v) hydrogen peroxide(which were adjusted to pH 2.0) were added to the residue from bound to oxides. The mixture was heated to 85 °C in a water bath for 2 hours with occasional agitation and allowed to cool down. Another 3cm³ of 30% hydrogen peroxide, adjusted to pH 2.0 with HNO_3 , was then added. Residues from bound to organics were oven dried at 105°C. Digestion was carried out with a mixture of 5cm³ conc. HNO_3 (70% w/w), 10cm³ of hydrofluoric acid (40% w/w) and, 10cm³ of perchloric acid (HClO_4 , 60% w/w). The solution of each form was aspirated into AAS and the results displayed at the read out meter of the AAS.

The results of laboratory analysis were analyzed using descriptive statistics such as mean to determine the mean concentration of heavy metals and standard deviation. The bioavailability of heavy metals in the spinach was evaluated using equation 1.

$$bf = \frac{x}{y} \quad (1)$$

where bf is the bioavailability, x is the heavy metal values in soil and y is the heavy metals values in spinach (Mohammed, 2018). The potential health risk of heavy metals intake via ingestion were evaluated based on the estimated daily intake (EDI) as described in Adedokun *et al.* (2016), hazard quotient (HQ) and, hazard index (HI) described by United State Environmental Protection Agency (USEPA, 2011). The EDI was evaluated using equation 2.

$$EDI = \frac{C_{\text{metal}} \times D_{\text{food intake}}}{BW_{\text{average}}} \quad (2)$$

where C_{metal} is the metals concentration in spinach in mg kg⁻¹, $D_{\text{food intake}}$ is the daily intake of spinach in kg/P and BW_{average} . The average daily consumption of 0.2 kg of average spinach was assumed in the study and average adult body weight was considered to be 60 kg (Iwanyanwu and Chioma, 2019). For the evaluation of hazard risk, the non-carcinogenic and carcinogenic effect of heavy metals were applied to ingestion exposure path way. The non-carcinogenic risk was evaluated by determine the Hazard Quotient (HQ) as expressed in equation 3.

$$HQ = \sum \frac{EDI}{RFD} \quad (3)$$

where HQ is the hazard quotient, EDI is the estimated daily intake for all the heavy metals and RFD is the reference dose which is assumed to be a

day-to-day consumption of heavy metals throughout the life time that would not cause adversarial health effect to human (Dee *et al.*, 2019). Based on the USEPA IRIS (2006), the following RFD for Cd (0.001 mg/kg/day), Cu (0.040 mg/kg/day), Zn 0.300 mg/kg/day), Pb 0.0053 mg/kg/day), Cr (1.5 mg/kg/day) and, Ni (0.020 mg/kg/day) were adopted for this work. The carcinogenic risk was evaluated by summation of the HQ for all the heavy metals under investigation as expressed in equation 4.

$$HI = HQ_A + HQ_B + HQ_C + HQ_n \quad (4)$$

where HI is the hazard index, HQ_A is the target HQ for A intake, HQ_B is the target HQ for B intake, HQ_C is the target HQ for C intake and, HQ_n is the target HQ for n intake. If HI is < 1 its assumed there is no significant risk of non-carcinogenic effect. It is further stipulated that if the HI is > 1 there is potentials of non-carcinogenic effect may occur. However, if HI is within the range of threshold values ($10^{-4} - 10^{-6}$) thus, cancer risk is acceptable (Ogunbanjo *et al.*, 2016).

RESULTS AND DISCUSSIONS

Table 1: Partition of Heavy Metal in the Study Area

Heavy Metals	Forms of Heavy Metals in mg kg ⁻¹										
	Exchangeable 7.53%		Carbonate Bond 63.57%		Fe-Mn Oxide 9.39%		Organically bond 8.12%		Residual 11.46%		Sum of the mean
	Mean	±Sd	Mean	±Sd	Mean	±Sd	Mean	±Sd	Mean	±Sd	
Cd	0.04	0.01	0.05	0.01	0.09	0.07	0.37	0.05	0.37	0.24	0.92
Cu	0.05	0.02	0.04	0.04	0.18	0.27	0.10	0.07	0.36	0.18	0.73
Zn	0.24	0.35	0.52	0.69	0.57	0.61	0.56	0.76	2.59	2.04	4.48
Pb	3.52	2.3	4.05	1.88	3.23	2.17	5.14	4.16	30.9	13.71	46.83
Cr	0.21	0.12	0.42	0.74	0.39	0.19	0.18	0.27	1.73	0.76	2.92
Ni	0.41	0.38	0.37	0.44	0.25	0.30	0.30	0.37	0.91	1.17	2.24

