

**SPECIATION OF HEAVY METALS IN SOIL AND THEIR PHYTO-  
AVAILABILITY IN EDIBLE PART OF SOME SELECTED VEGETABLE SPECIES  
CULTIVATED ALONG MAJOR HIGHWAYS IN LAGOS, NIGERIA**

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## **Abstract**

This study investigated five heavy metals speciation and soil-plant transfer to edible leafy plants species on roadside Vegetable farmland. Ten soil samples and five varieties of Vegetable species (Water Lettuce, Scent leaf, Curry leaf, Bush okra and African Spinach) were collected from two major roadsides vegetable farmland located at LASU Iyana-Iba road and Lagos Badagry expressway in Lagos, Nigeria. A five-step sequential extraction procedure was applied for the determination of the distribution of the heavy metal (Pb, Cu, Zn, Fe, Cd) in soil samples collected. The mean percentage order of mobility and bio-availability of these metals were: Cd>Pd>Zn>Cu>Fe. The results showed that Cu (98.89±13.22 mg/kg) and Fe (1272.93±352.90 mg/kg) were predominantly associated with residual fractions while Pb (11.18±0.79 mg/kg, 11.11±0.79 mg/kg) and Cd (5.61±1.39 mg/kg, 5.85±1.66 mg/kg) were associated with exchangeable and Fe–Mn oxide fractions respectively. A comparison of the result of total extractible metals with standard set by USEPA reveals that Cu (457.1±64.06 mg/kg) and Cd (28.27±6.21 mg/kg) level in the vegetable farmland were above the critical permissible limit of 250mg/kg and 3.0mg/kg respectively for agricultural soil and therefore portend a health risk. The order of decreasing level of concentration for all the metals in the vegetable species is given as; Fe>Cu>Pb>Cd>Zn. The result also revealed that plant species accumulated Cu (180.9± 65.61 mg/kg), Cd (11.349±1.27 mg/kg) and Pb (14.85±5.21 mg/kg) above the threshold limit of 10 mg/kg, 0.1-1.2 mg/kg, and 5.0 mg/kg respectively suggested by USEPA. At present, the study indicated that Pb and Cd are potentially bioavailable in the soil with Cd present at chronic level while the vegetables species were heavily contaminated with Cu, Cd and Pb at chronic level which may pose health risk at consumption. Therefore it is recommended that cultivation and consumption of vegetables in the study areas should be discouraged.

**Key words:** Heavy metal, Speciation, Mobility, Roadside vegetable soil, Lagos

## INTRODUCTION

In recent years, advancement in technology has led to high levels of industrialization leading to pollution of the environment with heavy metals (Olukanmi and Adeoye, 2012). Sources of heavy metals in soils in urbanized areas mainly include natural occurrence derived from parent materials and human activities which are associated with activities such as atmospheric deposition, industrial discharges, waste disposal, waste incineration, urban effluent, long-term application of sewage sludge, fertilizer application in soil, and vehicle exhausts (Olukanmi and Adeoye, 2012, Bilos et al., 2001; Hlavay et al., 2001; Koch and Rotard, 2001). Depending on the concentration, heavy metals can either be essential nutrients or toxic to biota and their contamination of the environment is of major concern because of their toxicity and threat to human life and the environment (Olajire *et al.*, 2003, Saken *et al.*, 2010).

Cultivation and sales of vegetables are often undertaken along highways with increased risk of pollution from vehicular emission and atmospheric deposition (Olabanji et al 2013). In many cities in the developing world, lack of access to land make other lands including hazardous places such as road verges, banks of drainage channels and dumpsites converted to vegetable gardens (Olukanmi and Adeoye, 2012). All setbacks along major highways are used by farmers for vegetable cultivation. It has been reported that topsoil and roadside soil near heavy traffic in urban areas are indicators of heavy metal contamination from atmospheric deposition (Arowolo et al., 2000; Xiangdong et al., 2001). Metals such as Pb, Cd, Cu, and Zn are good indicators of contamination in soils because they appear in gasoline, car component, oil lubricants and industrial incinerator emissions (Popoola et al., 2012). Lead contamination of roadside soil and vegetation is considered to arise from organic tetraalkyl lead additives: tetramethyl lead, tetraethyl lead, and mixed alkyls triethylmethyl lead, diethyldimethyl lead and ethyltrimethyl lead. Methylcyclopentadienyl manganese tricarbonyl (MMT) has now largely replaced lead additives as antiknock compound in regular leaded gasoline. However, motor vehicle tyre wear and fossil fuel combustion are now the emerging sources of lead and Cadmium in the roadside environment (Ozkan et al 2005). Also Cadmium is used in carburators of motor vehicle as alloy and is released after combustion (Olajire and Ayodele 1997). Excessive accumulation of heavy metal in agricultural land

through traffic emission may results in soil contamination and elevated heavy metal uptake by crops, and thus affects food quality and safety (Ikeda *et al.*, 2000). Trace metals contamination in plants could also be traced to the air particulate deposition on plants and soil from which metals are taken up by the root or foliage. Aerial deposition on leaf surfaces and metal accumulation on the hairy and rough surfaces by rain and dust are exposure routes for plants, because the transportation of ionic metals from the leaf surface via ionic channels to other locations in the plant depend on the mobility of the metal in the xylem and phloem. When plants are polluted with metals, it serves as exposure routes for herbivores and man (Marschner, 1995).

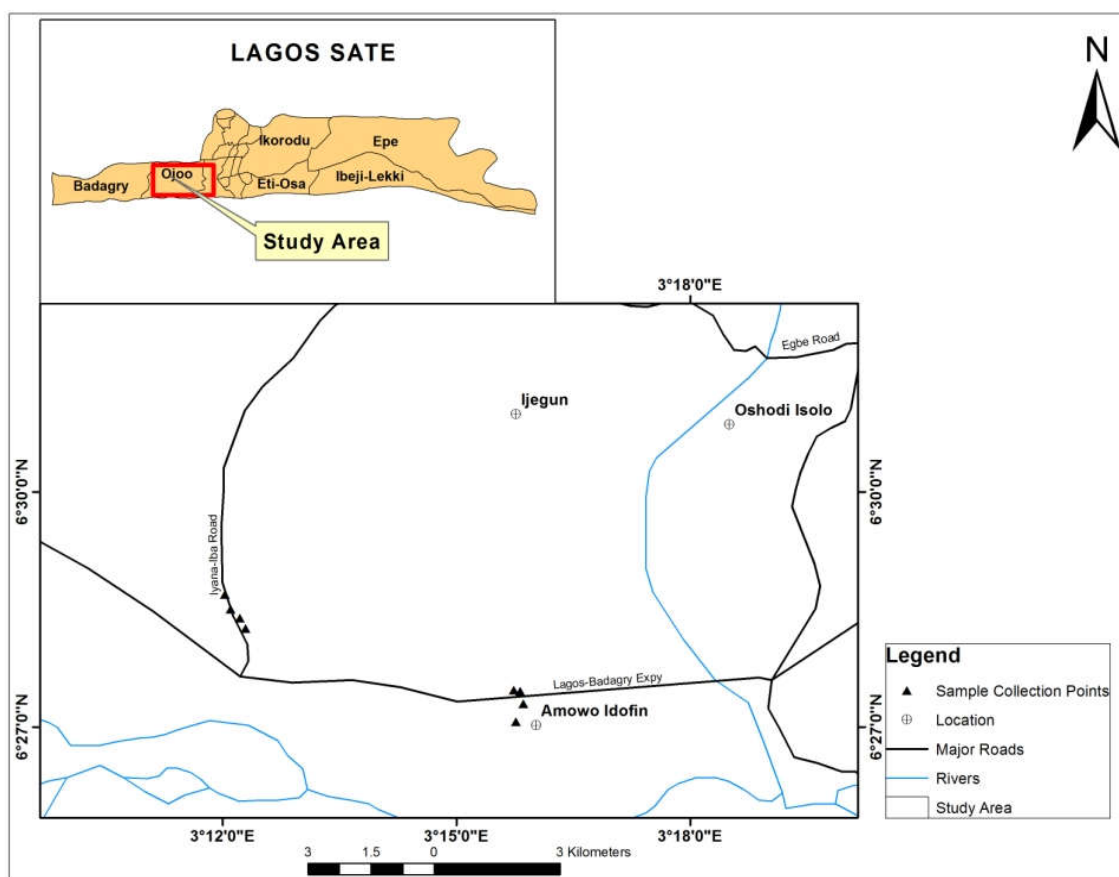
The uptake of metal by plants roots depends on the form the metals exist in the soil and the nature of the soil and the plant species. Thus, metal mobility and plant availability are very important when assessing the effect of soil contamination, plant metal uptake, and toxicity (Chandrasekhar *et al.*, 2001). Total metal concentrations in the soil may indicate the overall level of metals in soils, but they provide no information regarding the chemical nature or potential mobility and bioavailability of a particular element, capacity for remobilization and the behavior of the metals in the environment (Tessier *et al.*, 1979; Vijver *et al.*, 2004; Powell *et al.*, 2005; Kalis *et al.*, 2007; Ping *et al.*, 2008;). Therefore, measurements of labile trace metal species in environmental samples are essential for the assessment of pollution or trace element cycling (Kabata-Pendias, 2004; Gupta and Sinha, 2006; Iwegbue *et al.*, 2007).

