

Heavy Metal Speciation and Health Risk Assessment of Soil and Jute Mallow (Corchorus olitorus) Collected From a Farm Settlement in Ikorodu, Lagos, Nigeria

Olatunji Mojeed Makanjuola^{1*}, Babatunde Saheed Bada¹, Oriyomi Olalekan Ogunbanjo², Olanrewaju Olusoji Olujimi¹, Oluseyi Adeboye Akinloye¹, Moyosoluwa Odunayo Adeyemi³

¹Department of Environmental management and Toxicology, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria ²Department of Chemical Sciences, Tai Solarin University of Education, Ijagun, Ogun State, Nigeria

³Department of Geology, Crawford University, Igbesa, Ogun State, Nigeria

Email: *tunji.makanjuola@yahoo.com

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Abstract

There is an increasing global concern for adverse effects of inorganic fertilizer and pesticides applied to agricultural soils. This study investigated metal speciation in soil and health risk assessment of Jute mallow (Corchorus olitoriuos) from a farm settlement in Ikorodu, Lagos State. Soil samples were collected according to the set standard procedure, sequentially extracted and analyzed for selected heavy metals using standard methods. Results showed that chromium (Cr) was associated with reducible fraction (Fe-Mn) for top soil, while cadmium (Cd), manganese (Mn), and copper (Cu); lead (Pb) and nickel (Ni); and Cr were predominantly bound to carbonate, reducible and residual mineral components respectively for sub-soil. The results of Contamination Factor (CF), Contamination Degree (CD), Pollution Load Index (PLI) and Geoaccumulation Index $(\mathrm{I}_{\mathrm{geo}})$ showed that the soil samples were not polluted for all the investigated metals. The Cd level in the soil (13.54 \pm 1.21 mg·kg⁻¹) and vegetables $(0.83 \pm 0.05 \text{ mg·kg}^{-1})$ were above the USEPA critical permissible limit of 3.0 mg·kg⁻¹ and 0.1 - 1.2 mg·kg⁻¹ respectively. The daily intake of estimated selected heavy metals from the vegetable ranged from 8.8 \times 10 $^{-03}$ to 1.4 \times 10 $^{-02}$ for adult and 3.8 \times 10 $^{-03}$ to 1.1 \times 10 $^{-02}$ for children while the Hazard Quotient (HQ) for adults ranged from 5.4×10^{-05} to 1.1 \times 10⁻⁰¹ and that of children ranged from 8.3 \times 10⁻⁰³ to 1.4 \times 10⁻⁰². The cancer risk (CR) values of heavy metals in the soil ranged from 1.02×10^{-11} to $9.90 \times$ 10^{-10} and 4.45×10^{-09} to 8.61×10^{-09} for children and adults respectively. The level of cancer risk was below the threshold values $(10^{-4} - 10^{-6})$ which USEPA considered as unacceptable risk. The consumption of Jute mallow grown at Ikorodu Farm Settlement is assessed to be free of risk. Hence heavy metal analysis should be included in routine soil analysis before planting.

Keywords

Inorganic Fertilizer, Pesticides, Health Risk, Jute Mallow, Heavy Metals

1. Introduction

In Nigeria, the rate of increase in human population which, according to the National Population commission, stood at 88.6 million people in 2006, (and is projected to hit 160 million within the next one decade) does not enjoy a corresponding rate of increase in food supply [1] [2]. This thus creates a huge food supply deficit among Nigerians as food demand far outstripped the level of supply, creating an immense pressure on the available food items with the attendant increases in market prices [1]. Availability of food is a major issue in food security and in order to provide for more food, more lands are cultivated and fertilizer and pesticides are increasingly used. Vegetables are part of human diet to take up a lot of essential nutrients and certain trace elements in a short period. In this situation, safety of vegetables is very important [3] [4].

Findings reveal that vegetable farmers use a wide range of pesticides at different levels to reduce losses from pests and diseases. However, despite the contribution of pesticides to agricultural production, pesticides are of major environmental concern. Many pesticides and chemicals are not biodegradable, they bioaccumulate in the food chain and detrimental to human and the ecosystem [5] [6]. The repeated applications of these agrochemicals potentially contributed to the accumulation of heavy metals in agricultural soils as some of these fertilizers and pesticides contain heavy metals such as Cd, Pb, Zn [7]. The accumulation of heavy metals in soil of the study area could either directly endanger the natural soil functions, or indirectly endanger the biosphere by bioaccumulation in the food chain, and ultimately endanger human health [8].

It is commonly acknowledged that total soil heavy-metal concentration alone is not a good measure of bioavailability and is not a very helpful tool to determine the potential risk associated with soil contamination. Therefore, chemical speciation, which plays a vital role in determining the bioavailability of toxic metal in a soil solution, is often used as a predictor of metal bioavailability to soil organisms and plants [9]. The chemical forms of the metal control its bioavailability or mobility. The exchangeable and acid extractable fractions are mobile fractions that are easily bioavailable [10]. This bioavailable metals in the soil provides rough estimate of metal uptake by plants (especially edible plants) and their risk assessment.

Heavily contaminated soils may pose long-term risks to ecosystems and human health [11] [12] [13] via the increased uptake and accumulation of heavy metals in plant tissues [14] [15] [16]. Risk assessment has emerged in recent years as a powerful tool in the analysis of environmental and/or occupational hazards [17] [18]. This discipline is becoming increasingly important in modern toxicological and epidemiological practice, both in terms of hazard evaluation as well as at the level of efficient disease control and prevention [19] [20] [21]. Environmental analysis has largely contributed in this direction by careful monitoring of contaminant distribution over space and time [22] [23].

Several studies recently have examined heavy-metal transfer from soil to vegetables [24] [25] [26] [27]. Many studies have also reported that the bioavailability of soil metal to vegetable is controlled by soil properties, soil metal speciation, and plant species [28] [29] [30]. However, not so much has been done on effect of fertilizer and pesticide application on redistribution and bioavailability of heavy metal in soil and vegetable and their possible associated health risk. It is on this background that this study seeks to determine effect of fertilizer and pesticide application on metal speciation in soil and vegetable and to assess the health risk of human exposure to heavy metal from soil and vegetable.

