Urban vegetable farming: Anthropic level, bioavailability, and health implication associated with bioaccumulated trace metals in selected vegetables in Ilorin, Nigeria

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ABSTRACT: Urban horticulture is of growing importance in developing and developed countries around the world; however, contamination of urban horticultural products can exceed the precautionary values, posing significant human health risks due to dietary exposure to high levels of the pollutants. In this study, samples of rhizosphere soil and corresponding vegetables have been collected from an urban garden in Ilorin, Nigeria, to assess the contamination level of trace metals as well as the health risk, associated with dietary intake of contaminated vegetables, in adult sub-population. The range of Cu, Pb, and Cd in garden topsoil was 14.0-52.50, 33.00-121.40, and 1.00-4.50 mg/kg, respectively. The metals sources were both anthropogenic and lithogenous, though the long-term accumulation of trace metals in the soil led to significant soil-plant transfer as evident in the levels of metals in some of the vegetables. The estimated daily intakes (EDI) of Cu and Pb through vegetable consumption were far below the recommended tolerable daily intakes (TDI) and the hazard quotient (HQ) values were within the safe zone for the adult population. In contrast, the EDI of Cd for the vegetables was several folds greater than the TDI, thus greatly contributing to a high hazard index (HI>1.0), observed in all vegetables. Therefore, risk assessment of trace metal ingestion through consumption of the vegetables in the adult sub-population depicts serious health hazards with Cd, mainly contributing to vegetable contamination in the studied area.

Keywords: anthropogenic, bioaccumulation, bioavailability, hazard index, trace metal.

INTRODUCTION
Urban horticulture is of growing importance in developing and developed countries around the world; however, contamination of urban horticultural products can exceed the precautionary limits and pose significant human health risks due to dietary exposure to high levels of organic and inorganic

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contaminants, associated with soil pollution. Soil acts as a sink and also a source of pollution, capable of transferring pollutants first to the ground water and food chain, and then to the human and/or animals (Khan et al., 2010). Once trace metals are accumulated in the soil as a result of anthropogenic activities, they pose potential risks to the ecosystem, agricultural products, and also human health due to their non-biodegradable and persistent nature (Vega et al., 2004; Khan et al., 2008; Zeng et al., 2011). Depending on the concentration of the metals and properties of the soil, uptake of bioavailable portions of metals into plants is inevitable which can pose toxic threats to biota, cause soil degradation, decrease plant yield, and bio-magnify along the food chain (Vega et al., 2004; Luo et al., 2011). When released from specific sources in an uncontrolled manner, mobile metals can be taken up by vegetables, grown for consumption, from the soils whilst scavenging for nutrients at varying degrees (Luo et al., 2011). There is broad evidence that urban and garden soils can contain high amounts of trace metals (Alloway, 2004; Charlesworth et al., 2010). These soils are, therefore, considered the main sites for human exposure to trace metals (De Miguel et al., 2007). Previous studies have shown that chronic intake of even low-level toxic metals over time can lead to nervous, cardiovascular, renal, and neurological impairment as well as bone diseases (Steenland & Boffetta, 2000; Jarup, 2003).

Vegetables (fruits, leaves, roots, and stems) are of high importance to people's diet in Nigeria as they are the major ingredients in several native soups, taken daily alongside carbohydrates. They are, therefore, often grown widely in home gardens, fallow plots, or farms across the country at different seasons and varying levels. Due to the ubiquitous nature of metals in the environment, vegetables are prone to threats of severe exposure. Elevated metal concentrations in vegetables can originate mainly from deposition of air pollution particulates or fumes on leaf surfaces and soils. The magnitude of metal accumulation in vegetables depends on the location of the vegetable farm and soil properties (pH, CEC, and organic matter) (Luo et al., 2011). Slightly acidic and acidic soils have been shown to increase heavy metal mobility and bioavailability to plants by enhancing desorption from soil components into soil solution (Zeng et al., 2011).

Vegetables' bioaccumulation of essential metals (e.g. copper and iron) from soils with elevated levels or non-essential anthropogenic metals (e.g. arsenic, lead, and cadmium) at low concentrations, can cause toxicity to biota and humans who consume these vegetables as a source of food and nutrition. Unsurprisingly, Agbenin et al. (2009) showed that such metals can accumulate in tissues of vegetables to unsafe levels despite being below the allowable concentration of the metals in agricultural soils. Within the markets, Sobukola et al. (2010) found heavy metal concentrations within tolerable limits in fruits and vegetables in a city in Nigeria. However, Lokeshappa et al. (2012) discovered elevated concentrations of Cd, Cr, Pb, Se, and Zn in agricultural products (e.g. potato and spinach) around Powai area of Mumbai, India. Vegetables, cultivated in irrigated soils or near rivers receiving effluents, can take up heavy metals in sufficient quantities to pose potential risks to consumers and biota around the region (Bahemuka & Mubofu, 1999; Ikeda et al., 2000; Khan et al., 2008). With regards to human exposure, soil to plant transfer represents a major pathway for contamination and eventual disease manifestation. It is hence vital to assess the potential health risks by determining the transfer of essential and non-essential metals from soils to vegetables in an urban garden (Jolly et al., 2013). According to Ite et al. (2014), monitoring and assessment of heavy metals' concentrations in the environment result in effective understanding of

biogeochemical processes and gauging ecosystem health.

The objective of the current study is to investigate the potential effects of irrigation, industrial, and vehicular activities within an urban settlement on the surrounding environment and food products, particularly, specific metal contaminants. We have determined the total and bioavailable metal (Cu, Pb and Cd) concentrations in soil within an urban garden and categorized the potential sources. In addition, we have analyzed the edible vegetable varieties for these specific metals and have further investigated the soil-to-plant transfer coefficient for each metal. Results are useful to understand the source, mobility, fate, and uptake of metals into edible vegetables, all of which are critical for assessing the risk to humans, depending on the vegetables, themselves, as sources of nutrition in order to protect local community from health hazards.