Although there are many studies on detection of concentration of toxic trace metals in roadside environment in different part of Nigeria (Akinola and Adedeji, 2007; Amusan *et al.*, 2003; Abechi *et al.* 2010; Arowolo *et al.*, 2000; Atuanya and Oseghe, 2006; Awofolu 2005; Olukanmi and Adeoye, 2012; Atayese *et al.*, 2009; Adu *et al.*, 2012), there is no report on speciation studies of heavy metals in the roadside soil under study. It is on this background that this study seeks to investigate the presence of different chemical forms of heavy metals in soil and their bioavailability on edible part of some vegetable species cultivated along some major high ways in Lagos, Nigeria.

## **MATERIALS AND METHODS**

### **Description of the Study Area**

This study was conducted in Lagos, southwest Nigeria. The State lies between the sedimentary belt of South-Western Nigeria on longitude 20° 42' E and 3° 22' E and between latitude 6° 22' N and 6° 22' N. The area has a bimodal rainfall pattern which peaks in June and September. Lagos is a major industrial and commercial hub in Nigeria with a population density of 2,578person/Km<sup>2</sup> which is responsible for about 70% of the nations industries and commercial activities (Olukanmi and Adeoye, 2012). It is characterized by the heaviest traffic on major highways along where the commercial vegetable cropping takes place. The geophysical map showing the different sampling points in the study area is shown in figure 1



**Figure 1:** Map of the study area showing the sampling points

### **Chemicals and apparatus**

Chemicals and apparatus used for the study included: Acetic acid, Hydroxylamine hydrochloride, Perchloric acid, Ammonium acetate, Nitric acid, Hydrofluoric acid, Hydrogen peroxide, glassware, weighing balance (Gallenkamp 80), pH meter (Fisher Hydrus 300 model), mechanical shaker (Model TT 12F, Techmel and Techmel, Texas, US), electric

heater, centrifuge (Model TGL-16G, Shanghai, China), atomic absorption spectrophotometer (Buck Scientific Model 200A, Norwalk, Connecticut, US).

### **Sample Collection**

Two sites situated along busy roads were selected. Specifically, the sites were Lagos State University-Iba road and Lagos-Badagry Expressway (figure 1). A total of ten soil samples were collected at the two locations and the sample were collected in triplicate. Consent was gained and permission obtained from the vegetable farmers to get soil samples from the farmland. At each site, the vegetable farmland was divided into five sections. Composite samples were obtained by mixing sub-samples from five random points within each section and three composite samples were prepared for each section. Soil samples were collected from each portion of cultivated part by digging out a monolith of 10 × 10× 20cm size. The soil samples were brought back to the laboratory, air dried, crushed with porcelain mortar and pestle and passed through 2 mm mesh size sieve and were stored at room temperature before analyses (Sharma et al., 2009).

Five species of vegetables were randomly collected from different part of the farmland at each location and were transported to the laboratory. The species of vegetables collected includes; Water Lettuce (*Launaea taraxacifolia*), Scent leaf (*Ocimum gratissimum*), Curry leaf (*Thymus vulgaris*), Bush okra (*Corchorus olitorius*) and African Spinach (*Amaranthus Hybridus*). Non-edible portions of these vegetables were removed and the edible parts were washed and air dried, and then oven dried at 60°C. The sample were crushed with porcelain mortar and pestle and sieved through a 2 mm mesh size sieve.

### **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 Strowbel *et al.*, 2005. The soil moisture content was determined according to the procedure outlined by APHA (1998) while the cation exchange capacity of the soil samples were determined by ammonium saturation method described by Robertson *et al.* (1999). Organic carbon and the organic matter were determined according to the procedure outlined by Jackson (1958) while SO<sub>4</sub><sup>2-</sup> was quantified by procedure described by Butters and Chenery (1959). CO<sub>3</sub><sup>2-</sup> was determined using rapid titration method otherwise known as acid neutralization method.

### **Sequential Extraction of Heavy Metals**

A large number of sequential extraction methods have been reported, many of which are variant on Tessier procedure (Tessier *et al.*, 1978) 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 Tessier *et al.* (1979) and modified by Uba *et al.*, (2008). The steps and operationally defined fractions of metals are summarized in Table 1.

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<sup>-1</sup> using a Rotavit shaker (Selecta). After each extraction step, the suspensions were centrifuged at 3000 min<sup>-1</sup> (Heraeus SAPATECH centrifuge) for 30 min. The supernatants were carefully removed and stored in polyethylene bottles at 4<sup>o</sup>C. The residues were washed with ultrapure water before the addition of the next extracting agent.

The heavy metals content of each fraction was analyzed using Atomic absorption spectrophotometry (Perkin-Elmer Model Analyst 2002). The following metals were analyzed for; Pb, Cd, Fe, Zn, and Cu. All samples were run in triplicates.

**Table 1:** Sequential extraction method for metal speciation used in the present study (Tessier *et al.* 1979)

Steps	Fraction	Reagents	Duration of treatment and temperature
1	Exchangeable	8 ml of 1 M NaOAc, pH = 8.2	2 h at 20 <sup>o</sup> C
2	Carbonate bound	8 ml of 1 M NaOAc, pH = 5	6 h at 20 <sup>o</sup> C
3	Fe/Mn oxide bound	20 ml of 0.04 M NH <sub>2</sub> OH.HCl	6 h at 96 <sup>o</sup> C
4	Organic matter	(a) 3 ml of 0.02 M HNO <sub>3</sub> + 5 ml of 30% H <sub>2</sub> O <sub>2</sub>	(a) 3 h at 85 <sup>o</sup> C

	bound	(b) 3 ml of 30% H <sub>2</sub> O <sub>2</sub>	(b) 3 h at 85 <sup>o</sup> C
		(c) 5 ml of 3.2 M NH <sub>4</sub> Oac	(c) 30 min at 20 <sup>o</sup> C
		3 ml of HNO <sub>3</sub> + 0.7 ml of HClO <sub>4</sub> + 0.8 ml of HCl + 1 ml	Microwave
5	Residual of HF		digestion (20 min)

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**Source:**

**Quality Assurance**

The quality assurance procedures and precautions were ensured for the reliability of the results. Samples were carefully handled to avoid contamination. Glass wares were soaked in 10% HNO<sub>3</sub> overnight and were washed with liquid soap, and rinsed properly. The reagents were of analytical grades and deionised water was used throughout the study. Reagent blank determinations (deionized water and acids) were used to correct the instrument readings. The most sensitive wavelength for each element was selected for analysis, and calibration of AAS was done using multi- elemental solution prepared by serial dilution of 20, 10, 5, 3, 2 and 1 ppm with r<sup>2</sup> value above 0.9 before the analysis of the samples.