2. Materials and Methods

2.1. Study Area

This study was conducted in a farm settlement in Ikorodu, Lagos state, Nigeria. Ikorodu Farm settlement is on the designated areas for farming in Lagos State. It is located in Ikorodu, its geographical coordinates falls within 6°40'0" North, 3° 40'0" East. The farmers in the Settlement are into several aspects of agriculture, ranging from crops farming and animal husbandry which cut across snail farming, poultry production, piggery, grass cutter farming, Vegetable farming and others. It is bounded in the North by Agbowa-Ikosi town; in the South by Isiu town, in the East by Gberigbe town, while in the West by Ode-Remo town with considerable land mass of approximately 502 square kilometres. The map of the area was shown in **Figure 1**.

2.2. Sample Collection

Soil samples were collected randomly at 0 - 15 and 15 - 30 cm depth after land clearing, before the application of fertilizer and pesticide. The sample was collected at the uphill, hill wash and valley bottom. Two (2) weeks later after fertilizer application, pesticide application soil sample was collected at the same depth. Soil and vegetable samples were collected 4 weeks after pesticide application (**Table 1**).

2.3. Physicochemical Analysis of Soil Samples

Soil pH was determined using pH meter at a ratio of 1:2.5 soil/water according to the procedure described by [31]. The soil moisture content was determined according to the procedure outlined by [32] while the cation exchange capacities of the soil samples were determined by ammonium saturation method. Organic carbon and the organic matter were determined according to the procedure

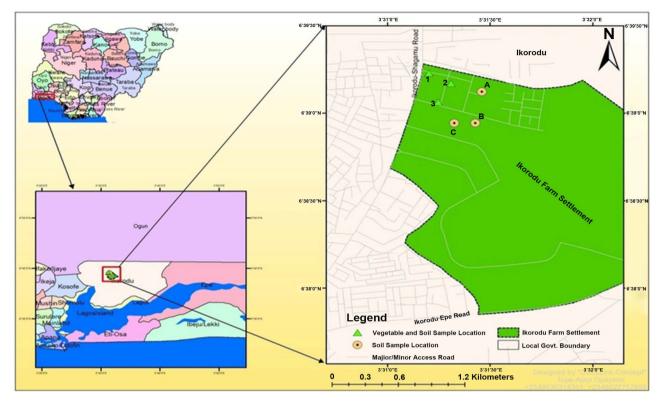


Figure 1. Map of the study area showing sampling points (field study).

Table 1. S	Sample colle	ection of soil	and vege	table at ikor	odu farm	settlement.

S/N	Commlo	Depth/Number of Sample						
	Sample —	Stages of Sample Collection	0 - 15	15 - 30				
1	Soil	Immediately after land clearing	3	3				
2	Soil	2 weeks after fertilizer application	3	3				
3	Soil and vegetable	2 weeks after pesticide application	3	3				
4	Soil and vegetable	4 weeks after pesticide application	3	3				

outlined by [33]. Total Nitrogen was determined by the regular macro-Kjeldahl method while Phosphorus was determined according to Bray-1 method [34].

2.4. Sequential Extraction of Heavy Metals

A large number of sequential extraction methods have been reported, many of which are variant on Tessier procedure [35] in which the exchangeable metals and those nominally associated with different reagents. In defining the desired partitioning of metals, care was taken to choose fractions likely to be affected by various environmental conditions; the five fractions (Exchangeable, Carbonate bound, Reducible, Oxidizable, Residual) were selected in this study and this method was developed by [35] and modified by [36].

The sequential extractions were carried out on 1 g of soil, in 85 ml polypropylene centrifuge tube to simplify centrifuge-washing of the residue after each extraction and to minimize contamination risks and any loss of the solids through the successive extraction steps. The sample suspensions with extractant were stirred at 220 min⁻¹ using a Rotavit shaker (Selecta). After each extraction step, the suspensions were centrifuged at 3000 min⁻¹ (Heraeus SAPATECH centrifuge) for 30 min. The supernatants were carefully removed and stored in polyethylene bottles at 4°C. The residues were washed with ultrapure water before the addition of the next extracting agent.

2.5. Vegetable Digestion

Digestion of the vegetable was carried out according to the method described by [37] with some modifications. Five milliliter (5 ml) of concentrated nitric acid and five ml of hydrogen peroxide were added to one gram of the vegetable sample and heated on a hot plate at a temperature of 60°C to near dryness. Ten milliliter (10 ml) of deionized water was then added to the mixture and then filtered. The digested sample was made up to 100 ml and stored for analysis.

2.6. Chemical Analysis

The concentration of Pb, Cd, Cu, Zn and Fe present in the soil extracts and vegetable digest were assayed using AAS (Buck Scientific Model 200 A) with air acetylene flame. The calibration of AAS was done using multi-elemental solution prepared by serial dilution of 20, 10, 5, 3, 2 and 1 ppm with r^2 value above 0.9 before the analysis of the samples. As samples were aspirated into the flame, the heavy metals of interest present in the sample absorbed some of the light from the hollow cathode lamp reducing the intensity of the light transmitted. The computer data system of the machine converted the intensity of light into the absorbance which was directly proportional to the concentration of the heavy metals present in the sample. The metal concentration in mg/l was converted to mg/kg using the following equation:

$$Metal \operatorname{conc} \cdot (mg/kg) = \frac{\operatorname{metal} \operatorname{conc} \cdot (mg/l) \times \operatorname{dilution} \operatorname{factor}(l)}{\operatorname{mass of the sample}(kg)}$$
(1)

2.7. Data Analysis

Descriptive (Mean and Standard deviation) and inferential (ANOVA) statistics were used. Duncan was used to compare means using statistical analysis system (SAS). The data were expressed as mean \pm standard deviation. The significant differences between groups were compared to find out the major biogeochemical processes controlling the distribution and partitioning of metals.

2.8. Potential Human Health Risk of Metals in the Study Sites

The health risk assessment model used in this study to calculate the exposure risk to children and Adults from heavy metals in soil is based on those models developed by [38] and the Dutch National Institute of Public Health and Environmental Protection [39] which defines guidelines or screening levels of con-

taminants in soils in urban exposured scenarios. Human exposure to heavy metals in soil can occur via the following three main paths: a) direct ingestion of substrate dust particles (CDI_{ing}); b) inhalation of suspended dust particles through mouth and nose (CDI_{inh}); c) dermal absorption of heavy metals in particles adhered to exposed skin (CDI_{dermal}). The dose received through each of the three paths was calculated using the following Equations (2)-(4) [38] [40].