The carbonate bond forms of heavy metals shows that, Cu (0.04 mg kg⁻¹) has the lowest concentration, while Pb (4.05 mg/kg) recorded highest mean values. The concentration level of heavy metals for the entire fraction followed order as: Pb > Zn > Cr > Ni > Cd > Cu. High concentrations of Pb in carbonate form indicates that Pb is greatly obtainable by the soil microbes and plant in the area. This is contended by Kanat *et al.* (2018) that heavy metals in carbonate form is naturally available to soil microbes and plant. Carbonate bond heavy metals have the highest percentage (63.57%) among the five forms of heavy metals. High percentage of heavy metals in carbonate form indicates that, 63.57% of the concentration of the selected heavy metals are available to be used by soil microbes and plant grown in the area.

The oxide form of heavy metals shows that, Pb (3.23 mg kg⁻¹) has the highest concentration with lowest values in Cd (0.09 mg

The sequential extraction of Cd, Cu, Zn, Pb, Cr and, Ni were evaluated, thereby the mean values, standard deviation and coefficient of variability were presented in table 1. The distribution of heavy metals in the area shows that there is variability in the mean values among the heavy metal and also across the forms in which the heavy meals exist. This is probably due to the fact that, some were found abundantly in nature, while some are rare and can be toxic if found above the threshold limit and also due to sources of soil contaminant in the area (Mohammed, 2015).

The exchangeable forms (Table 1) show that Pb (3.52 mg kg⁻¹) is found to be higher followed by Ni (0.41 mg kg⁻¹) this indicates that Pb recorded higher concentration in exchangeable form than Cd (0.04 mg kg⁻¹), Cu (0.05 mg kg⁻¹), Zn (0.24 mg kg⁻¹), Cr (0.21 mg kg⁻¹) and Ni (0.41 mg kg⁻¹). This implies that Pb can easily be absorbed and exchanged with cation present in the soil colloid and therefore can be available for plant uptake for metabolic activity. The mean value of heavy metals in exchangeable forms followed the order: Pb (3.52) > Ni (0.41) > Zn (0.24) > Cr (0.21) > Cu (0.05) > Cd (0.04).

kg⁻¹). This form of heavy metals has 9.39% among the form of heavy metals. The Pb in oxide form has been reported as the major heavy metals under reducible condition. High Pb concentration in oxide form indicate high anthropogenic source of Pb in the area. The concentration level of heavy metals in oxide form followed the order: Pb > Zn > Cr > Ni > Cu > Cd.

The organically bond heavy metals constituted 8.12% of the heavy metals forms and also observed that, Pb (5.14 mg kg⁻¹) recorded the highest mean value with Cu (0.10 mg kg⁻¹) having low mean value. The concentration of heavy metals under organically form followed the order as: Pb > Zn > Cd > Ni > Cr > Cu. The residual form shows that Cu (0.36) has the lowest mean value with Pb (30.90) having the highest concentration level. The residual form is considered as background level of heavy metals in the soil of the area thus, the values of Cd (0.37), Cu (0.36), Zn (2.59), Pb (30.90), Cr (1.73) and, Ni (0.91) are hereby considered as

background level of heavy metals in the soil of the area.

The concentration of heavy metals in the area were compared with the European Union Regulator values (CEC, 2001). Table 2 shows that all the selected heavy metals in soil of the study

area were found to be lower than the E.U values, this indicates that the level of the heavy metals in soil of the area was below the threshold and probably may not pose an ecological risk in the area.