**Statistical Analysis**

Descriptive statistics was used for data analysis, using Statistical Package for the Social Sciences (SPSS, version 18.0, Inc., Chicago, USA). The data were displayed as mean ± standard deviation. Correlation analysis (CA) and Principal component analysis (PCA) were also carried out using SPSS to find out the major biogeochemical processes controlling the distribution and partitioning of metals.

**RESULT**

The result of the physico-chemical properties (pH, Moisture content, CEC, organic matter, organic carbon, % carbonate and % Sulphate) of the soil in the two studied sites are shown in table 2. The mean of pH, organic carbon, organic matter, cation exchange capacity, % carbonate and % sulphate of the soil are: 6.9±1.14, 2.94±0.88%, 5.87±1.76%,



3.36±0.87cmol/kg, 2.32±0.54%, and 33.7±9.59% respectively. The result shows that there was significant difference ( $p<0.05$ ) among the physico-chemical parameters in the two study locations.

The result obtained from metal speciation of each farm land at the two study locations for five elements were presented in table 3a and 3b and graphically in figure 2. The mean percentage order of mobility and bio-availability of these metals were: Cd>Pb>Zn>Cu>Fe (Figure 3). The result revealed that the total extractible Cu, Zn and Pb in the farmland were significantly ( $p<0.05$ ) higher in the site 2 compared to the site 1. The paired sample T-test of mean concentration of total extractible metals between the two roadsides vegetable farmland also shown that there was significant difference between the concentration of metals in two study sites except for Fe and Cd ( $P<0.05$ ). Table 4 shows the geoaccumulation Index values and pollution intensity of metals in the soil of the study sites. Cd and Pb in the soil under study fall within the category of very seriously polluted and moderately polluted respectively. Additionally, Zn and Cu are within the class of unpolluted to moderately/highly polluted respectively. According to geoaccumulation index, the degree of contamination from strong to weak in the studied soil was: Cd>Cu>Pb>Zn. Table 5 presents the risk assessment of metals associated with exchangeable and carbonate fraction of the soil in the study sites. The table reveals that the percentage of all metals associated with exchangeable and carbonate component of soil under study falls within medium risk (11-30%).

Moreover, the results of total heavy metals concentration (mg/kg) in the edible part of plant species are shown in table 6. The concentrations of Cu and Cd for all vegetable species were significantly higher in the site 2 compare to site 1 while Fe and Pb for all vegetable species were significantly higher in site 1 compare to site 2 ( $P<0.05$ ). The order of decreasing level of concentration for all the metals in the vegetable in both locations is given as; Fe>Cu>Pb>Cd>Zn.

The results of Biological accumulation coefficient (BAC) are presented in figure 4. The result shown that all the vegetable species studied had BAC<1 for all the metals.

Correlation and Principal component analysis (PCA) were used to obtain additional information on the behavior of physico-chemical properties and heavy metals in the soil. First, non-parametric correlation analysis was conducted on total extractible heavy metals and soil physicochemical parameters to obtain relationship that exist between the two parameters.

The result of the correlation and Principal component analysis were presented in table 7 and table 8 respectively.

**Table 2:** Physico-chemical parameters of the soils in the studied sites, mean±SD (n=3)

SITES	pH	Moisture Content (%)	CEC (cmolc/kg)	TOC (%)	TOM (%)	Carbonate (%)	Sulphate (mg/kg)
			3.52±0.13 <sup>cd</sup>				
<b>1A</b>	8.2±0.10 <sup>d</sup>	4.2±0.06 <sup>b</sup>	<sup>e</sup>	2.77±0.16 <sup>c</sup>	5.55±0.37 <sup>c</sup>	2.54±0.12 <sup>d</sup>	28.98±0.76 <sup>c</sup>
<b>1B</b>	8.8±0.06 <sup>e</sup>	8.73±0.25 <sup>c</sup>	1.7±0.41 <sup>a</sup>	3.3±0.35 <sup>d</sup>	6.6±0.70 <sup>d</sup>	2.94±0.01 <sup>f</sup>	23.67±1.20 <sup>a</sup>
<b>1C</b>	5.4±0.15 <sup>a</sup>	2.18±0.13 <sup>a</sup>	4.34±0.21 <sup>f</sup>	2.61±0.16 <sup>c</sup>	5.23±0.32 <sup>c</sup>	1.99±0.11 <sup>c</sup>	34.6±0.20 <sup>e</sup>
<b>1D</b>	6.7±0.15 <sup>c</sup>	8.73±0.15 <sup>c</sup>	2.13±0.06 <sup>b</sup>	3.69±0.10 <sup>e</sup>	7.38±0.20 <sup>e</sup>	2.88±0.11 <sup>f</sup>	43.27±0.65 <sup>g</sup>
<b>1E</b>	8.2±0.10 <sup>d</sup>	4.27±0.31 <sup>b</sup>	3.48±0.05 <sup>cd</sup>	3.48±0.11 <sup>de</sup>	6.96±0.22 <sup>de</sup>	2.91±0.00 <sup>f</sup>	54.83±1.79 <sup>h</sup>
			<sup>e</sup>				
<b>2A</b>	5.9±0.52 <sup>b</sup>	2.07±0.03 <sup>a</sup>	4.49±0.05 <sup>f</sup>	3.97±0.01 <sup>f</sup>	7.94±0.02 <sup>f</sup>	1.96±0.05 <sup>c</sup>	29.7±1.08 <sup>d</sup>
<b>2B</b>	6.2±0.06 <sup>b</sup>	4.43±0.21 <sup>b</sup>	3.24±0.01 <sup>c</sup>	1.02±0.18 <sup>a</sup>	2.04±0.36 <sup>a</sup>	2.06±0.03 <sup>c</sup>	25.53±0.64 <sup>b</sup>
<b>2C</b>	6.8±0.10 <sup>c</sup>	2.07±0.02 <sup>a</sup>	3.77±0.15 <sup>e</sup>	3.33±0.06 <sup>d</sup>	6.67±0.12 <sup>d</sup>	2.74±0.13 <sup>e</sup>	29.63±0.76 <sup>d</sup>
<b>2D</b>	5.9±0.06 <sup>b</sup>	4.4±0.17 <sup>b</sup>	3.33±0.15 <sup>cd</sup>	3.2±0.10 <sup>d</sup>	6.4±0.20 <sup>d</sup>	1.72±0.02 <sup>b</sup>	39.23±0.51 <sup>f</sup>
<b>2E</b>	6.9±0.06 <sup>c</sup>	4.3±0.20 <sup>b</sup>	3.63±0.05 <sup>de</sup>	1.98±0.04 <sup>b</sup>	3.96±0.08 <sup>b</sup>	1.47±0.12 <sup>a</sup>	27.7±0.81 <sup>c</sup>
<b>Avg</b>	<b>6.9±1.14</b>	<b>4.54±2.43</b>	<b>3.36±0.87</b>	<b>2.94±0.88</b>	<b>5.87±1.76</b>	<b>2.32±0.54</b>	<b>33.7±9.59</b>

**Key 1:** CEC: Cation exchange capacity, **TOC:** Total organic carbon, **TOM:** Total organic matter **Key 2:** 1A-1E: Sampling points at LASU Iyana-iba roadside vegetable farmland, 2A-2E: Sampling points at Lagos Badagry roadside vegetable farmland.