MATERIALS AND METHODS

Study area

This study was carried out at the peak of dry season, (October 2014- January 2015) in the densely-populated residential area of Ilorin, North-central Nigeria, which has a tropical climatic condition with two distinct seasons (rainy and dry seasons). The rainy season spans from April to early October with a mean temperature of 25°C to 30°C and annual precipitation of 1000 mm to 1500 mm. The dry season, however, commences from late October and finishes in late March with a mean temperature of 33°C to 34°C. Relative humidity ranges from 75% to 80% in the rainy season, its mean humidity accounting to 65% in the dry season. The population of Ilorin was estimated to be 864,755 in 2006 (NPC, 2006) with 44 registered industries (Ibrahim et al., 2014).
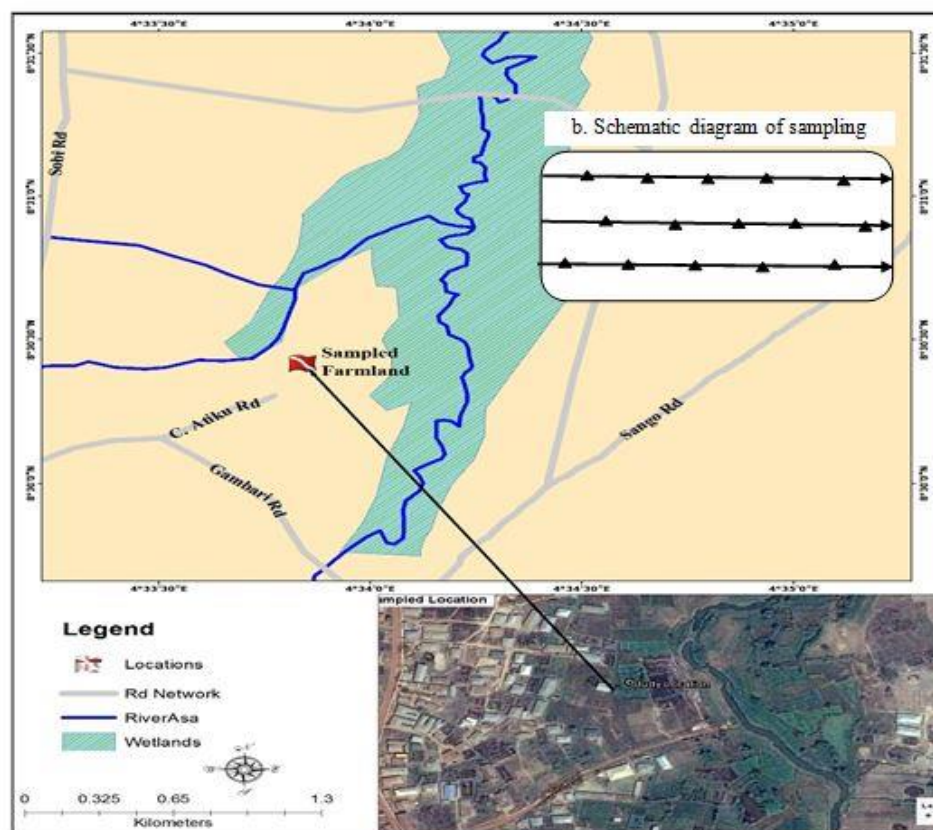

Fig. 1. Map of Ilorin, Nigeria showing the location of the vegetable farmland. Inset: Schematic diagram of sampling design

The study was carried out on a vegetable farmland, approximately 1000m×600m. It is located at the bank of Asa River in Ilorin and is regularly flooded in the rainy season (Fig. 1). The Asa River flows south-north through residential areas, serving as a significant source of water for domestic, economic, agricultural, and environmental purposes (Ahaneku & Animashaun, 2013; Ibrahim et al., 2013). Irrigation water for the vegetable farm in the dry season comes from the Asa River through the use of overlay pipes with motorized pumps. The water quality of Asa River is poor as it has been reported to be grossly-polluted by trace metals such as Cd, Cu, Ni and Pb (Ibrahim et al., 2013). The farm was segmented into four parts; each, cultivated with one of the following vegetables: jute mallow (*Corchorus olitorius* L.), plume cockscomb (*Celocia argentea* L.), cabbage (*Brassica oleracea* L.), and amaranth (*Amaranthus spinosus* L.).

Sampling and chemical analysis

Three transects were demarcated on each vegetable segment (*C. olitorius, C. argentea, B. oleracea* and *A. spinosus*) respectively. Five stands of each vegetable-type were collected randomly with their corresponding rhizosphere soil (0-15 cm depth) along each transect in each segment and properly tagged. All the vegetable samples were collected during 41 days of planting (DOP), except for cabbage, which was collected during 30 days after transplant. Samples of the rhizosphere soil were air-dried, pulverized, and passed through a 2-mm mesh, prior to chemical analysis. Vegetable samples were washed with clean water; root parts were excised and discarded while the shoots were oven-dried at 60°C to constant weight.