Table 2: Comparison of Heavy Metal of the Area with EU Values

Heavy Metals	Mean Values (mg kg ⁻¹)	EU Values (mg kg ⁻¹)
Cd	0.92	3
Cu	0.73	140
Zn	0.280	300
Pb	46.84	400
Cr	2.92	180
Ni	2.24	75

The result obtained in this research is in line with the results obtained by Mohammed (2010) who discovered that Cd, Pb, Cu, Mo, and Zn was found to be lower than E.U value. This is probably due to slow rate of accumulation of these heavy metals in the area. However, despite the low mean values of all the heavy metals compared to E.U values(CEC, 2001), care should be taken to avoid further buildup of these heavy metals (Cd, Cu, Zn, Pb, Cr and Ni) which may cause ecological risk due to their gradual accumulation and bioavailability in the soil of the area.

Concentration of Heavy Metals in Spinach

The mean values of heavy metals analyses from the biomass (leaves and stems) of spinach

was evaluated and presented in table 3. The mean value of Ni (100.02 mg kg⁻¹) was found to be higher than all the selected heavy metals under investigation followed by Pb (59.02 mg kg⁻¹) with Cu (0.21 mg kg⁻¹) being the lowest among the heavy metals. The orders of heavy metals concentration in spinach follow: Ni > Pb > Cd > Zn > Cr > Cu. High mean values of Ni (100.02 mg/kg) in spinach indicates high bioavailability of Ni which can easily be transferred to the consumers through food chain and accumulates gradually to form an ecological risk. This implies that the consumers of spinach grown in the area may likely be at risk of the Ni and Pb hazard due to their bioavailability status.

Table 3: Mean concentration of heavy metals in spinach

Heavy Metals	Spinach (mg kg ⁻¹)
Cd	2.71
Cu	0.21
Zn	1.31
Pb	59.02
Cr	0.38
Ni	100.02

The heavy metals uptake via spinach by consumers depend on bioavailability of these heavy metals in soil. Despite the low level of Cd in spinach it may pose some ecological risk because Cd is rare in nature and can be toxic even at very low status (Brady and Weil, 2014).

Bioavailability of heavy metals in spinach

The bioavailability level of heavy metals (Table 4) shows that Ni (44.65 mg kg⁻¹) has the highest mean value of bioavailability followed by Cd (2.95 mg kg⁻¹) and Pb (1.26 mg kg⁻¹), whereas Zn (0.29 mg kg⁻¹) and Cu (0.29 mg kg⁻¹) have the same value, while Cr (0.13 mg kg⁻¹) has the lowest values.

Table 4: Mean Bioavailability level of heavy metals in spinach and Soil

Heavy Metals	Spinach (mg kg ⁻¹)	Soil (mg kg ⁻¹)	Bioavailability Factors
Cd	2.71	0.92	2.95
Cu	0.21	0.73	0.29
Zn	1.31	4.48	0.29
Pb	59.02	46.83	1.26
Cr	0.38	2.92	0.13
Ni	100.02	2.24	44.65

This indicated that Ni is more available for uptake by soil microbes and spinach, followed by Cd and Pb. This implies that high bioavailability of Ni and Cd is probably due to the high concentration of Ni and Cd in spinach and can easily transfer to the human body through ingestion and may consequently affect the human health system (Ali *et al.*, 2019). The bioavailability of heavy metals follows the order: Ni > Cd > Pb > Zn & Cu > Cr. The current status of Ni and Cd in spinach are pervasive in the environment with harmful effect on human health and therefore their presence in spinach is a public health concern.

The bioavailability status of heavy metal and their uptake by spinach depend on soil pH, OC, CEC and clay content of the soil (Table 5). The mean values pH (6.08) is considered as slightly acidic and is ideal for most crops because it is within the range that can favour the availability, solubility of heavy metals. This implies that the pH status enhance the dissolution of heavy metals which can easily be taken by spinach for their metabolic processes. This is supported by Mohammed (2017) who explained that the pH range of 6.0 to 6.5 influences the availability and solubility of heavy metals and other essential nutrient.