**Key 3:** Values in the same column followed by the same superscript are not significantly (P<0.05) difference (DMRT)

**Table 3a:** Heavy metal concentration in each fraction of the soil samples (mg/kg), mean±SD (n=3)

SAMPLE	FRACTIONS	Cu	Zn	Fe	Pb	Cd
<b>1A</b>	Exchangeable	64±2.65	5.04±0.04	663.3±5.77	10.13±0.15	5.43±0.489
	Carbonate	66.3±1.15	5.05±0.046	643.3±15.28	10.2±0.26	6.69±0.343
	Reducible	65.7±1.53	4.97±0.035	790±137.48	10.03±0.06	7±0.052
	Oxidizable	68±3.46	5.2±0.191	620±17.32	10.13±0.12	7.28±0.131
	Residual	73.3±3.21	5.27±0.023	740±36.06	10.27±0.15	7.31±0.21
	Total Metal	337.3±6.66 <sup>a</sup>	25.53±0.13 <sup>a</sup>	3457±133 <sup>a</sup>	50.77±0.25 <sup>a</sup>	33.71±0.61 <sup>e</sup>
	Non Residual (%)	78.3	79.3	78.6	79.8	78.3
	Residual (%)	21.7	20.7	21.4	20.2	21.7
	Mobile Fraction (%)	38.6	39.5	37.8	40.1	36
<b>1B</b>	Exchangeable	73±3	5.18±0.062	690±17.32	10.23±0.21	7.65±0.021
	Carbonate	76±1.73	5.15±0.01	673.3±23.09	10.07±0.12	7.88±0-151
	Reducible	76±1	5.15±0.02	1130±295.13	10.07±0.12	7.79±0.229
	Oxidizable	74.7±1.53	5.17±0.035	680±55.68	10.23±0.12	7.99±0.119
	Residual	98±2.63	5.22±0.015	1793.3±5.77	10.17±0.06	8.17±0.228
	Total Metal	397.7±8.51 <sup>b</sup>	25.96±0.15 <sup>b</sup>	4967±267 <sup>d</sup>	50.740.10 <sup>a</sup>	39.48±0.61 <sup>g</sup>
	Non Residual (%)	75.4	79.8	63.9	80	79.3
	Residual (%)	24.6	20.2	36.1	20	20.7
	Mobile Fraction (%)	37.5	40	27.4	40	39.3
<b>1C</b>	Exchangeable	78.7±2.52	5.21±0.026	633.3±15.28	10.33±0.06	8.65±0.321
	Carbonate	79.3±0.58	5.27±0.083	656.7±15.28	10.3±0.1	9.51±0.432
	Reducible	77±0	5.35±0.023	1343.3±155.23	10.23±0.15	9.44±0.308
	Oxidizable	78.7±2.08	5.34±0.072	693.3±15.28	10.27±0.21	4.96±0.005
	Residual	84.3±4.16	5.41±0.04	880±170.59	10.4±0.1	4.86±0.025
	Total Metal	398±8.00 <sup>b</sup>	26.58±0.17 <sup>c</sup>	4207±35.1 <sup>b</sup>	51.53±0.25 <sup>a</sup>	37.42±0.52 <sup>f</sup>
	Non Residual (%)	78.8	79.6	79.1	79.8	87.1
	Residual (%)	21.2	20.4	20.2	20.2	12.9
	Mobile Fraction (%)	39.7	39.4	30.7	40	48.5
<b>1D</b>	Exchangeable	87±2.65	5.33±0.04	646.7±20.82	10.87±0.15	4.68±0.199
	Carbonate	88±2	5.32±0.023	633.3±25.17	10.63±0.12	4.54±0.167
	Reducible	86.7±0.58	5.33±0.025	1470±50	10.67±0.21	4.56±0.07
	Oxidizable	91±5.29	5.3±0.025	906.7±81.45	10.57±0.21	4.4±0.015
	Residual	99.7±2.31	5.3±0.026	1646±57.73	10.7±0.2	4.38±0.057
	Total Metal	452.3±5.86 <sup>c</sup>	26.59±0.11 <sup>c</sup>	5303±142 <sup>e</sup>	53.47±0.38 <sup>b</sup>	22.55±0.47 <sup>a</sup>
	Non Residual (%)	78	80	69	80	80.5
	Residual (%)	22	20	31	20	19.5
	Mobile Fraction (%)	38.6	40.1	24.1	40.2	40.9
<b>1E</b>	Exchangeable	90±3.61	5.23±0.01	706.7±15.28	11.03±0.31	4.51±0.127
	Carbonate	90.7±1.15	5.2±0.051	710±10	10.9±0.17	4.51±0.081
	Reducible	88.7±2.08	5.28±0.015	1303.3±61.1	10.73±0.12	4.66±0.081
	Oxidizable	90.3±0.58	5.32±0.036	676.7±11.55	10.93±0.15	4.6±0.031
	Residual	92.7±1.53	5.36±0.031	873.3±32.15	11.03±0.12	4.64±0.067
	Total Metal	452.3±2.31 <sup>c</sup>	26.4±0.13 <sup>c</sup>	4303±87.4 <sup>b</sup>	54.63±0.25 <sup>c</sup>	22.92±0.27 <sup>a</sup>
	Non Residual (%)	79.5	79.6	79.5	79.8	79.7
	Residual (%)	20.5	20.4	20.5	20.2	20.3
	Mobile Fraction (%)	39.9	39.5	33.2	40.2	39.4

Values in the same column followed by the same superscript are not significantly (P<0.05) difference (DMRT)

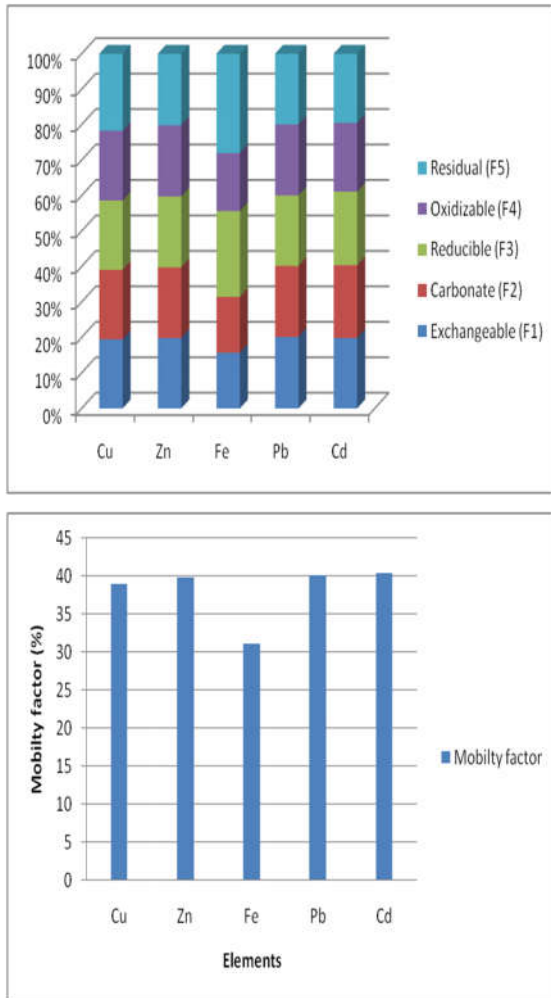
**Key:** 1A-1E: Sampling points at LASU Iyana-Iba roadside vegetable farmland, 2A-2E: Sampling points at Lagos Badagry roadside vegetable farmland.

