

Full Length Research Paper

Speciation of heavy metals in soil, and their phytoavailability in edible part of *Amaranthus hybridus* cultivated along major roads in Ile- Ife, Nigeria

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Accepted 7 May 2013

Heavy metal content in soil and *Amaranthus hybridus* cultivated on it were determined by speciation method and acid dissolution. The atomic absorption spectrophotometer was used to quantify the metals in the soil and vegetable. The mobilisation of metals from soil to plants as indicated by the metal contents in the soil and vegetables decreased in this order Fe > Mn > Zn > Cu > Pb > As ≥ Cd. The metals concentration ranges in the soil and vegetables as follows: {Fe (12.540-20.915), Mn (1.727-2.506), Zn (0.717- 1.571), Cu (0.292- 0.569), Pb (0.019-0.030) As (0.016-0.033) and Cd (0.015- 0.028)} µg/g : {Fe (7.359-11.205), Mn (0.964-1.580), Zn (0.542- 1.220), Cu (0.010- 0.272), Pb (0.015-0.085) As (0.012-0.019) and Cd (0.012- 0.018)} µg/g respectively. The total metal concentration found in the vegetables was more than the metal uptake from the soil, indicating contamination of the vegetables from other sources. The heavy metals concentrations were within the safe limit of WHO/FAO. There was no statistical significant difference between the metal uptake by vegetable and total metal in the vegetable at 95 and 99% of probability level. At present the vegetables may not pose health risk but the plots needed to be monitored from time to time.

Key words: Heavy metals, soil, *Amaranthus hybridus*, metal uptake.

INTRODUCTION

Cultivation and sales of vegetables are often undertaken along highways with increased risk of pollution from vehicular emission and atmospheric deposition. The rapid industrialization and unorganized urbanization in this century is responsible for the increase in metal contamination of soils especially in developing countries. The environment is a dynamic system; pollution of one component of the system by heavy metals can spread

throughout the entire system based on the interactions and the existing synergy in the environment (Dube et al., 2001).

Amaranthus hybridus, otherwise known as “pigweed”, is an herbaceous plant with rough, hairy and ovate wavy margin leaves that are alternatively arranged (Akubugwo et al., 2007). It is one of the most popular vegetable grown and eaten by the people of south west Nigeria and

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cultivated throughout the year. *A. hybridus* leaves and stem with other ingredients are used to prepare soup (Oke, 1983; Mepha et al., 2007). It has been found to contain all the classes of food (proteins, fat, fibre, carbohydrate and calorific value, mineral elements, vitamins, amino acids) in appreciable quantities with low level of toxicants (Akubugwo et al., 2007).

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). Trace metals contamination in plants could 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).

Many researchers have established direct relationship between atmospheric metals deposition and increase in metal concentration in plants and top soils, especially in urban centres where there are emitting factories. Since the atmosphere is not partitioned, airborne submicron particles are also deposited on plant surfaces, constituting a substantial, but unknown, contribution to the atmospheric pollution and metal deposition on other ecosystem. (Anderson et al., 1978; Jassir et al., 2005; Sharma et al., 2008a, b; 2009). Vegetables planted along the road side are susceptible to vehicular emission containing heavy metals during production, transporting and marketing because the emission will be deposited on the plant surfaces and raised the metal concentrations (Jassir et al., 2005; Sharma et al., 2008a, b; 2009).

Some trace metals such as (Zn, Se, Mo, Mn and Cu) are essential in plant nutrition, but plants growing in a polluted environment can accumulate trace elements at high proportions that can be deleterious to human health (Wong et al., 2003; Khillare et al., 2004; Marshall, 2004; Sharma et al., 2008a,b).

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 behaviour of the metals in the environment (Vijver et al., 2004; Powell et al., 2005).

Metal speciation of the soil is taken to mean the fractionation of the total metal content into exchangeable (bound to exchangeable sites of clay minerals), acid extractable (bound to carbonates and hydroxides), reducible (bound to Fe/Mn oxides), oxidizable (bound to organic matter/ sulfides) and residual (bound to clay

minerals) forms. The chemical forms of the metal control its bioavailability or mobility. The exchangeable and acid extractable fractions are mobile fractions that are easily bioavailable (Norvell, 1984). This bioavailable metals in the soil will provide rough estimate of metal uptake by plants (especially edible plants) and their risk assessment.