Soil organic matter (OM) was determined by loss on ignition (LOI) at 450°C, pH, and electric conductivity (EC) were measured in soil suspension (1:5 w/v), using a digital pH-meter and electric conductivity meter respectively. Mechanical analysis of the soil samples was done, using the method of Bouyoucos (1962); total nitrogen (TN) and total phosphorus (TP) were determined in accordance to the Kjeldahl method of Bremner (1965), and Bray and Kurtz (1945) respectively. The exchangeable metal fraction of rhizosphere soil was carried out by single extraction technique (Tessier et al., 1979). Briefly, 1 g of the soil sample was shaken continuously in 8 ml of 1 M $MgCl_2.6H_2O$ for 60 min at room temperature. Total metal content (bulk concentration) was determined by digesting 1 g of soil sample in 10 ml of concentrated HNO_3. The mixture was boiled gently for 30-45 min to oxidize all easily-oxidizable matter. After cooling, 5 ml of 70% $HClO_4$ was added and the mixture was heated gently until dense white fumes appeared (Hseu, 2004). The anthropogenic metal portion of the soil was determined by subjecting 1 g of the sample to 0.53 N HCl digestion (Karbassi et al., 2008), while lithogenous metal fraction was determined as the difference between the total (bulk) and anthropogenic metal concentrations (Karbassi et al., 2008). Total metal content of the vegetables was determined in 1 g of pulverized sample according to the method of Hesu (2004), described earlier. All digests were filtered and diluted to 25 ml with distilled H_2O and concentrations of Cu, Pb, and Cd were determined by Atomic Absorption Spectrophotometry (AAS) (Perkin Elmer A Analyst 200). The AAS was calibrated prior to metal analysis using a certified working standard solution (CPI international, USA) and metal concentration was determined only when the correlation coefficient (r^2)> 0.980. For quality assurance, procedural blanks, duplicate digestion, and certified reference materials (IAEA SL1-soil and IAEA 359-cabbage) were run alongside the soil and vegetable samples. The accuracy of the analysis was about ±4% and ±3% for all elements in certified reference soil and plant respectively.

Statistical analysis and metal pollution models

Data in this study were subjected to Analysis of Variance to check significance and significant means were separated by Duncan Multiple Range Test, using Statistical Software for Social Sciences (SPSS ver. 20). Principal Component Analysis (PCA) Biplot was presented, using Paleontological Statistics Software Package for Education and Data Analysis version 2.17b.

To assess the degree of metal pollution of the garden soil, geo-accumulation index (I_{geo}) (Muller, 1979; Zhuang & Gao, 2014), and the newly developed pollution index ($Ipoll$) by Karbassi et al. (2008) were employed.

$$\text{Igeo} = \log_2 \left[\frac{Cn}{1.5Bn} \right] \qquad (1)$$

where C_n is the metal content in soil sample and B_n, the geochemical background/crustal concentration for each element. A constant, 1.5, was introduced to buffer the possibility of lithological variability (Abrahim & Parker, 2008). The geochemical background concentration by Bowen (1979) was adopted (Cu -50 mg/kg, Pb -14 mg/kg and Cd -0.3 mg/kg).

$$\text{Ipoll} = \log_2 \frac{Bn}{Lp} \qquad (2)$$

where B_n and L_p represent bulk concentration (mg/kg) and lithogenous portion (mg/kg) respectively. Lithogenous portion is the difference between the total metal content (bulk concentration) and the anthropogenic metal portion. The pollution index for $Igeo$ and $Ipoll$ has seven categories: >5- extremely polluted; 4-5- strongly to extremely strongly polluted; 3-4- strongly polluted; 2-3- moderately to strongly polluted; 1-2- moderately polluted; 0-1- unpolluted to moderately polluted and $Ipoll$ < 0- unpolluted soils (Muller, 1979; Karbassi et al., 2008).

Soil-plant metal transfer

Transfer factor coefficient (TC) was calculated to assess the mobility of the metal in the soil-plant system. It describes the concentration of a metal in the plant, relative to the concentration in the soil, and was determined according to Kachenko and Singh (2006).

$$\text{TC} = \frac{\left[\text{Eplant} \right]}{\left[\text{Esiol} \right]} \qquad (3)$$

where E_{plant} is the concentration (mg/kg dw) of a metal, measured in the vegetable biomass, and E_{soil} is the $MgCl_2$ extractable concentration (mg/kg dw) of the same metal in the rhizosphere soil.

Non-carcinogenic health risk of vegetable consumption

In addition to the soil-plant transfer, the estimated daily intake of metal (EDI) and human non-carcinogenic health risk (HI) were determined to evaluate the potential risk of vegetable consumption to adult consumers, using the following equation (Cao et al., 2010; Orisakwe et al., 2012):

$$\text{HQ} = \frac{\text{EDI}}{\text{RfD}}; \quad \text{EDI} = \frac{\left[\text{Cmetal} \times \text{Dfood intake} \right]}{\left[\text{BAverage weight} \right]} \qquad (4)$$

$$\text{HI} = \text{HQ}_1 + \text{HQ}_2 + \text{HQ}_3 + ... \text{HQ}_n \qquad (5)$$

where the C_{metal}, $D_{food\ intake}$, and $B_{average\ weight}$ represent the metal concentration (mg/kg) in vegetable, daily intake of vegetable (kg/person), and average body weight (kg), respectively. Data on per capita consumption of vegetables in Nigeria was scarce; however, Hart et al. (2005) showed varying daily intake due to location, season price, availability, and culture. An average daily intake was used, hence the adopted average daily vegetable intake for adults equaled to 0.086 kg/person/day, with the average adult body weight considered to be 64.41 kg (Mbada et al., 2009). RfD is the oral reference dose (mg/kg bw/day), which are 4.0×10^{-2} for Cu, 3.5×10^{-3} for Pb, and 1.0×10^{-3} for Cd (USEPA, 2007).

The risk of non-carcinogenic toxic effects is assumed to be of no potential risk if the HI< 1.0, whereas there should be some concerns for potential health risk when the HI> 1.0.