**Table 3b:** Heavy metal concentration in each fraction of the soil samples continued

SAMPLE	FRACTIONS	Cu	Zn	Fe	Pb	Cd
2A	Exchangeable	90.7±3.51	5.37±0.021	693.3±20.82	11.33±0.12	4.97±0.129
	Carbonate	91.3±2.31	5.39±0.061	703.3±5.77	11.3±0.1	4.96±0.06
	Reducible	92±1	5.47±0.02	960±104.4	11.3±0	4.99±0.065
	Oxidizable	94±2	5.46±0.035	726.7±5.77	11.63±0.21	4.79±0.023
	Residual	95.3±1.15	5.44±0.031	1446.7±181.48	11.5±0.1	4.83±0.04
	Total Metal	459.3±5.69 <sup>c</sup>	27.14±0.15 <sup>d</sup>	4530±271 <sup>bc</sup>	57.070.50 <sup>d</sup>	24.55±0.11 <sup>b</sup>
	Non Residual (%)	79.4	80	68.1	79.8	80.3
	Residual (%)	20.6	20	31.9	20.2	19.7
	Mobile Fraction (%)	39.2	39.7	30.8	39.7	40.5
2B	Exchangeable	99±4	5.31±0.04	710±10	11.7±0.26	4.86±0.078
	Carbonate	96±1.73	5.34±0.032	703.3±11.55	11.6±0.35	4.91±0.085
	Reducible	96.3±0.58	5.33±0.035	933.3±136.5	11.63±0.06	5.09±0.168
	Oxidizable	97±2.65	5.28±0.051	750±10	11.63±0.06	5.05±0.029
	Residual	107.3±7.57	5.3±0.038	1356.7±146.4	11.67±0.32	5.19±0.03
	Total Metal	483.7±1.53 <sup>d</sup>	26.56±0.05 <sup>c</sup>	4453±249 <sup>bc</sup>	59.73±0.64 <sup>f</sup>	25.26±0.48 <sup>bc</sup>
	Non Residual (%)	78.3	80	69.5	80	79.3
	Residual (%)	21.7	20	30.5	20	20.7
	Mobile Fraction (%)	39.3	40.1	31.7	40	38.9
2C	Exchangeable	98.67±2.08	5.32±0.046	733.3±5.8	12.3±0.2	5.26±0.066
	Carbonate	97.67±1.15	5.43±0.036	720±10	11.97±0.21	5.26±0.051
	Reducible	100.33±3.51	5.43±0.061	940±60.8	11.8±0.1	5.27±0.056
	Oxidizable	101±1	5.49±0.015	716.7±15.3	11.93±0.12	5.01±0.05
	Residual	114±4.36	5.49±0.052	1536.7±37.9	11.73±0.31	5±0.04
	Total Metal	505±6.56 <sup>e</sup>	27.16±0.16 <sup>d</sup>	4647±68.1 <sup>cd</sup>	59.33±0.29 <sup>f</sup>	25.8±0.12 <sup>c</sup>
	Non Residual (%)	77.7	78.3	66.9	80.3	80.6
	Residual (%)	22.3	21.7	33.1	19.7	19.4
	Mobile Fraction (%)	38.4	39.5	31.3	40.6	40.7
2D	Exchangeable	105.7±4.04	5.53±0.05	766.7±15.28	11.93±0.15	5.08±0.133
	Carbonate	105.3±2.08	5.54±0.006	773.3±5.77	11.9±0.1	5.21±0.067
	Reducible	104.3±1.53	5.51±0.015	1090±108.17	11.87±0.21	5.37±0.112
	Oxidizable	104±3.46	5.47±0.045	773.3±11.55	11.8±0.2	5.42±0.04
	Residual	111±6.08	5.41±0.017	1260±101.49	11.83±0.25	5.51±0.064
	Total Metal	533.3±2.52 <sup>f</sup>	27.45±0.11 <sup>e</sup>	4663±171 <sup>cd</sup>	58.23±0.59 <sup>e</sup>	26.61±0.26 <sup>d</sup>
	Non Residual (%)	79.1	80.3	73	80.1	79.3
	Residual (%)	20.9	19.7	27	19.9	20.7
	Mobile Fraction (%)	39.7	40.3	33	40.1	38.7
2E	Exchangeable	105±1.73	5.47±0.012	733.33±5.77	11.93±0.06	4.98±0.076
	Carbonate	105.7±1.15	5.5±0.006	743.33±5.77	12.2±0.1	4.98±0.01
	Reducible	105±1	5.54±0.046	906.67±56.86	11.87±0.31	4.95±0.056
	Oxidizable	103.3±1.53	5.55±0.045	753.33±5.77	11.9±0.17	4.86±0.023
	Residual	113.3±4.73	5.55±0.072	1196.67±142.95	11.2±1.13	4.83±0.015
	Total Metal	532.3±5.51 <sup>f</sup>	27.61±0.12 <sup>e</sup>	4333±185 <sup>bc</sup>	59.03±1.29 <sup>ef</sup>	24.6±0.16 <sup>b</sup>
	Non Residual (%)	78.7	79.9	72.4	81	80.4
	Residual (%)	21.3	20.1	27.6	19	19.6
	Mobile Fraction (%)	39.6	39.7	34.1	40.8	40.5

Values in the same column followed by the same superscript are not significantly (P<0.05) difference (DMRT)

**Key:** 1A-1E: Sampling points at LASU Iyana-Iba roadside vegetable farmland, 2A-2E: Sampling points at Lagos Badagry roadside vegetable farmland.



**Fig: 2:** Percentages of metals in each soil fraction **Fig: 3:** Potential mobility of metals in the soil

**Table 4:** Geoaccumulation Index values and pollution intensity of metals in the soil of the study sites

Element	Average crustal values (Hakanson 1980)	mean conc. of metal in soil	I <sub>geo</sub> value	I <sub>geo</sub> grade	Pollution intensity
Cu	50	455.1	2.6	4	Moderately to highly

					polluted
<b>Zn</b>	70	26.7	-2.4	1	Uncontaminated
<b>Fe</b>	----	4486.3	----	--	----
<b>Pb</b>	12.5	55.5	1.6	3	Moderately polluted
<b>Cd</b>	0.15	28.2	7	7	Very seriously polluted

**Table 5:** Risk assessment of metals associated with exchangeable and carbonate fraction of the soil in the study sites

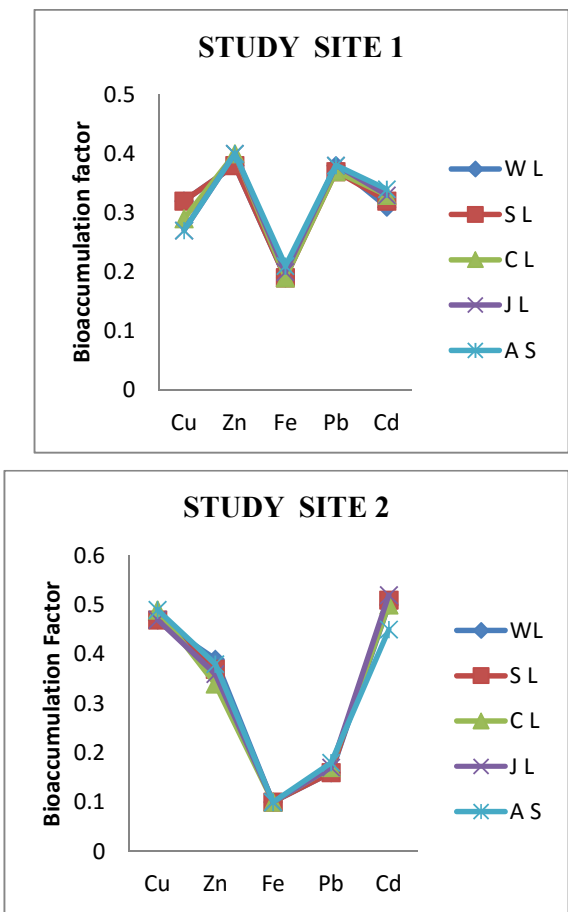
Element	Fraction	% Average	Critical (%)	Risk Assessment Code
Cu	Exchangeable	19.5	11-30	medium risk
	Carbonate	19.6	11-30	medium risk
Zn	Exchangeable	19.9	11-30	medium risk
	Carbonate	20	11-30	medium risk
Fe	Exchangeable	15.7	11-30	medium risk
	Carbonate	15.7	11-30	medium risk
Pb	Exchangeable	20.1	11-30	medium risk
	Carbonate	20	11-30	medium risk
Cd	Exchangeable	19.8	11-30	medium risk
	Carbonate	20.5	11-30	medium risk