Table 5. Bioavailability Factors

Bioavailability Factors				
	pH (CaCl ₂)	Clay (%)	CEC (Cmolkg ⁻¹)	OC (%)
Mean	6.08	8.00	15.55	1.07

This was further explained by Brady and Weil (2014) that at high pH more hydroxyl ion (OH⁻) associated themselves and thereby more H⁺ will be produced which will be exchanged with cation heavy metals in the soil solution. The clay content is 8.08 % which is considered as medium level based on ranking of London (1991). The clay status facilitates the adsorption of cation heavy metals (Cu²⁺, Zn²⁺ and, Cr²⁺). This implies that the adsorption of heavy metals by soil colloid is moderate based on the clay status of the soil. The mean value of CEC (5.55 Cmol kg⁻¹) in soil of the area ranked low based on the ranking of London (1991), this is probably attributed to the low organic carbon in the soil. This explained that low CEC in the soil indicated that the soil has low clay and organic colloids (Tan, 2006). The value of CEC obtained in this work is higher than values obtained by Mohammed (2010); Adamu (2014). This indicates that there is gradual increase in the exchangeable cation due to the pH level. This is explained by Brandy and Weil (2014) that cation exchange capacity of the soil increases with increase of exchangeable cation and exchangeable acidity. The low CEC values implies that low or few cation heavy metals were adsorbed and then

exchange within soil ecosystem and would undergo isomorphic substitution slowly due to few exchangeable heavy metals present in the soil solution. The mean value of organic carbon content is 1.07 % and is considered low based on the ranking of London (1991). This implies that the uptake of heavy metals in area by spinach gradually due to the low OC status because at low OC the adsorption and exchange of available cation heavy metals will be low.

Human Health Risk

The estimated daily intake (ingestion) of heavy metals shows that Pb recorded high value, while Cd, Cu, Zn Cr and Ni recorded low values (Table 6). This implies that Pb is vastly accessible and can be ingested by the consumers of vegetables grown in the area. These results coincided with the results of table 1 where Pb was found to be higher among the five forms of heavy metals in the area. The EDI of Ni is the least among the heavy metals which indicates that there is low ingestion of Ni for the consumers of the spinach grown in the area therefore, the EDI in the following order: Pb > Cr > Ni > Cd > Cu > Zn.

Table 6: Estimated Daily Intake of Heavy Metals

Heavy Metals	C _{metal}	D _{food intake}	BW _{average}	EDI
Cd	0.92	0.2	60	0.0031
Cu	0.73	0.2	60	0.0024
Zn	0.28	0.2	60	0.0009
Pb	46.84	0.2	60	0.1561
Cr	2.92	0.2	60	0.0097
Ni	2.24	0.2	60	0.0075

The results of HQ analyses revealed that Pb has the highest HQ values (29.4), followed by Cd (3.1), Ni (0.37), Cu (0.06), Cr (0.006) and, Zn (0.003). This implies that Pb has high risk of non-carcinogenic effect and Zn has less non-carcinogenic effect among the heavy metals considered in this study. The HQ values also revealed that Pb and Cd may pose a health risk, while Ni, Cu, Cr and Zn may pose less or no any health hazard for the consumers of the spinach grown in the area. This is adduced by Raiet *et al.* (2019) who explained that HQ values of less than 1 is considered as safe level and conversely, the HQ values of greater than one could pose a health hazard for the consumer of the spinach grown in the study area. The HQ showed the following order of position Pb > Cd > Ni > Cu > Cr > Ni. The HQ values obtained in this work is higher than the HI values reported by Ogunbanjo *et al.* (2016). However, the carcinogenic effect (HI values) obtained is 32.9 which is by far greater than 1. This indicates that there is greater potential risk of cancer for the consumers of the spinach grown in the study area. It was reported that if the HI level is within the threshold values of 10^{-4} to 10^{-6} it was believed that the cancer risk is acceptable (Ogunbano *et al.* (2016). This implies that there is potential cancer risk for the consumers of spinach that grown in the study area since the HI values is 3.6×10^{-2} .

CONCLUSION

There is gradual accumulation of heavy metals in the soil, therefore the background level of heavy metals in the area was determined as a residual form and can be used in estimating the level of anthropogenic form of heavy metals. The low bioavailability level of Cu, Zn, Pb, Cr in the study area result from pH and CEC and OC level of the soil in the area which influence, their solubility and availability in the soil. Ample quantity of the heavy metals are accessible by the crop grown in the area and consequently, there is a serious threat with regard to carcinogenic effect of the heavy metal in the area.

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