RESULTS AND DISCUSSION

Soil properties

The geology of the study area consists of Precambrian basement complex rock and the soil type is loamy in texture with several common features, as shown in Table 1. The analyzed soil samples had an average pH and OM of 6.45 and 2.20%, respectively. In fact, the soil pH value is actually optimal for efficient growth of such vegetables (Laboski et al., 2006), exhibiting moderate OM levels to provide micronutrients. Such pH levels are of importance as they limit the mobility of metals, found within such soils since near basic soils ensure lower metal bioavailability and mobility to biota (Siebielec et al., 2006; Takáč et al., 2009). In addition, the level of OM was moderately low, when compared to the soils in neighboring locations (Ogunkunle et al., 2015) and states (Fasina et al., 2007; Awotoye et al., 2011); and as it had lost fertility following water erosion, OM decomposition (through high temperature and humidity) and poor land use management was being practiced by the farmers. The OM content can alter the concentrations of exchangeable and dissolved metal content in the soils, thus governing metal bioavailability in the soil (Liu et al., 2009).

The TN and TP contents of the soil were also considerably low, with their average levels equal to 0.61% and 1.37 mg/kg, respectively. Considering the recommended levels of nitrogen and phosphorus, required for optimum vegetable growth (1.8% and 26-45 mg/kg respectively) by Omotoso (1973) and Laboski et al. (2006), the vegetable farm requires addition of appropriate concentrations and rates of nutrients for enhanced growth and yield. The deficiency of such macronutrients and micronutrients can expose plants, grown on these soils, to toxicity from another element. The non-saline soil contained much coarse sand, reflected in the low-level EC (Table 1), explaining the high eroding ability of the soil that requires proper management.

The soil texture comprising sand, silt, and clay that in average amounted to 84.0%, 7.73% and 8.75%, respectively. The fine components of the soil (silt and clay) were considerably low in content, comprising a total mean of 16.48%, previously shown to be the amount of either clay or silt in more fertile soils (Fasina et al., 2007). Precisely, clay content was always below 9% indicating leaching of minerals and nutrients through erosion, owing to topography, high seasonal rainfall, coupled with high temperatures (Ajibade & Ojelola, 2004; Fasina et al., 2007). On the other hand, the soil had substantial amount of sand ranging from 81% to 90%, thus explaining the level of erosion occurring within the area.

Concentration of metal portions in the garden soil

The total (bulk) and $MgCl_2$-extractable (exchangeable) concentrations of the studied metals (Cu, Pb and Cd) varied widely within the urban vegetable farm soil. The mean total concentrations of trace metals in the soil followed the following sequence: Pb> Cu> Cd (Table 1). Some of the concentrations exceeded the permissible limits for trace metals in agricultural soils. For instance, the total Cu concentration ranged from 14.0 to 52.5 mg/kg with an average of 37.1 mg/kg (Table 1). Similarly, the total Pb concentrations ranged from 33.0 to 121.4 mg/kg with an average of 83.3 mg/kg. Cd showed a much lower concentration, i.e. 1.0 to 4.5 mg/kg with an average amount of 2.27 mg/kg in soil, but due to the potency, such levels are considerably high. The individual mean concentrations of the metals were well below the mean concentrations, found in urban soils in other parts of Nigeria (Ogbonna & Ogbonna, 2011; Chiroma et al., 2014). However, the level of trace metals in this study were well above those, found in soils of urban vegetable gardens in the literature (Jia et al., 2010; Chen et al., 2014; Adamo et al., 2014). Interestingly, mean Pb concentration increased considerably, compared to the previous mean

concentration (32.7 mg/kg) in the same area though a different location (Ogunkunle et al., 2015), indicating increasing input of Pb into the river, used for irrigation on this vegetable farm. The mean concentrations of Pb and Cd were above their respective crustal values and Canadian Soil Quality Guidelines for agricultural soils by the Canadian Council of Ministers of the Environment (CCME, 2007). In particular, mean Cd concentration exceeded the UK soil guideline value (EA, 2009) for allotments (1.8 mg/kg) with soil OM of 6% and lower than the Dutch intervention value for remediation.

The MgCl$_2$-extractable (exchangeable) concentrations of the trace metals were also determined to quantify fractions available for uptake into edible vegetables and elucidate potential risk. The bioavailable forms of the metals followed the same sequence as total concentration in the soil; Pb> Cu> Cd. Although Pb and Cu were more bioavailable fractions, compared to Cd. The latter (Pb and Cu)was bioavailable for either equal to or less than 23% of the mean total concentrations, while at least 37% of mean total Cd concentration was bioavailable in the soils. Ogunkunle et al. (2013) showed that at least 86% of average total concentration of essential nutrient (Cu) in cement-polluted acidic soil was bioavailable. In contrast to other studies, Cu bioavailability did not

exceed 4% of total concentration in acidic urban soil (Takáč et al., 2009). Although these reported studies did not determine the state of Cu in the soils, Cu complexes with oxides and carbonate, as well as with OM is bioavailable, while Cu complexes with clay mineral fractions is non-bioavailable (Pakula & Kalembasa, 2013; Romić et al., 2014). Hence, high Cu bioavailability in the study of Ogunkunle et al. (2013) was definitely due to the higher OM and low pH that encouraged mobility of Cu. However, with regards to Cd, higher OM content leads to a more Cd-organic-bound matrix, reducing the bioavailability (Liu et al., 2009), though the OM content in this study was moderately low, resulting in higher Cd bioavailability. This supports previous works, claiming that the soil properties and state of heavy metals in soils alter the extent of bioavailability for uptake or toxicity to biota (Liu et al., 2009; Pakula & Kalembasa, 2013; Romić et al., 2014).