**Table 6:** Heavy metals concentration (mg/kg) in edible part of plant species in the studied sites, mean±SD (n=3)

SITES	Samples	Elements				
		Cu	Fe	Cd	Zn	Pb
1	<b>African Spinach</b>	108.7±3.06 <sup>a</sup>	933.3±25.2 <sup>a</sup>	10.5±0.00 <sup>c</sup>	10.47±0.06 <sup>b</sup>	19.7±0.35 <sup>cd</sup>
	<b>Bush okra</b>	110.7±2.08 <sup>a</sup>	903.3±15.3 <sup>a</sup>	10.33±0.06 <sup>bc</sup>	10.4±0.17 <sup>ab</sup>	20.03±0.21 <sup>d</sup>
	<b>Curry leaf</b>	116±1.73 <sup>a</sup>	846.7±11.5 <sup>a</sup>	10.2±0.10 <sup>ab</sup>	10.33±0.06 <sup>b</sup>	19.37±0.21 <sup>c</sup>
	<b>Scent leaf</b>	129.7±8.50 <sup>b</sup>	823.3±11.5 <sup>b</sup>	10.13±0.11 <sup>ab</sup>	10.07±0.06 <sup>ab</sup>	19.77±0.23 <sup>cd</sup>
	<b>Water Lettus</b>	130.7±5.03 <sup>b</sup>	850±17.3 <sup>b</sup>	9.93±0.11 <sup>a</sup>	10±0.10 <sup>ab</sup>	20±0.35 <sup>d</sup>
	<b>Average</b>	<b>119.1±10.4</b>	<b>871.3±45.73</b>	<b>10.2±0.21</b>	<b>10.3±0.21</b>	<b>19.8±0.27</b>
2	<b>African Spinach</b>	251.7±3.72 <sup>c</sup>	442.5±14.0 <sup>c</sup>	11.67±0.21 <sup>d</sup>	10.6±0.85 <sup>b</sup>	10.4±0.40 <sup>b</sup>
	<b>Bush okra</b>	250.2±9.66 <sup>c</sup>	437±6.51 <sup>c</sup>	13.2±0.10 <sup>f</sup>	10.07±0.66 <sup>ab</sup>	9.47±0.32 <sup>a</sup>
	<b>Curry leaf</b>	250.5±7.07 <sup>c</sup>	460.5±10.2 <sup>c</sup>	12.57±0.29 <sup>e</sup>	9.6±0.30 <sup>a</sup>	10.37±0.51 <sup>b</sup>
	<b>Scent leaf</b>	241.7±9.67 <sup>c</sup>	456.7±10.6 <sup>c</sup>	12.8±0.10 <sup>c</sup>	10.47±0.31 <sup>b</sup>	9.5±0.26 <sup>a</sup>
	<b>Water Lettus</b>	240.3±6.11 <sup>c</sup>	454.8±7.10 <sup>c</sup>	12.57±0.35 <sup>e</sup>	10.33±0.43 <sup>b</sup>	9.53±0.31 <sup>a</sup>

Average	246.9±5.42	450.3±10.04	12.56±0.56	10.21±0.49	9.85±0.49
USEPA Standard	10		0.1-1.2	100	5

**Key:** Values in the same column followed by the same superscript are not significantly (P<0.05) difference (DMRT)



**Fig:4** Biological accumulation coefficient (BAC) of plants for all the metals in the studied sites

**Key:** WL-Water lettuce, SL-Scent leaf, CL-Curry leaf, JL-Jute leaf, AS-African spinach

**Table 7:** Correlation coefficients obtained from spearman's analysis

	Cu	Zn	Fe	Pb	Cd	pH	MC	CEC	TOC	TOM	CO <sub>3</sub>	SO <sub>4</sub>
Cu	1											
Zn	<b>.897**</b>	1										
Fe	.416	.306	1									
Pb	<b>.943**</b>	<b>.858**</b>	.186	1								
Cd	-.695*	-.573	-.236	-.699*	1							
Ph	-.436	-.649*	-.098	-.464	.278	1						
MC	-.207	-.402	.556	-.426	.134	.568	1					
CEC	.169	.424	-.552	.371	-.167	-.590	-.967**	1				
TOC	-.214	-.121	.284	-.282	-.034	.292	.264	-.247	1			
TOM	-.214	-.121	.284	-.282	-.034	.292	.264	-.247	1.00**	1		
CO <sub>3</sub>	-.500	-.678*	.236	-.547	.146	.661*	.503	-.558	.596	.596	1	
SO <sub>4</sub>	.076	.044	.114	-.051	-.443	.018	.077	-.070	.551	.551	.315	1

\*\*Correlation is significant at the 0.01 level (2-tailed), \*Correlation is significant at the 0.05 level (2-tailed).



**Table 8:** Varimax Rotated Component matrix for the Total extractible metals and physicochemical parameters of the soil

Parameters	Extracted components		
	PC1	PC2	PC3
Cu	<b>0.966</b>	0.060	-0.114
Zn	<b>0.929</b>	-0.205	-0.054
Fe	0.459	0.737	0.181
Pb	<b>0.907</b>	-0.158	-0.170
Cd	-0.770	<b>0.017</b>	-0.271
Ph	-0.577	0.476	0.179
Moisture content	-0.233	0.932	0.093
CEC	0.231	-0.946	-0.080
TOC	-0.119	0.169	<b>0.923</b>
TOM	-0.119	0.169	<b>0.923</b>
CO <sub>3</sub>	-0.503	0.462	0.561
SO <sub>4</sub>	0.167	-0.024	<b>0.792</b>
% of Variance	34.8	24	23.7

**Extracted Method:** Principal component analysis

**Rotation Method:** Varimax with Kaiser Normalization

Rotation converged in 4 iterations

## DISCUSSION

The study revealed that the mean pH of the vegetable farmland varied between acidity and alkalinity in the study sites. pH plays a role in soil microbial reactions, the observed pH values may well have implications on the soil alkalinity and availability and uptake of metals by plants and microorganisms. Most metals in the pH range of 6.0-9.0 are not always in free form (Porteus 1985). The pH of almost all the soil samples studied fell within this range. This would eventually influence lower release of heavy metals into the sub-soil and ground water.

The mean of total organic carbon (TOC) and cation exchange capacity (CEC) values were generally low. Low organic carbon (matter) and CEC exhibited by soil in this study could be due to high proportion of sand. Cation exchange capacity is known to decrease proportionally with increase in sand in most soil samples because there is always a lesser exchange sites that effect retention of heavy metals in sand compared to clay and organic matter. Low CEC and TOC implied high leachability of heavy metals from the soil to underground water posing health hazard to humans and other animals that drink this water. Cation exchange capacity gives the soil a buffering capacity which may slow down the leaching of nutrient cations and positively charged pollutants because they affect both soluble and exchangeable metal levels (Yoo and James, 2002). While soil organic carbon is not a requirement for plant growth, the levels of organic matter in soils influence a number of soil chemical and physical processes in the soil and it is an important indicator of the soil as a rooting environment (Okalebo *et al.*, 1993).