For cancer risk, only the carcinogen risk for inhalation exposure modes was considered in the model, and was used in the assessment of cancer risk [41] [42].

$$CDI_{ing} = C_{UCL} \times \frac{R_{ing} \times F_{exp} \times T_{exp}}{ABW \times T_{avg}} \times 10^{-6}$$
(2)

$$CDI_{lnh} = C_{UCL} \times \frac{R_{lnh} \times F_{exp} \times T_{exp}}{PEF \times ABW \times T_{avg}}$$
(3)

$$CDI_{dermal} = C_{UCL} \times \frac{SAF \times A_{skin} \times F_{exp} \times T_{exp}}{ABW \times T_{ave}}$$
(4)

where CDI (mg·kg⁻¹·day⁻¹) is the Chemical daily intake through ingestion (CDI_{ine}) , inhalation (CDI_{inh}) , dermal contact (CDI_{dermal}) R_{ine} is the ingestion rate at 200 mg·day⁻¹ for children (1–6 years) and 100 mg·day⁻¹ for adults [43]; R_{inh} is the inhalation rate at 7.6 m³·day⁻¹ for children and 20 m³·day⁻¹ for adults [42]. Exposure frequency (F_{exp}) in this study was 180 day-years⁻¹ [44] while exposure duration (T_{exp}), in this study, was 6 years for children and 24 years for adults [45]. Average body weight (ABW) was 15 kg for children and 70 kg for adults [43] while *PEF* is the particle emission factor taken to be $1.36 \times 10^9 \text{ m}^3 \cdot \text{kg}^{-1}$ for both children and adults [46]. Skin surface area (A_{skin}) was 2800 cm² for children and 3300 cm^2 for adults [46] and SAF is the skin adherence factor given as 0.2 mg cm²·h⁻¹ for children and 0.07 mg·cm²·h⁻¹ for adults [47]. Dermal absorption factor (DAF) (unitless) was 0.001 for both children and adults [48]. T_{avg} is the average time [fornon-carcinogens T_{avg} = 365 9 Texp; for carcinogens T_{avg} = 70 × 365 = 25,550 days [43]. C_{UCL} (exposure-point upper confident limit content $[mg \cdot kg^{-1}]$) which is the upper limit of the 95% confidence interval for the mean was calculated using equation v [43].

$$C_{UCL} = X + t_{1-\infty,df} \frac{s}{\sqrt{n}}$$
(5)

where X is the arithmetic mean, s is the standard deviation and n is the number of samples. In this study, quantified risk or hazard indexes for both carcinogenic and non-carcinogenic effects were applied to each exposure pathway in the analysis. The chemical daily intake (CDI) for different exposure pathways was calculated for each element and subsequently divided by the corresponding reference dose yields a hazard quotient (HQ) (non-cancer risk). For carcinogens, the chemical daily intake (CDI) was multiplied by the corresponding slope factor to produce an estimate of cancer risk. Hazard index (HI) is equal to the sum of HQ. If the value of HI (non-cancer risk) is < 1, it is believed that there is no significant risk of non-carcinogenic effects; if the value of HI > 1, there is a chance that non-carcinogenic effects may occur [49]. If the value of HI (cancer risk) falls within the range of threshold values $(10^{-4} - 10^{-6})$, the cancer risk is acceptable [50]. Therefore, hazard index methods and cancer risk methods were used to assess the human exposure to heavy metals in the study area.

$$HQ = \frac{CDI_{ing}}{RfD_o} = \frac{CDI_{dermal}}{RfD_o \times GIABS} = \frac{CDI_{inh}}{RfD_i \times 100 \ \mu\text{g/mg}}$$
(6)

2.9. Potential Daily Intake of Vegetable at the Study Site

The methodology for the estimation of non-carcinogenic risks was provided in the USEPA Region III's Risk-based Concentration Table [51]. The non-carcinogenic risk for each individual metal through vegetables consumption were assessed by the target hazard quotient (*THQ*) (US Environmental Protection Agency [43], which is the ratio of a single substance exposure level over a specified time period (e.g., sub-chronic) to a reference dose (*RfD*) for that substance derived from a similar exposure period. The equation used for estimating the target hazard quotient is as follows:

$$DIR = C_{\text{(metal conc.)}} \times C_{\text{(factor)}} \times D_{\text{(veg intake)}}$$
(7)

where $C_{(\text{metal conc})}$ = heavy metal concentration in vegetable (mg·kg⁻¹);

 $C_{(\text{factor})} = \text{conversion factor (0.085)};$

 $D_{(\text{vegetable intake})} = \text{Daily intake of vegetable } (\text{kg·person}^{-1} \cdot \text{day}^{-1}).$

$$THQ = \frac{E_{fr} \times ED \times DIR}{RfD \times BW \times AT}$$
(8)

In order to assess the overall potential for non-carcinogenic effects from more than one heavy metal, a hazard index (*HI*) has been formulated based on the Guidelines for Health Risk assessment of Chemical Mixtures of US Environmental Protection Agency [46] as follows:

$$HI = \sum TTHQ = TTHQ_{veg1} + TTHQ_{veg2} + \dots + TTHQ_{veg n}$$
(9)

where, *THQ* is the target hazard quotient; *EFr* is the exposure frequency (365 days/year); *ED* is the exposure duration (70 years); *C* is the metal concentration in foods (mg·kg⁻¹·fw); *RfD* is the oral reference dose (mg·kg⁻¹·day⁻¹); *AT* is the averaging time for non-carcinogens (365 days/year × number of exposure years). The oral reference doses were based on 1.5, 0.02, 0.04, 0.0003, 0.0005, and 0.004 mg·kg⁻¹·day⁻¹ for Cr, Ni, Cu, As, Cd, and Pb, respectively [51] [52]. If the *THQ* is less than 1, the exposed population is unlikely to experience obvious adverse effects. If the *THQ* is equal to or higher than 1, there is a potential health risk and related interventions and protective measurements should be taken.