Sources of metals in the garden soil
Although, soils may show elevated levels of heavy metal pollution, categorization of pollution sources is of vital importance for risk assessment and management. Hence, this study has deduced the lithogenous and anthropogenic concentrations and fractions of individual trace metal pollutant persistence in soil (Tables 1). Only Cu

Table 1. Physico-chemical parameters and metal portions of the garden topsoil

Physico-chemical parameter (n=10)							
pH	OM (%)	EC (dS/m)	Total N (%)	Total P (mg/kg)	Sand (%)	Silt (%)	Clay (%)
6.45±0.12	2.20±0.13	0.23±0.02	0.61±0.18	1.37±0.18	84.0±2.56	7.73±1.03	8.75±2.81

Metal portion (n=45)	Cu	Pb	Cd
Total (mg/kg) [*]	37.1 ± 12.57[b]	83.3 ± 27.62[a]	2.27 ± 0.90[c]
Range	14.0-52.5	33.0-121.4	1.0-4.5
MgCl$_2$-extractable (mg/kg)	7.3 ± 2.05[b]	18.7 ± 2.62[a]	0.85 ± 0.38[c]
% MgCl$_2$-extractable	19.7%	22.4%	37.4%
Anthropogenic (mg/kg)	24.1 ± 13.1[b]	61.0 ± 26.9[a]	1.12 ± 0.26[c]
Lithogenous (mg/kg)	13.2 ± 9.10[a]	22.3 ± 12.19[a]	1.15 ± 0.93[b]
Anthropogenic portion (%)	64.96	73.23	49.34
Lithogenous portion (%)	35.04	26.77	50.66

Note: [*] Value is mean± standard deviation; Mean values in each row with the same superscript are not statistically different at *P* < 0.05.

showed statistical significant anthropogenic input (*P<* 0.05), in comparison to lithogenous sources in the soil, while Pb and Cd showed no statistical difference (*P>* 0.05) between both anthropogenic and lithogenous inputs. Despite a large fraction of anthropogenic Pb input, the wide variation within the soil illustrates that there were some hot-spot localized areas having significant anthropogenic inputs. To support the latter claim, heavy metal pollution index showed that anthropogenic source of Pb was a moderately to strongly caused pollution (Fig. 2.). The soils in this study are often irrigated with water from the Asa river, confirmed to be contaminated with complex compositions of effluents from diverse industrial upstream (Ibrahim et al., 2013; Ogunkunle et al., 2015). On the other hand, non-anthropogenic source of

Cd showed levels of moderate to strong pollution, whilst the anthropogenic inputs were only moderate (Fig. 2.). Individually, the concentrations of anthropogenic and lithogenous trace metals (Cu, Pb, Cd) inputs were below the CCME soil quality guidelines, but anthropogenic inputs (irrigation) are currently accumulating overtime, hence proper monitoring is required. More specifically, Cd levels require monitoring as both mean concentration of anthropogenic and lithogenous inputs are close to the CCME soil quality guideline for Cd (1.4 mg/kg) in agricultural soils (CCME, 2007). Herman et al. (2000) showed that under-estimation of the 'metal accumulation index' is a possibility due to high level lithogenous metal source in soil as anthropogenic inputs may come from both localized (irrigation) and transboundary sources.
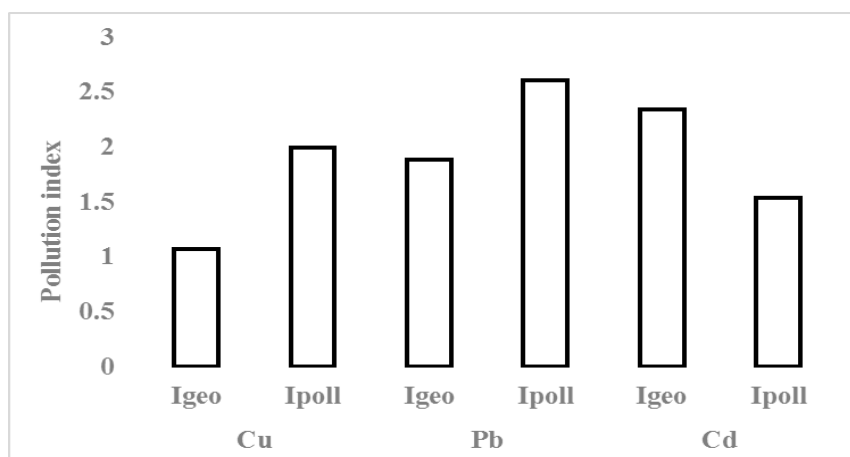

Fig. 2. Pollution index of metals in topsoil of the vegetable garden

Concentrations of metals in edible vegetables
Four species of edible vegetables (jute mallow, plume cockscomb, cabbage, and amaranth) were sampled and analyzed to determine the level of metal accumulation in the leafy tissues that can potentially pose threats to humans through consumption. The amount of trace metals, found within vegetable biomasses, exceeded the maximum levels for contaminants in vegetables, set by World Health

Organization (FAO/WHO, 2011). According to the FAO/WHO standards for contaminants in vegetables and accompanied oils, maximum limits of Cu, Pb, and Cd should not exceed 0.4, 0.3, and 0.2 mg/kg, respectively (FAO/WHO, 2011). Among the trace metals, Cu is the only micronutrient, thus it is expected that vegetables will require it for reproductive growth, resulting in the highest metal uptake by the vegetables (Fig. 3). Although there was no statistical difference (*P>* 0.05) in concentrations

accumulated by the vegetables; cabbage had the highest accumulation range (1.5-6.8 mg/kg). Pb was only found within plume cockscomb with a mean concentration of 1.9 mg/kg, which stood above FAO/WHO maximum limits along with the harvested vegetables in other studies (Sobukola et al., 2010; Tyokumbur & Okorie, 2011; Mutune et al., 2014). This was however lower than the concentrations, found in other literature (Biling et al., 2008). It is suggested that Pb would have accumulated within root zone which was excluded in the analysis, as Pb has been shown to bind to root surfaces and cell walls, limiting its translocation to shoots or leaves (Cobb et al., 2000; Liu et al., 2010). In addition, difference in Pb accumulation is also attributed to the differences in absorption strength and species of the vegetables despite the length of exposure (Ciura et al., 2005; Tan et al., 2011).