The concentrations of total extractible Cu in the study areas were all below the toxic limit of 250mg/kg set by USEPA (1986) for agricultural lands indicating that the soil is not polluted with Cu. The results also indicated that majority of Cu in the soil was associated with the residual fraction (i.e bound to silicates and dentrial materials) having an average of 21.61% which is similar to the reports of Gupta and Chen (1975), Harrison *et al.* (1981) and Iwegbue (2007). The result is at variant to Ashraf *et al.*, 2011 and Yeongkyoo *et al.*, 2009 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 bioavailable to the environment. Next in importance for Cu content was Oxidizable fraction which has average percentage of 19.7% (Table 3). These indicate the effectiveness of organic matter as a scavenger of Cu in soil. A number of studies on speciation of Cu have shown that it is mainly bound to the

oxidizable phase, occurring as organic complexed metal species (Perdo et al., 1993; Kotoky et al., 2003; Horsfall and Spiff, 2005; Tucker et al., 2003; Segarra et al., 2008; Osakwe and Egharevba, 2008, Fytianos and Lourantou 2004). The high percentage of copper in this fraction would be relatively immobile in the soils (Froster, 1985; Garcia-Magarraya and Sosa, 1994). This is because organic matter especially holds copper so much that its availability can be very low in organic soils. Copper levels bound to exchangeable and reducible fractions were an average of 19.51% each while the level found in the carbonate fraction was an average of 19.61%. The association of Cu with different fractions was observed to be in the order Residual > Oxidizable > Carbonate > Exchangeable & Reducible (Table 3).

Zinc contents in the both location were within the permissible limits of 30-300mg/kg for agricultural lands set by USEPA (1986). The percentage mobile phase was high indicating that the Zn will be readily bio-available to the environment. It was however noted that Zn was almost equally distributed among various soil fractions.

The majority of Fe in the soils was associated with the residual fraction (28%) (Table 3). This is consistent with the results of Horsfall and Spiff, (2005); Gupta and Chen, (1975); Ramos *et al.*, (1994); Abeh *et al.*, (2007); Segarra *et al.*, (2008). The residual fraction is considered the most stable, less reactive and less bioavailable since it is occluded within the crystal lattice layer of silicates and well crystallized oxide minerals (Abeh *et al.*, 2007; Schawarzenbach *et al.*, 1993). The fraction can be taken as a guide to the degree of pollution of the soil. The smaller the percentages of the metal present in this fraction, the greater the pollution of the area (Horsfall and Spiff, 2005). The high percentage of iron found in residual fraction is an important repository of iron in the soil. In sandy soil that contains little clay, iron oxide could be leached through the soil and impact ground water quality. Appreciable quantity of Fe was also found in the reducible fraction (24.2%). This fraction could be considered relatively stable, slowly mobile and poorly available but could change with variations in redox conditions. It may become more soluble under reducing conditions and less soluble under oxidizing ones (Horsfall and Spiff, 2005). The considerable level of iron in Fe-Mn oxide fraction can be explained by the precipitation effect of Fe-Mn oxyhydroxides in water. Under strong oxidizing conditions and neutral pH value, Fe<sup>2+</sup> can be transformed into Fe<sup>3+</sup> rapidly precipitated as Fe oxyhydroxide (Stumm and Morgan, 1981).

Organic fraction with average Iron content of 16.28% is next in abundance after reducible fraction. The low iron concentration reported here is at variance to the result obtained by

Urunmatsoma and Ikhuoria, 2005. Organic compounds of heavy metals can be directly or indirectly introduced into soil through the formation of complexes and can be taken up by plants. Organic content is associated with the production of gas, and in sandy soil that contains little clay, organic matter and phosphate can leach through the soil and impact ground water (Urunmatsoma and Ikhuoria, 2005). The concentrations of iron found in carbonate and exchangeable fraction have average percent of 15.56% and 15.53% respectively. The iron concentration reported here is in agreement with the result obtained by Abeh et al., (2007). Low iron content in this fraction has been reported (Horsfall and Spiff, 2005; Urunmatsoma and Ikhuoria, 2005; Zhang et al., 2010). The carbonate and exchangeable fractions are released into solutions of low pH, which can be related to stomach conditions (Evans et al., 1992). The association pattern of iron in the different phases were in the order residual > Reducible > Oxidizable > exchangeable > carbonate (Table 3 and Figure 2).

About 80% of Pb was found in the non-residual fraction (Table 3) 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 extractable Pb from all the sampling points in both study areas falls below 140mg/kg set by Canadian soil quality for residential area. The potential bioavailability of the metal is in the following order Exchangeable > Carbonate > Oxidizable > Residual > Reducible. The relatively high level of lead extracted in exchangeable and carbonate fracture is however not encouraging because they are the active forms which are easily mobilized and readily bioavailable. The high levels observed here are not consistent with the reports of Sheppard and Thilbault (1992) and Kabala and Singh (2001).

Total extractable cadmium levels in the study area were above the critical permission of 3.0mg/kg for agricultural soil (MAFF, 1992; USEPA, 1986). Cadmium was found to be mostly associated with the reducible fraction with the percentage average of 20.90%. The percentage of cadmium observed in this fraction is similar to that reported by Horsfall and spiff (2005); Iwegbue (2011). This fraction could be considered relatively stable but could change with variations in redox condition (Horsfall and Spiff, 2005). Jenne (1968) proposed that hydrous oxides of manganese and iron exert the principal control on the fixation of cadmium, nickel, copper and zinc in soils and freshwater sediments. An appreciable amount of cadmium was found in exchangeable and carbonate fraction (19.8% and 20.5%

respectively). This suggests that cadmium is potentially available to some extent in these soils.

The Muller Index of Geoaccumulation,  $I_{geo}$  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 polluted. Grade 6 indicates a 64-fold enrichment over the background values (Singh *et al* 1997). The result from the study shows that the soil were very seriously or moderately polluted by Cd, Pb and Cu whose contamination classes, in most of the soil, were: >5 (very seriously polluted), 1-2 (moderately polluted) and 2-3 (moderately polluted to highly polluted), respectively. Zn belong to class <0, which suggested that the soil were uncontaminated with Zn.

The risk assessment code (RAC) is a criteria used to indicate potential release of metals from the exchangeable and carbonate soil components. Soil which can release exchangeable and carbonate fractions, less than 1% of the total metal will be considered safe for the environment. On the contrary, soil releasing in the same fraction more than 50% of total metal has to be considered highly dangerous and can easily enter food chain (Perin *et al* 1985). The code as applied to the present study shown that all exchangeable and carbonate metals in the study sites come under the medium risk category which implies that they can easily enter the vegetable species cultivated on the farmland.

The result of total heavy metals concentration (mg/kg) in the edible part of plant species shows that different plant species absorbed metals at varying concentrations. Similar observations were reported by Shauibu and Ayodele (2002) and Ebong *et al.* (2008) which revealed the influence of plant species on the rate of uptake of various metal species in line with earlier reports of Kabata-Pendias and Pendias (2001). Since the rate of metal uptake is greatly influenced by plant species, the transfer factors of the metals by each plant species are desirable for classification of the plants' phytoaccumulation, phytostabilization and phytoextraction potentials (Chehregani and Malayeri, 2007; Ayari *et al.*, 2010; Malik *et al.*, 2010).

The results of Cu concentrations (108mg/kg-250mg/kg) showed that most of the plant species accumulated higher concentration of Cu than the normal limits (10.0mgkg<sup>-1</sup>). Values obtained in this study compared favourably with the values reported by Malik *et al.* (2010) for some plant species with the exception of some such as *Parthenium hysterophoirus* L. and

*Partulaca oleracea* L. whose values were exceedingly higher (Malik *et al.*, 2010). However, the values were lower when compared to those reported by Cui *et al.*, (2007) for some other plants species at contaminated sites. Cu is an essential metal for normal plant growth and development. It participates in numerous physiological processes and is an essential co-factor for many metalloproteins, although it is toxic when in excess (Prasad and Strzalka, 1999; Yruela, 2005). Cu concentration exceeding 40mgkg<sup>-1</sup> of dry matter could induce toxicity in plants and cause toxic effects in animals (sheep) feeding on them (Annenkov, 1982).