3. Results and Discussion

The descriptive statistics result of the physico-chemical properties at the study location is presented in Table 2 and Table 3 while the result of metal speciation of the soil for both top and sub soil for six elements and for all soil treatment is

shown graphically in Figure 2.

The result revealed that the total extractable cadmium levels in the study area were above the critical permission of 3.0 $\text{mg}\cdot\text{kg}^{-1}$ for agricultural soil [53] [40]. Cadmium was found to be mostly associated with the residual fraction in the top soil and carbonate fraction in the sub soil with percentage range of 34.7% to 44.9% and 33.6% to 46.2% respectively (Figure 2). The high percentage of Cadmium in residual fraction in the top soil shows that Cd is occluded in crystalline structures and has high stability. This result is in agreement with the observation of several researchers [54] [55]. By these criteria, cadmium must be considered quite mobile and biologically available in the soil samples. The availability of this metal in the sequentially extracted fractions in the top soil shows the order; Residual (34.7% to 44.9%) > Carbonate (23.1% to 29.8%) > Exchangeable (3.4% to 31.5%) > Reducible (6.51% to 20.0%) > Oxidizable (0.74% to 1.81%) (Figure 2). These extractable metals may find their way through the food chain into human body. Cadmium in the body is known to affect several enzymes [56]. It is believed that the renal damage results in proteinuriais, the result of Cd adversely affecting enzymes responsible for reabsorption of proteins in kidney tubules [57].

Table 2. Moisture content, pH, e	electrical conduct	tivity, organic carbo	n, of the farm settlement.
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	Sample	MC	pH	EC (µs/cm)	OC	O.M
Land clearing	Topsoil	$6.42 \pm 2.27b$	$7.06\pm0.05a$	176.2 ± 2.00b	1.59 ± 0.06ab	3.18 ± 0.12ab
	Subsoil	17.53 ± 11.1a	6.75 ± 0.26bc	$131.2\pm28.0b$	1.16 ± 0.23bc	2.32 ± 0.46bc
Fertilizer application	Topsoil	11.48 ± 6.65ab	7.05 ± 0.1a	162.3 ± 6.65b	1.30 ± 0.16bc	2.60 ± 0.33bc
	Subsoil	7.99 ± 3.52ab	6.96 ± 0.096ab	141.3 ± 25.1b	0.99 ± 0.20c	$1.99 \pm 0.41c$
Pesticide application	Topsoil	9.52 ± 2.72ab	$6.62\pm0.20c$	398 ± 311a	1.56 ± 0.27ab	$3.11 \pm 0.55 ab$
	Subsoil	8.95 ± 6.46ab	6.95 ± 0.094ab	$167.8\pm58.0\mathrm{b}$	1.163 ± 0.36bc	$2.33\pm0.73 bc$
Harvesting	Topsoil	10.3 ± 1.38ab	$7.13\pm0.18a$	163.1 ± 39.2b	1.91 ± 0.37a	$3.82\pm0.74a$
	Subsoil	7.58 ± 2.09ab	6.92 ± 0.017ab	149.6 ± 55.6b	$1.57\pm0.255 ab$	3.153 ± 0.51ab

MC = Moisture content, EC = Electrical conductivity, OC = Organic carbon, OM = Organic matter. Values in the same column followed by the same superscript are not significantly (P < 0.05) different.

Table 3. Average concentration	of elements in the top	psoil and subsoil from th	he farm settlement.

	Sample	P (mg/kg)	Na	Mg	Ca	TN
Land clearing	Topsoil	52.38 ± 3.00a	$1.20 \pm 0.20a$	1.03 ± 0.42ab	1.10 ± 0.2a	0.7 ± 0.03cd
	Subsoil	$56.03\pm6.07a$	1.07 ± 0.21ba	$1.23 \pm 0.23a$	1.07 ± 0.21ba	$0.60\pm0.07d$
Fertilizer application	Topsoil	53.3 ± 5.41a	1.10 ± 0.2 ba	1.13 ± 0.2a	1.17 ± 0.3a	$1.03 \pm 0.07 bc$
	Subsoil	53.16 ± 0.57a	1.03 ± 0.32 ab	1.13 ± 0.45a	$0.97 \pm 0.35a$	$1.04 \pm 0.23 bc$
Pesticide Application	Topsoil	52.69 ± 3.53a	0.97 ± 0.15abc	1.07 ± 0.15a	0.91 ± 0.03ab	0.91 ± 0.10bcd
	Subsoil	50.57 ± 2.37a	$1.0 \pm 0.1 \text{ ab}$	1.0 ± 0.26ab	1.0 ± 0.26a	1.18 ± 0.36b
Harvesting	Topsoil	56.9 ± 4.18a	$0.70c \pm 0b$	0.77±0.15ab	0.73±0.21ab	1.62±0.36a
	Subsoil	56.13 ± 3.48a	$0.6 \pm 0.3c$	$0.47 \pm 0.31 \mathrm{b}$	$0.47 \pm 0.21 \mathrm{b}$	1.07 ± 0.15bc

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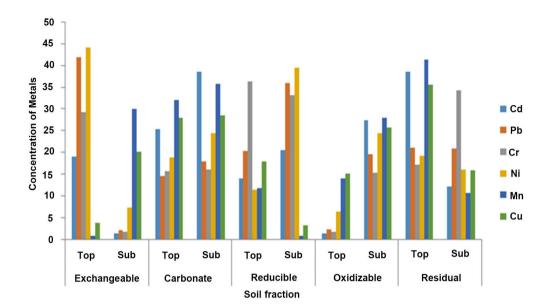


Figure 2. Percentage metals in each fraction of the soil samples.

More so, about 80% of lead was found in the non-residual fraction while high percentage of the total extractable fraction contributed to the mobile phase (exchangeable and carbonate phase) and as such implicates higher risk for lead contamination. However, total extractible Pb from all the sampling points in both study areas falls below 140 mg·kg⁻¹ set by USEPA for agricultural soil. Pb was found to be mostly associated with the exchangeable fraction in the top soil with percentage range of 27.6% to 44.9% (**Figure 2**). A high percentage of exchangeable Pb in the top soil might increase the potential of Pb mobility and bioavailability in these soils. The potential bioavailability of the metal in the top soil is in the following order Exchangeable (27.6% to 53.7%) > Reducible (16.7% to 24.4%) > Residual (15% to 33.7%) Carbonate (10.2% to 19.3%) > Oxidizable (1.26% to 2.83%) (**Figure 2**).