With regards to Cd, previous studies have shown that not only is it very toxic, but it also has the ability to translocate efficiently to shoot biomass of the vegetables (Brown et al., 1996; Tan et al., 2011; Jacob & Kakulu, 2012). Despite the low mean concentration of Cd in the soils and near neutral pH value, significant proportion of the trace metal was found within the edible fraction of all the vegetables, compared to the other metals (Pb and Cu). The lowest mean of Cd, found in the vegetable (plume cockscomb), was higher than the maximum limit, set by FAO/WHO (1.4 mg/kg), being some folds higher than the maximum concentration, found in lettuce and amaranth in urban vegetable gardens elsewhere in Nigeria (Agbenin et al., 2009). This implies that the amount of Cd found in the vegetable, irrespective of source, is within unsafe levels. Although much of Cd can be associated with the root zone of some vegetables (Sękara et al., 2005; Tan et al., 2011), there was no significant difference ($P< 0.05$) in the level of uptake and accumulation into shoot and leaves by the individual vegetable species. This does not rule out the potential deposition of Cd-containing dust particulates or fumes on the leaves. However, seasonal variations (hot, cool, wet, or dry), pH, competition with other metals (calcium, zinc), and precipitation (phosphate) can also alter the uptake of Cd into vegetables (Brown et al., 1996; Tan et al., 2011). The bioavailable/exchangeable fraction of Cd seemed low but was in best agreement with the fractions found in the vegetables compared to other metals; there was strong correlations existing between bioavailable Cd fraction of the soil and biomass concentrations of Cd in all the vegetables (Fig. 4), showing that it is mainly the exchangeable/soluble fraction of Cd that will translocate into leaves and the extraction procedure can be a useful tool for prediction.