The elevated range of Fe (436mg/kg-933.3mg/kg) in the various plant species obtained in this study could be attributed to the importance of the metal in plant growth and the general abundance of the metal in the earth's crust (Harrison and Chirgawi, 1989; Kabata-Pendias and Pendias, 2001). However, since most of the plant species studied are edible, the elevated Fe levels calls for concern as it can cause some health implications such as vomiting, upper abdominal pain, diarrhea, dizziness, shock, haemochromatosis, diabetes, diseases of the liver, lungs and kidney, haepatoma and cardinomyopathy to the consumers at chronic levels (Dupler, 2001, Ferner, 2001; Khan *et al.*, 2008).

Cadmium levels at the study sites for the various plant species (9.93-12.8mg/kg) exceeded the values reported by Yusuf *et al.* (2003), Udosen *et al.* (2006) and Ebong *et al.* (2008). The Cd range recorded in the studied plant species is high enough to cause phytotoxicity because according to Vecera *et al.* (1999), Cd phytotoxicity occurs when the level is above the range of 0.10-1.20mg/kg. Although, Cd is not an essential element for plants, they generally exhibit measurable Cd concentrations, particularly in roots, but also in shoots, most probably as a result of inadvertent uptake and translocation (Assuncao *et al.*, 2003). The continuous survival of these plant species in the farmland with high level of Cd in shoots above the normal limits suggested their adaptation to Cd contaminated soils and possibly development of mechanisms for the metal detoxification (Ghosh and Singh, 2005).

The results of Zinc concentrations (9.30-10.5mg/kg) showed that most of the plants species accumulated higher concentration of Zn than those reported by Ebong *et al.* (2008). However, the values were still below the permitted limit (100mgkg<sup>-1</sup>) in shoots as given by Zu *et al.* (2004) and were lower when compared with the results reported for some species of plants by Malik *et al.* (2010). In non-tolerant plants, Zn toxicity is apparent in soils with high Zn content which could result to inhibition of root elongation and chlorosis in young leaves. Soil

pH, soil organic matter and soil hydrology primarily govern the availability of Zn (Kabata-Pendias, 2004; Iwegbue *et al.*, 2007).

Lead (Pb) levels in the studied plant species (9.4-20.03mg/kg) were extremely higher than the values reported by Amusan *et al.* (2005) and Ebong *et al.* (2008) for some other plant species. The results however showed that most of the plants species accumulated higher concentration of Pb than their normal limits (5.0mgkg<sup>-1</sup>) in shoot as given by Zu *et al.* (2004). This high concentration of Pb could have toxic effects on the plants e.g. Pb inhibits activities of many enzymes, upsets mineral nutrition and water balance, changes in hormonal status and affects membrane structure and its permeability (Sharma and Dubey, 2005). Visual nonspecific symptoms of Pb toxicity include stunted growth, chlorosis and blackening of the roots system (Sharma and Dubey, 2005).

Biological accumulation coefficient (BAC) is used as an indicator of high heavy metals accumulation potentials for plant species which usually may be attributed to well developed cellular mechanisms for heavy metal detoxification and tolerance (Hall, 2002; Ghosh and Singh, 2005). Tolerance of heavy metals to plants has been defined as the ability of the plants to survive in a soil toxic to other plants and this is manifested by an interaction between the plants genotype and its environment (Macnair *et al.*, 2000). Biological Accumulation Coefficient (BAC) values greater than one (>1) are used to evaluate the potential of plant species for phytoextraction, phytostabilization and phyto remediation (Yoon *et al.*, 2006; Cui *et al.*, 2007; Li *et al.*, 2007). Additionally, plant species with BAC values > 1 for any metals are regarded as efficient in accumulating such metals and when the plant is able to accumulate up to 1000mg/kg of metal and above, the plant is classified as a hyperaccumulator (Baker and Brooks, 1989). Results of the study (Figures 4) show that all the plant species studied had BAC<1 for all metals. Similar results were reported by several others (Chunilall *et al.*, 2005; Cui *et al.*, 2007; Li *et al.*, 2007; Malik *et al.*, 2010). The BAC values obtained in this study for the plant species studied were low compared to the values reported for some other plant species by other workers (Shu *et al.*, 2000; Archer and Caldwell, 2004; Wei *et al.*, 2006; Malik *et al.*, 2010). It is evident from this study that all the vegetable species are not efficient in accumulating some of the heavy metals.

### **Correlation and Principal component Analysis**

Correlation and Principal Component analysis were used to confirm the sources of heavy metal in the soil. First, non-parametric correlation analysis was conducted on total extractible heavy metals and soil physicochemical parameters to obtain relationship that exist between the two parameters. The heavy metals showed no significant positive correlation with the soil physicochemical parameters indicating that the enrichment of heavy metal in the soil is not influence by soil physicochemical properties (table 4). Statistical analysis result also showed significant correlation between heavy metals, such as between Cu and Zn, Pb and Cu, Pb and Zn, suggesting that they are from the same anthropogenic source. However, Cd did not show positive correlation with other metals, implying that its source is different from other metals, probably from vehicular emission, wear and tear of car tyres etc.

Principal component analysis was also used to obtain additional information on the behavior of heavy metals. Three principal components (PC1, PC2, and PC3) with eigen values higher than 1.0 were extracted from the PCA. PC1 explains 34.8% of the total variance and characterized by the strong positive loading in Cu, Zn and Pb (table 5) which further confirmed the fact that they are from the same anthropogenic source. PC2 shows a very weak positive loading in of Cd showing that this metal is added to the soil from different source. PC3 explains 23.6% of the total variance and is characterized by a strong positive loading in Total organic carbon (TOC), Total organic matter (TOM), CO<sub>3</sub>, and SO<sub>4</sub> indicating that they did not influence the enrichment of the soil with the heavy metals.



## CONCLUSION

The results of the physiochemical parameters of the soil revealed that the pH of the soil varied from weakly acidic to alkaline while Total organic carbon (TOC) and cation exchange capacity (CEC) values were generally low. The results of speciation analysis showed that Cu, Zn and Fe were predominantly associated with residual fractions while Pb and Cd were associated with exchangeable and Carbonate fractions respectively. Since metals associated with carbonate can be remobilised and become available to the biota when the pH conditions of the soil system change, the soils studied could stand the risk of contamination by Cadmium. The high mobility factor values indicate that the metals have high mobility as well as high availability and can be leached easily from the soil. Overall, the results indicated the order of mobility and bioavailability of these metals as: Cd>Pb>Zn>Cu>Fe. A comparison of the result of total extractible metals with standard set by USEPA reveals that Cd level in the vegetable farmland is above the critical permissible limit of 3.0mg/kg for agricultural soil which portend a health risk. The result also implicated the plant species to accumulate Cu, Fe, Cd and Pb above the threshold limit suggested by USEPA (1986). The result from the study based on Muller Index of Geoaccumulation,  $I_{geo}$  shows that the soil were very seriously or moderately polluted with Cd, Pb and Cu whose contamination classes, in most of the soil, were: >5 (very seriously polluted), 1-2 (moderately polluted) and 2-3 (moderately polluted to highly polluted), respectively. Zn belong to class <0, which suggested that the soil were uncontaminated with Zn. The risk assessment of the soil in the study site shown that all exchangeable and carbonate metals come under the medium risk category which implies that they can easily enter the vegetable species cultivated on the farmland.

However, based on BAC values, it is evident from this study that all the vegetable species are not efficient in accumulating some of the heavy metals and therefore did not possess potential for phytostabilization and phyto-extraction. Statistically, metal like Cu, Zn, and Pb are significantly well correlated suggesting that they are possibly from the same anthropogenic source. However, Cd did not show positive correlation with other metals, implying that its source is different from other metals, possibly form atmospheric deposition such as vehicular emission, industrial stack emission etc.

At present, the study indicated that Pb and Cd are potentially available in the soil with Cd present at chronic level while the vegetables species were heavily contaminated with Cd and Pb at chronic level which may pose health risk at consumption. There is a great and urgent

need to carry out further monitoring, and to take suitable remediation measures to minimize the spread of pollution.

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