The total extractable Chromium in the soil was below 750 mg·Kg⁻¹ limit permissible by [58] and [59] for domestic gardens, agricultural and residential areas. The Cr content was strongly associated with the reducible fraction in the top soil with percentage range of 29.3% to 44.8%. The potential bioavailability of the metal for top soil is in the following order; Reducible (29.3% to 44.8%) > Exchangeable (16.7% to 38.0%) > Residual (17.2% to 18%) > Carbonate (14% to 17.9%) > Oxidizable (0.54% to 2.85%).

The level of Nickel in the farmland fell within the permissible limit of 150 mg·Kg⁻¹ set by [59] for residential and agricultural lands. Most of the Ni was found in the exchangeable in the top soil with percentage range of 26.4% to 51.7% (**Figure 2**). High concentration of Ni in exchangeable fraction for top soil indicated that Ni was in active speciation [60], which suggests that Ni in these mediums has strong activity and bioavailability. This result is at variance with the work of [61] [62] [63] where they reported a high concentration of Ni in other soil fractions other than exchangeable fraction. The potential bioavailabil-

ity of the metal for top is in the following order: Exchangeable (26.4% to 51.7%) > Carbonate (15.2% to 25.5%) > Residual (17.9% to 22.7%) > Reducible (8% to 14.9%) > Oxidizable (0.58% to 14.3%).

The concentrations of total extractible Cu in the farmland were all below the toxic limit of 250 mg·kg⁻¹ set by [64] for agricultural lands indicating that the soil is not polluted with Cu. The results also indicated that majority of Cu in the top soil was associated with the residual fraction (*i.e.* bound to silicates and detrital materials) having a percentage range of 25.7% to 42.6% (Figure 2) which is similar to the reports of [65] and [36]. The result is at variant to [66] and [67] in which their findings revealed Cu to be mostly abundant in the oxidizable fraction. Heavy metals with high abundance in the residual phase are not easily bio-available to the environment. The association of Cu with different fractions was observed to be in the order for the top soil; Residual (25.7% to 42.6%) > Carbonate (21.9% to 36.4%) > Reducible (12.8% to 21.6%) > Oxidizable (6.1% to 24.7%) > Exchangeable (1.24% to 5.95%).

On the other hand, appreciably high amount of Cadmium found in carbonate fraction in the sub soil suggested that cadmium is potentially available to some extent in these soils because metals in this fraction are usually thought to be readily available for plants uptake. By these criteria, cadmium must be considered quite mobile and biologically available in the soil samples. The availability of this metal in the sequentially extracted fractions in the sub soil shows the order; Carbonate (33.6% to 46.2%) > Oxidizable (24.7% to 29.9%) Reducible (3.8% to 33.7%) > Residual (7.0% to 20.5%) > Exchangeable (1.22% to 1.75%) > Oxidizable (0.74% to 1.81%) (Figure 2). Cadmium reduces the activity of delta aminolevulinic acid synthetase, arylsulfatase, alcohol dehydrogenase, and lipoamidedehydrogenase, whereas it enhances the activity of delta aminolevulinic acid dehydratase, pyruvate dehydrogenase, and pyruvate decarboxylase [68].

Lead was found to be mostly associated with the reducible fraction in the sub soil with percentage range of 15.8% to 55.4% respectively (**Figure 2**). Pb in reducible fraction constituted more than 32% of total concentration for all samples in the sub soil which is consistent with work of some researchers that showed reducible fraction of Pb to be the most important compound form in soil [60] [70] [71]. Fe-Mn oxides are important scavengers of heavy metals in soils (Ping *et al.*, 2008). This is because Pb element exists as Pb (II) in the earth's surface, which could intensely absorb on the surface of Al, Fe, Mn oxides, and silica. The potential bioavailability of the metal in the sub soil is in the following order: Reducible (15.8% to 55.4%) > Carbonate (14% to 55.4%) > Oxidizable (13.9% to 28%) > Residual (13.5% to 28%) > exchangeable (1.13% to 3%) for sub soil respectively (**Figure 2**).

The Chromium content was strongly associated with the residual fractions in the sub soil with percentage range of 20.8% to 39.9% respectively (**Figure 2**). High concentration of residual Cr in the sub soil could probably be envisage because through a series of reactions in soils, Cr could be easily transformed into insoluble hydroxide precipitates, which stayed in the residue [71] which is in agreement with those reported by other researchers [15] [72] but however differ from those reported by [61] for tannery sludge. The potential bioavailability of the metal for sub soil is in the following order; Residual (29.4% to 41%) > Reducible (20.8% to 39.9%) > Carbonate (13.8% to 17.5%) > Oxidizable (14.5% to 18.1%) > exchangeable (1.32% to 2.58%) in sub soil (**Figure 2**).

Most of the Nickel was found in the reducible fractions in the sub soil with percentage range 6.3% to 53% respectively (**Figure 2**). High concentration of Ni in the reducible fraction for both sub soil indicated that Ni was in active speciation [15], which suggests that Ni in these mediums has strong activity and bioavailability. This report is at variant to the work of [61] [62] [63] where they reported high concentration of Ni in other soil fractions other than reducible fraction. The potential bioavailability of the metal for sub soil is in the following order: Reducible (6.3% to 53%) > Oxidizable (19.1% to 33.8%) > Carbonate (16.1% to 36.1%) > Residual (6.9% to 26.7%) > exchangeable (1.50% to 18.6%) in sub soil (**Figure 2**).

However, it was inferred from the result that majority of extractable Cu in the sub soil was associated with the carbonate fraction which it's potential mobility and bioavailability. The association of Cu with different fractions was observed to be in the order for the sub soil; Carbonate (3.89% to 50.3%) > Oxidizable (17.6% to 33.4%) > Exchangeable (5.45% to 42.8%) > Residual (11.4% to 21.9%) > Reducible (1.97% to 4.95%) (**Figure 2**).