Transfer coefficient

Metal transfer to individual plants did not depend on the plant species; rather transfer was dependent on the nature of the metal (Fig. 5). Chen et al. (2014) showed that metal transfer depended on vegetable species-type and metal type. In this study, apart from cabbage, there was significantly-higher ($P< 0.05$) transfer of Cd to all the vegetables, compared to other metals (Pb and Cu). Based on the soil properties and source of metals, Cd showed a more mobile property in comparison to other metals, reflected in the 37% fraction of bioavailable fraction (Table 1). Hence the bioavailable fraction is a good determinant of the potential mobility of the metal in soils, as this study also confirmed the hypothesis that metals are absorbed and utilized by vegetables in dissolved and exchangeable phase (Aydinalp & Marinova, 2003; Chen et al., 2014). Only Cd had a mean transfer coefficient over 1.0, while transfer coefficient of both Pb and Cu was below 1. As a result, these studied vegetables are accumulators, specific to Cd in the soil, thus raising a concern on the risk to consumers but will depend on the amount consumed per day.
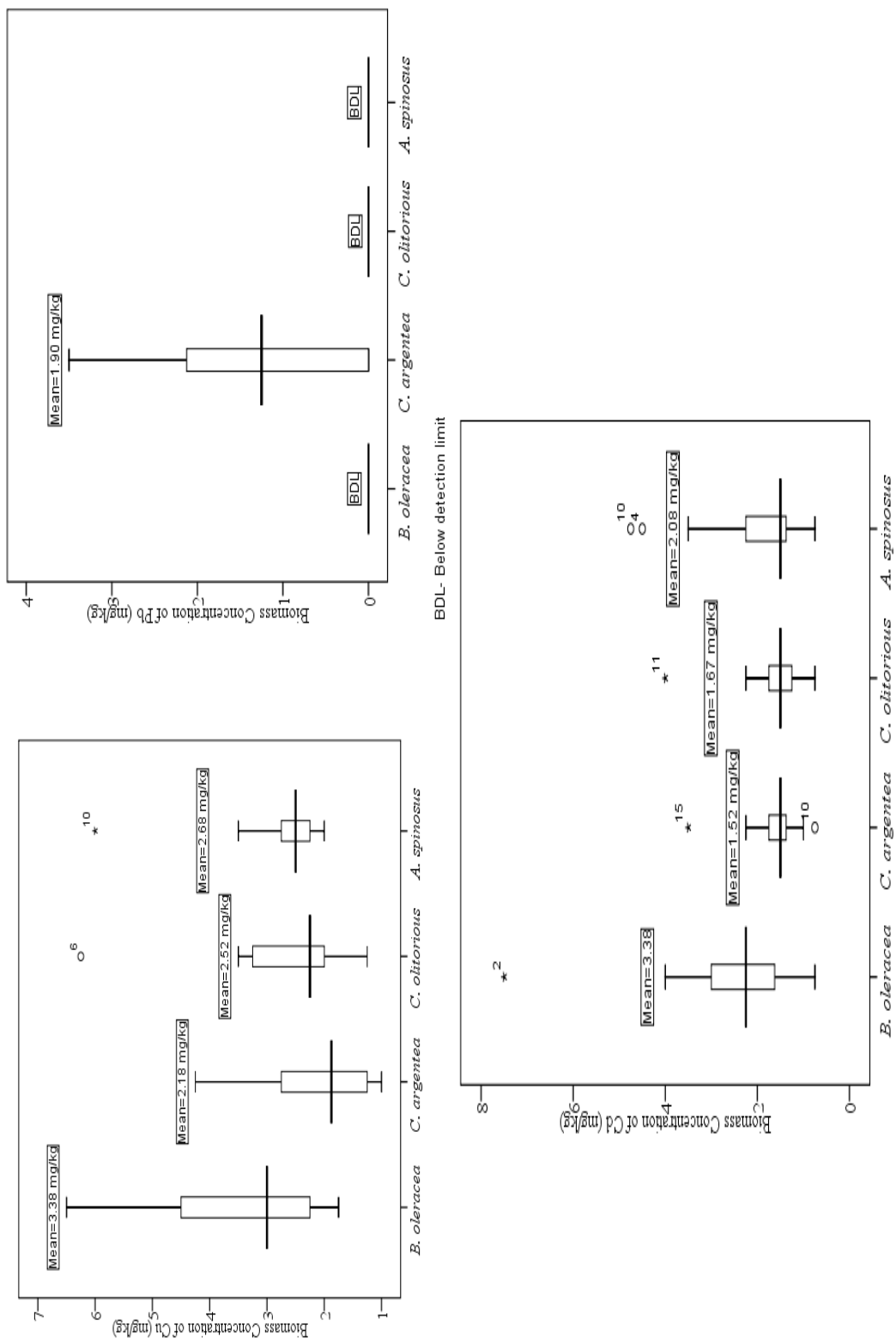
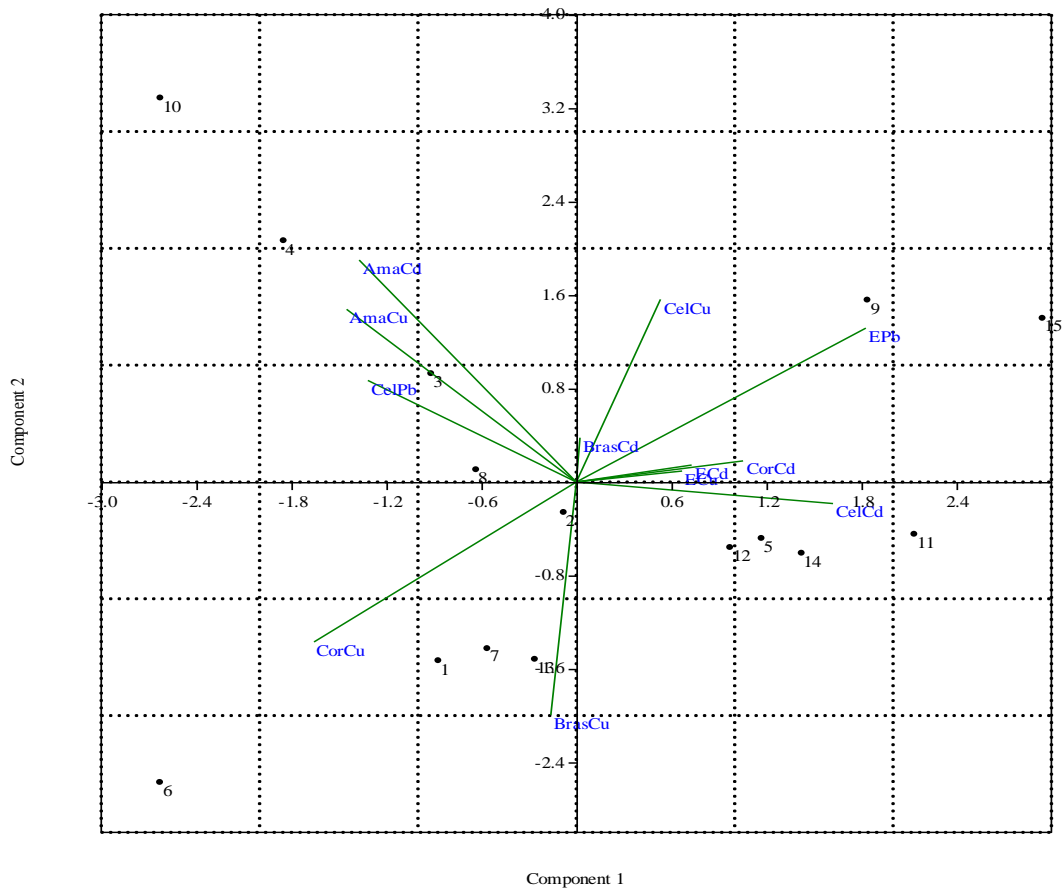**Fig. 3. Concentrations of Cu, Pb, and Cd in the shoot biomass of the leafy vegetables**