The Cadmium concentration was noted above the recommended value of 3.0 mg·kg⁻¹ for agricultural soil [43] [53] throughout the study area. Contamination of soil with Cd is increasingly becoming a major problem in developing countries worldwide. Concentration of Cd in Agricultural soil of south west, Nigeria ranged from 4.50 - 9.63 mg·kg⁻¹ [73], Peri-smelter soil in China ranged from 4.1 - 167.6 mg·Kg⁻¹ [63]; Industrial zone in North east China ranged from 0.76 - 81.20 mg·kg⁻¹ [74]; Dumpsites soil in Abia state, Nigeria ranged from 6.78 - 72.13 mg·kg⁻¹ [62] and so on.

The Muller Index of Geoaccumulation, Igeo indicating the level of contamination found in various soils, is widely recognized in Europe. I_{geo} consist of seven grading ranging from unpolluted to very seriously pollute. Grade 6 indicates a 64-fold enrichment over the background values [75].

The result from the study shows that the soil was not contaminated for all the metal analyzed in the soil (**Table 3**). Contamination factor (CF) is used to illustrate the contamination of particular toxic substance at a given site [76]. It can be observed from the result that the soil was practically not contaminated with all the metals studied in the soil at this site. The study revealed Ni as the most severe component causing moderate to very high contamination of the soil in the study site. A similar pattern was noted for contamination degree (CD) (**Table 4**), where sampling sites having dominant anthropogenic activities displayed high CD for nickel. This demonstrates regular monitoring of the farmland for the presence of trace elements especially nickel is required.

In geochemical investigations, PLI is used as a resourceful tool to measure and compare soil contamination. Analyzed soil at all the sampling points displayed higher PLI values for Ni and progressive deterioration in quality (**Table 4**). Higher PLI values in soil demonstrated substantial anthropogenic impacts on the soil quality whereas lower PLI values pointed to no considerable anthropogenic activities. This investigation strengthened employment of CD and PLI as effective instruments for assessing the environmental geochemistry of soil and could be used individually or in combination as they closely complemented each other. Furthermore, they easily convey information to the public and policy makers to ascertain the contamination load of the soil to take necessary remedial measures.

Heavy-metal exposure has potential and serious health risk to [77] Thus, in this study, the health risk of heavy metal exposure to humans was one of the main focus issues. The results of the carcinogenic and non-carcinogenic risk assessment for children and adults using the summation of mobile fractions are presented in (Table 5). For the non-cancer effects for adults; dermal exposure to Cd (4.28E+06) and ingestion route to Cr (1.01E-02) are the major exposure routes. The non-cancer distribution pattern for both ingestion and dermal routes was: Cd > Cr > Ni > Mn > Pb > Cu. Additionally, total exposure Hazard Index (HI) from ingestion, dermal contact, and inhalation for Cd, Pb and Mn were greater for children than for adults. Children are more susceptible to a given dose of toxin and are likely to inadvertently ingest significant quantities of metals because of their hand-to-mouth behavior, which has been widely regarded as a key metal exposure pathway for children [78].

Hazard Index (HI) values for analyzed elements to both adults and children decrease in the order of Mn > Cd > Cr > Ni > Pb > Cu. The HI summation for the sites using Mobile Fractions (F1 + F2 + F3 + F4) showed that Manganese poses a higher risk of non-cancer effects among the studied elements while Copper poses the lowest (Table 5). The sum of hazard index (Σ HI) for all of the metals and all routes for both adult and children is 6.15E+15. This HI value is > 1 and this is an indication that the soil poses non-cancer threat to human. The range reported for the non-cancer effects in the present study is at variance to the values reported by some authors [79] [80] [81], but also in agreement with [82]. Among the carcinogenic metals, only Cd, Pb, Cr and Ni are analyzed, and carcinogenic risk was assessed from calculated daily dose (CDI) multiplied by the corresponding SLF. The cancer risk for Children ranged from 1.02E-11 to 9.90E-10 and that of the Adult ranged from 4.45E-09 to 8.61E-09 respectively. The level of cancer risk for Cd, Pb Cr and Ni falls below the threshold values (10⁻⁴ to 10⁻⁶) which some environmental and regulatory agencies considered as unacceptable risk. It is noteworthy that the Σ CR for all the metals and routes for Children (1.08E-09) and Adults (1.32E-08) were lower than the 10^{-5} risk factor acceptable by some authorities [83].

Element	Soil (ppm)	CF	CD	PLI	Classification
Cd	10.3	0.11	0.21	0.001	Low contamination Factor/Polluted
Pb	6.93	0.35	0.65	0.017	Low contamination Factor/No Pollution
Cr	4.81	0.14	0.31	0.007	Low contamination Factor/No Pollution
Ni	8.66	0.43	0.74	0.006	Low contamination Factor/No Pollution
Mn	25	0.04	0.08	0.003	Low contamination Factor/No Pollution
Cu	4.48	0.18	0.39	0.01	Low contamination Factor/No Pollution

Table 4. Contamination factor (CF), Degree of contamination (CD) and Pollution load index (PLI) of metals in the soil of the study site.

 Table 5. Cancer risk and non-cancer risk of analyzed metals in the soil of the farm under study.