Fig. 4. PCA Biplot (Correlation matrix), showing the relation among extractable metal (E) and vegetable biomass metal concentrations
Note: EPb, ECu, and ECd are extractable metal concentrations of Pb, Cu, and Cd respectively while Ama, Cel, Cor, and Bras stand for Amaranthus, Celocia, Corchorus, and Brassica, respectively.
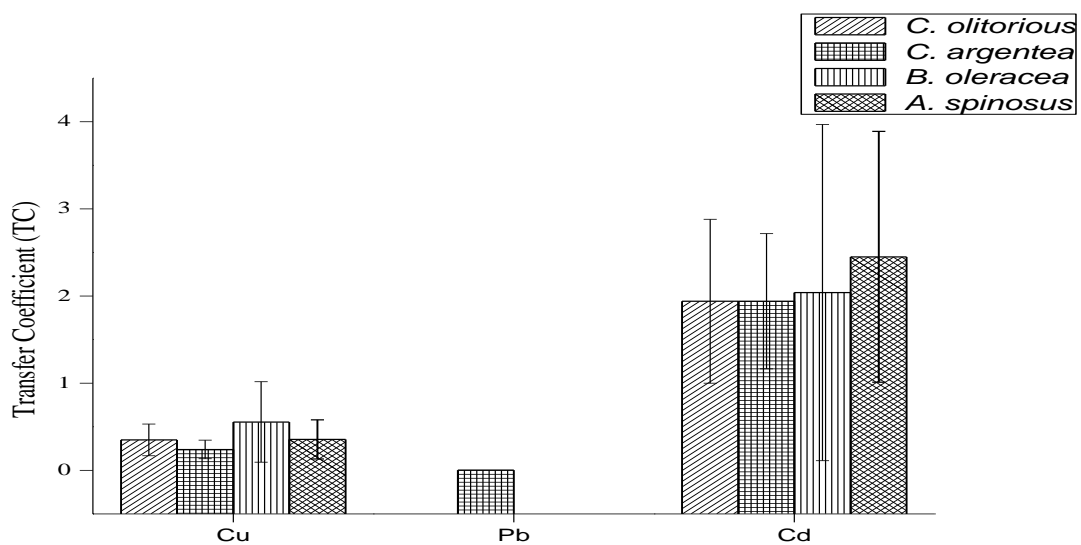

Fig. 5. Transfer coefficient (TC) of Cu, Pb, and Cd in the vegetables (Pb < detection limit in *C. olitorius*, *B. oleracea* and *A. spinosus*)

Daily intake of metal and potential human health risk

The implication of heavy metal contamination, uptake and bioaccumulation in vegetables cannot be overemphasized, owing to the disturbing effects. Literature shows considerable level of information on the phytotoxic effects of heavy metals such as Pb and Cd. Although not considered in this study, metal phytotoxicity can eventually decrease crop yield, owing to significant alterations in enzymatic activities, respiration, photosynthesis, genotoxicity, and considerable decrease in vegetable nutrient composition (Lagriffoul et al., 1998; Sinha et al., 2006; Pourrut et al., 2012). In addition, risk assessment of exposure to metal contaminated-vegetables taken by a population can inhibit the likelihood of proliferation of heavy-metal-associated diseases. Hence, this study also estimated the level of metal exposure by quantifying estimated daily intake (EDI) and the potential human carcinogenic risk to humans of the population in the urban area.

Limited data is available on the daily intake of individual vegetables in Nigeria; however, *B. oleracea* expressed the highest estimated EDI of metals (Cu and Cd), compared to other vegetables (Table 3). The EDI exceeded the tolerable daily intake (TDI) of 0.001 mg/kg/day for Cd in all the vegetables by at least 2-fold (USEPA, 2007; FAO/WHO, 2010). In addition, the present study showed that potential daily intake of vegetables, containing Cd from the urban garden, was also higher than that found in Khan et al.

(2008) and Orisakwe et al. (2012), thus likely to pose adverse health conditions. Despite the low dietary intake of vegetables in Nigeria compared to literature (Khan et al., 2008) and the WHO standard to prevent chronic diseases, Cd daily intake was still relatively high.

The hazard quotient (HQ) for Cu and Pb in the adult population of the study area showed negligible health risk as the HQ values were $\leq$ 0. HQ for Cd in all the vegetables indicated potential health risk to consumers in the area, as HQ values exceeded the recommended safe limit, equal to 1.0, by several folds. Therefore, long-term consumption of any of these Cd-contaminated vegetables may results in serious human health hazard and chronic exposure may lead to several health problems. It is known that long-term consumption of Cd-contaminated vegetable may result in organ defects, cell necrosis, kidney stones, acute gastrointestinal effects, bone damage, low birth weight, and increased rate of abortion (Godt et al., 2006). Heavy metal mitigation and/or remediation of the soils, particularly Cd is required.

CONCLUSION

The present study showed that anthropogenic activities have resulted in the release of trace metals in the local environment, causing elevated concentrations of trace metals in the surrounding soil and vegetables. Total and bioavailable concentrations of trace metals in the soil samples were in the following

Table 3. Estimated daily intake (EDI) and non-cancer health risk (HI) of metal through vegetable consumption.

	Estimated daily intake (mg/kg bw/day)			Hazard quotient (HQ)			Hazard index (HI)
	Cu	Pb	Cd	Cu	Pb	Cd	
B. oleracea	0.0045	0	0.0045	0.112	0	4.5	4.61
C. argentea	0.0029	0.0026	0.0020	0.072	0.74	2.0	2.81
C. olitorious	0.0034	0	0.0022	0.085	0	2.2	2.28
A, spinosus	0.0036	0	0.0028	0.090	0	2.8	2.89

order: Pb> Cu> Cd. The concentrations of Pb and Cd in the soils exceeded the Canadian Soil Quality Guidelines and United Kingdom Soil Guideline Values for agricultural soils, indicating some risks to the surrounding ecosystems. Although the soil pH was appropriate for vegetable cultivation, there was a severe deficiency of macronutrients and high coarse soil attributes. Despite the favorable pH, Cd was bioavailable and mobile enough to get accumulated in the vegetables. The bioavailable fraction served as a good determinant of the potential mobility of the metal in soils, as the absorbed metals were in the dissolved and exchangeable phase. The eventual uptake of heavy metals into the edible part of the vegetables exceeded the World Health Organization (WHO) maximum limits for metals in vegetables. Hence, risk assessment showed that chronic exposure to such vegetables was unsafe and proper management and remediation of soils should be carried out in order to reduce potential health risks, associated with the consumption of contaminated vegetables. Further, a long-term risk assessment needs to be carried out in order to assess the leachability and migration potential of these toxic metals in the soils.

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