Element	Cd	Cdcar	Pb	Pbcar	Cr	Crcar	Ni	Nicar	Mn	Cu
Type of distribution	LogN		LogN		LogN		Ν		LogN	LogN
95% UCL	1.649	1.649	1.294	1.294	1.072	1.072	2.988	2.988	2.187	1.045
RfD_{ing}	1.00E-01		3.50E-03		3.00E-03		1.10E-02		1.40E-01	4.00E-02
RfD_{inh}	2.0E-05				1.00E-01		7.66E-05		5.00E-02	
RfD_{dermal}	2.50E-05		3.50E-02		7.50E-05		4.40E-04		1.40E-01	4.00E-02
SF_{inh}		5.00E-01		5.00E-01		4.20E+01		8.40E-01		
Children										
$CDI_{ing} (mg \cdot kg^{-1} \cdot d^{-1})$	9.29E+07		7.30E+00		6.04E+00		1.68E-06		1.23E-06	5.89E-07
$CDI_{inh} (mg \cdot kg^{-1} \cdot d^{-1})$	2.60E-11		2.04E-11		1.69E-11		4.71E-11		3.44E-11	1.65E-11
CDI_{dermal} (mg·kg ⁻¹ ·d ⁻¹)	1.45E-02		1.13E-02		9.40E-03		2.62E-02		1.92E-02	9.16E-03
HQ_{ing}	9.29E+08		2.09E+03		2.01E+03		1.53E-04		8.79E-06	1.47E-05
HQ_{inh}	1.30E-05						1.69E-10		6.15E+15	6.88E-10
HQ_{dermal}	2.32E+04		3.23E-01		9.62E+03		1.49E+03		1.37E-01	
$HI = \Sigma HQ_i$	9.29E+08		2.09E+03		1.16E+04		1.49E+03		6.15E+15	1.47E-05
Cancer Risk		1.30E-11		1.02E-11		7.10E-11		9.90E-10		
Adult										
$CDI_{ing} (mg \cdot kg^{-1} \cdot d^{-1})$	1.16E-06		9.12E-07		7.55E-07		2.11E-06		1.54E-06	7.36E-07
$CDI_{inh} (mg \cdot kg^{-1} \cdot d^{-1})$	1.71E-10		1.34E-10		1.06E-10		4.21E-10		3.08E-10	1.47E-10
CDI_{dermal} (mg·kg ⁻¹ ·d ⁻¹)	2.68E+00		2.11E+00		1.67E+00		4.86E+00		3.56E+00	1.70E+00
HQ_{ing}	1.16E-03		2.61E-04		1.01E-02		4.80E-03		1.10E-05	1.84E-05
HQ_{inh}	8.34E-08				1.06E-11		5.50E+01		6.16E-02	
HQ_{dermal}	4.28E+06		6.03E+01		1.72E+06		2.75E+05		6.35E+01	4.25E+01
$HI = \Sigma HQ_i$	4.28E+06		6.03E+01		1.72E+06		2.75E+05		6.36E+01	4.25E+01
Cancer Risk		8.55E-11		6.70E-11		4.45E-09		8.61E-09		

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The estimated daily intake of metals from the Jute Mallow and the hazard quotient and hazard index for adult and children for were presented in (**Table 6**). Cadmium is a dangerous element because it can be absorbed via the alimentary tract; penetrate through placenta during pregnancy, and damage membranes and DNA [57]. Once in the human body, it may remain in the metabolism from 16 to 33 years and is connected to several health problems, such as renal damages and abnormal urinary excretion of proteins. Decrease in bone calcium concentrations and increase of urinary excretion of calcium have also been attributed to exposure to Cd, eventually causing death. It also affects reproduction and endocrine systems of women [84]. Vegetables may contribute to about 70% of Cd intake by humans, varying according to the level of consumption [85].

The daily intake of Cd for adult ranged between (0.023 and 0.026 mg·day⁻¹. person⁻¹) and children ranged between (0.016 and 0.018 mg·day⁻¹·person⁻¹) (Table 6) with RfD, established to 0.001 mg·kg⁻¹ of body weight per day, equivalent to 0.07 mg per day for a 70 kg adult [86]. The daily intake was higher than the tolerable daily intake (TDI) for the jute mallow. The toxic effects of Pb focus on several organs, such as liver, kidneys, spleen and lung, causing a variety of biochemical defects. The nervous system of infants and children is particularly affected by the toxicity of this Heavy metal. Adults exposed accidentally to excessive levels of Pb exhibit neuropathology. There is association between Pb in human body and the increase of blood pressure in adults [87]. Although Pb effects are more relevant for children, calculations for risk assessment were made for adults and children. The daily intake of Pb ranged from (0.020 - 0.038 mg·day⁻¹·person⁻¹) for adult and (0.014 - 0.026 mg·day⁻¹·person⁻¹) for children (Table 6) which is 15.5% of RfD value of 0.245 mg per day for a 70 kg adult. Pb concentrations were high in jute mallow. This value (0.025 and 0.521 mg per day) was below those reported in literature [88].

Cr is an important element for the insulin activity and DNA transcription. However, an intake below 0.02 mg per day could reduce cellular responses to insulin [89]. The daily intake, ranged from 0.012 to 0.023 mg·day⁻¹·person⁻¹ for adult and 0.079 to 0.099 mg·day⁻¹·person⁻¹ for children estimated, was lower than

	Table 6. Daily me	etal intake estimate and hazard c	uotient for bush okra in i	investigating site.
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Element	Cd	РЬ	Cr	Ni	Mn	Cu	HI
UL (mg·day ⁻¹ ·person ⁻¹)	6.4E-02	2.4E-01	1.05E-02	1.0E-00	1.1E+01	1.0E+01	
RfDo (mg·kg ⁻¹ ·day ⁻¹)	5.0E-04	4.0E-03	1.5E-00	2.0E-02	1.4E-02	4.0E-02	
Children							
DI	1.6E-02	1.9E-02	1.1E-02	1.1E-02	2.4E-01	3.8E-02	
HQ	8.1E-02	9.0E-02	3.6E-03	3.6E-03	8.3E-03	4.6E-03	2.6E+00
Adult							
DI	2.4E-02	8.8E-03	1.4E-02	2.1E-02	3.5E-01	5.7E-02	
HQ	1.1E-01	3.5E-02	5.4E-05	5.2E-03	1.3E-01	7.0E-03	2.9E-01
нQ	1.1E-01	3.5E-02	5.4E-05	5.2E-03	1.3E-01	7.0E-	-03

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the RfD established at 1.5 mg·kg⁻¹ per day (equivalent to 105 mg per day) [51]. This value was also lower than that recommended by the US National Council [90] for Cr^{3+} : from 0.05 to 0.2 mg. The daily intake of Cr estimated in this work was under than that reported in literature, which ranges between 0.013 and 0.098 mg per day [88] [91].

Ni does not have a specific function in humans; however, it is a co-factor for some microbial intestine enzymes. Ni content in the adult human body should remain below 0.1 mg per day, and excess may cause damages to DNA and cell structures [89]. The daily intake of Ni ranged from (0.012 - 0.026 mg·day⁻¹·person⁻¹) for adult and (0.0079 - 0.0099 mg·day⁻¹·person⁻¹) (Table 5) which represents approximately 40 % of RfD established in 0.02 mg·kg⁻¹ per day, equivalent to 1.4 mg per day for a 70 kg adult [86]. The daily intake was below the TDI of 1.4 mg per day and lower than that reported in literature (0.089 and 0.231 mg per day) [88] [91]).

Copper is an essential micronutrient required in the growth of both plants and animals. In humans, it helps in the production of blood haemoglobin. In plants, Cu is especially important in seed production, disease resistance, and regulation of water. Copper is indeed essential, but in high doses, it can cause anaemia, liver and kidney damage, and stomach and intestinal irritation. Copper normally occurs in drinking water from Cu pipes, as well as from additives designed to control algal growth. The daily intake of copper ranged from (0.05 -0.2 mg·day⁻¹·person⁻¹) for adult and (0.034 - 0.13 mg·day⁻¹·person⁻¹) for children of RfD established as 0.04 mg·kg⁻¹ per day, equivalent to 8.0 mg per day for a 70 kg adult [86]. The daily intake was below the TDI of 1.4 mg per day.

Although the HQ-based risk assessment method does not provide a quantitative estimate for the probability of an exposed population experiencing a reverse health effect, it indeed provides an indication of the risk level due to exposure to pollutants [92]. Many researchers consider the risk estimation method reliable [91] [93] [94] and it has been proven to be valid and useful. However, this HQ method considers only exposure to HMs via consumption of vegetables, without HQs for individual vegetables were all below 1.0 for all HMs. HQ for Cd, Pb, Cr, Ni, Mn and Cu ranged from 0.11 to 0.13; from 0.0036 to 0.047; from 7.5E–05 to 3.9E–05; from 7.1E–03 to 2.9E–03; from 9.5E–02 to 1.1E–01; and from 6.1E–03 to 2.5E–02 (Table to 1.1E–01 and from 4.3E–03 to 1.6E–02 for children. Cr values were lower than 0.00001 for children and adults. When the consumption habit of adults and children in the study site were analyzed, HQs for all HMs were below 1.0 (**Table 6**). So, the consumption of these vegetables can be considered safe with no risk to human health.

The sequence of HQ for adults and children followed the decrease order Cd > Mn > Pb > Ni > Cu > Cr (Table 6) for adult and Pb > Cd > Mn > Cu > Ni > Cr for children. However, the HQ for children was higher than that for adults, as verified by other researchers [95]. High Pb concentrations observed in many vegetables, may be attributed to crops located near roads of heavy traffic. The

main sources of this element to humans are inhalation of airborne Pb from vehicle emissions and from direct atmospheric deposition on soils, water, and crops, constituting the gateway into the food chain [96]. When the hazard index exceeds 1.0, there is concern for potential health effects [95]. Even though there was no apparent risk when each metal was analyzed individually, the potential risk could be multiplied for adults from 0.079 to 0.08; from 0.0025 to 0.34; from 4.6E–05 to 2.6E–05; from 4.9E–03 to 1.9E–03; from 7.0E–02 considering all HMs. HI for adults and children were in ranged 3.2E–01 to 2.4E–01 and 5.60E–01 to 1.7E–01, respectively (**Table 6**). Neither the HI suffered from ingestion of vegetables in the study site from HMs. The relative contributions of Cr, for adult and children were minimal which may be related to the high RfD of Cr (1.5 $mg\cdot kg^{-1}$ per day) [95] and [94].

4. Conclusion

Metal speciation and health risk assessment of soil and vegetable collected from Ikorodu farm settlemen of Lagos had been carried out. The results of speciation analysis showed that Pb and Ni, Cd, Mn and Cu were predominantly associated with exchangeable and residual fractions respectively, while Cr was associated with reducible fractions for top soil. Also, for sub soil; Cd, Mn and Cu, Pb and Ni, and Cr were predominantly bound to carbonate, Fe-Mn oxide and Silicate mineral components of the soil respectively. A comparison of the result of total extractible metals with standard set by USEPA reveals that Pb, Cr, Ni, Mn and Cu were below the threshold limit in the vegetable farmland while Cd level was above the critical permissible limit of 3.0 mg/kg for agricultural soil and therefore portend a health risk. The result also shows that the plant species investigated (Corchorus olitorius) accumulate all metals below the threshold limit suggested by USEPA (1986) except for Cd and Pb which exhibit higher concentration above the limit of 0.3 mg \cdot kg⁻¹ and 5 mg \cdot kg⁻¹. The concentration of total extractible metals in farmland was also compared to some other soil around the world, even though each area has its own geochemical characteristics. The investigation revealed Cd as the biggest contaminant and chief cause of concern. Four soil quality indices namely; contamination factors (CF), contamination degree (CD), pollution load index (PLI) and geo-accumulation index (Igeo) were further used to determine degree of anthropogenic influence on the soil quality. From the result, it can be deduced that the soil was practically not contaminated with all metals investigated in the soil except Cd which has very high contamination factor (CF), contamination degree (CD), pollution load index (PLI) and geo-accumulation index (Igeo). The health risk of heavy metal exposure to humans from the soil and vegetable was also investigated. The result reveals dermal and ingestion exposure route were the major exposure routes for adult and children respectively which can also serve as exposure route for cancer development. The Hazard index value (HI > 1) from the study shows that the soil poses non-cancer threat to human. The cancer risk Cd, Pb, Cr and Ni ranged from

1.02E–11 to 9.90E–10 and 6.70E–11 to 8.61E–09 for Children and Adult respectively.

The level of cancer risk of Cd, Pb Cr and Ni falls below the threshold values 10^{-4} to 10^{-6} which some environmental and regulatory agencies considered as unacceptable risk. Σ CR for all the metals and routes for Children (1.08E–09) and Adults (1.32E–08) were lower than the acceptable value of 10^{-5} . The finding of this study regarding DIR, HQ and HI showed that the consumption of bush okra grown at Ikorodu farm settlement was free of risk. But the situation could however change in future depending on the dietary pattern of the consumer and the volume of contaminant added to the ecosystem. It is therefore recommended that routine monitoring of the farmland should be carried out on regular bases. Additionally, Farmer need to be educated about the dangers associated with chemical used on the farm.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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