An increased interest in trace metal accumulation in plant systems has emerged and several researchers reported concentrations of a number of trace elements in the local crops and other plants as a consequence of anthropogenic emissions (Bernhard et al., 2004). Modern technologies increase with increasing pollution and contamination of human food chain and its awareness made the International and national regulations on food quality to lowered the maximum permissible levels of toxic metals in the food items (Radwan and Salama, 2006). Heavy metals are bioaccumulative and non-biodegradable with long biological half lives, and they do not have good mechanism of elimination in the body (Suruchi and Pankaj, 2011). Some metals are soluble in water and so at low concentration have damaging effects on man. Thus this study aimed at quantifying the amount of metal ions available for plant uptake in the soil, determining the concentration of the metals present in the edible parts (stem and leaves) of the vegetable and carry out the risk assessment of these metals on humans at consumption.

MATERIALS AND METHODS

Study area

The grid location of the sites from which different soil samples and vegetables were collected are shown in Table 1.

Sample collection

Consent was gained and permission obtained from the vegetable farmers to get soil samples from the farmland (Figure 1). Each plot was divided into four parts, soil samples were collected from each portion of cultivated part by digging out a monolith of 10 × 10 × 20 cm 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).

Vegetables were selected from the four different parts of the farmland and bought from the farmers on each site and were transported to the laboratory. Inedible portions of the vegetables were removed and the edible parts were washed and air dried, and then oven dried at 60°C for 3 min. The same was crushed with porcelain mortar and pestle and sieved through a 2 mm mesh size sieve.

Pretreatment and sterilization of apparatus

All the apparatus used, namely: Teflon tube, conical flask, and stirrer were washed thoroughly and then rinsed three times with distilled water and dried in a Gallenkamp oven. Other apparatus

Table 1. Grid Location of the sampling points.

Site	pH of soil	Distance from road (m)	GPS grid coordinates	
			Longitude (E)	Latitude (N)
A	7.1	8	4°30'50.30"	7°30'49.70"
B	7.7	4	4°32'08.03"	7°29'00.78"
C	6.7	3.6	4°31'57.97"	7°28'56.64"
G	7.9	2.5	4°31'29.68"	7°29'44.72"
E	8.3	2.2	4°32'09.45"	7°29'01.37"
F**(control)	8.3	17	4°30'50.36"	7°30'49.70"
D**(control)	7.4	18.2	4°30'44.54"	7°29'37.08"

**Figure 1.** Vegetable farmland.

used include filter paper, water bath and heater, micro pipette, glass beaker, shaker and a centrifuge.

Reagent used and their sources

The reagents include: Hydrochloric acid (BDH chemical Ltd, Poole, England) Glacial acetic acid (BDH chemical Ltd, Poole, England), Hydroxylamine hydrochloride (BDH chemical Ltd, Poole, England). Perchloric acid (BDH chemical Ltd, Poole, England) Ammonium acetate (Riede-de Haën, Germany). Nitric acid (BDH chemical Ltd, Poole, England).

Soil and vegetable dissolution

One gram of the soil sample was weighed into a Teflon beaker and a mixture of nitric and perchlorate acid ($\text{HNO}_3 + \text{HClO}_4$) was added in the ratio 1: 1.5 (2 ml: 3 ml), followed by addition of 3 ml HF for complete digestion of the silicate matrix and then heated to near dryness at about 200°C. 10 ml of deionised water was added before the solution was filtered and made up to 100 ml and then stored for analysis. 5 ml of nitric acid and 5 ml of hydrogen peroxide was added to one gram of the vegetable sample and was heated on a hot plate at a temperature of 60°C. 10 ml of deionised water was added to the mixture and then filtered. The digested sample was made up 100 ml and stored for analysis.

Speciation analysis

One gram of each soil sample was weighted from a representative sample selected by conning and quartering methods. The

extractions were made through five steps method of Tessier et al. (1979) by shaking for specified time. Centrifugation was carried out at 3000 rpm for 10 min by placing the sample in Teflon centrifuge tubes, followed by decantation and filtration. Deionised water was used to wash the residues following subsequent extractions in order to ensure selective dissolution and avoid possible interphase mixing between the supernatants. All samples were run in triplicates.

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 washed with liquid soap, and rinsed properly and reagents were of analytical grades. 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 (Buck model, at International Institute of Tropical Agriculture, Ibadan) 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.

Statistical analysis

Descriptive statistics was used for data analysis, using Statistical Package for the Social Sciences (SPSS, version 16.0, Inc., Chicago, USA) the significant differences between groups were compared using analysis of independent t-test at probability level of 95 and 99% confidence level. The data were displayed as mean \pm standard deviation.

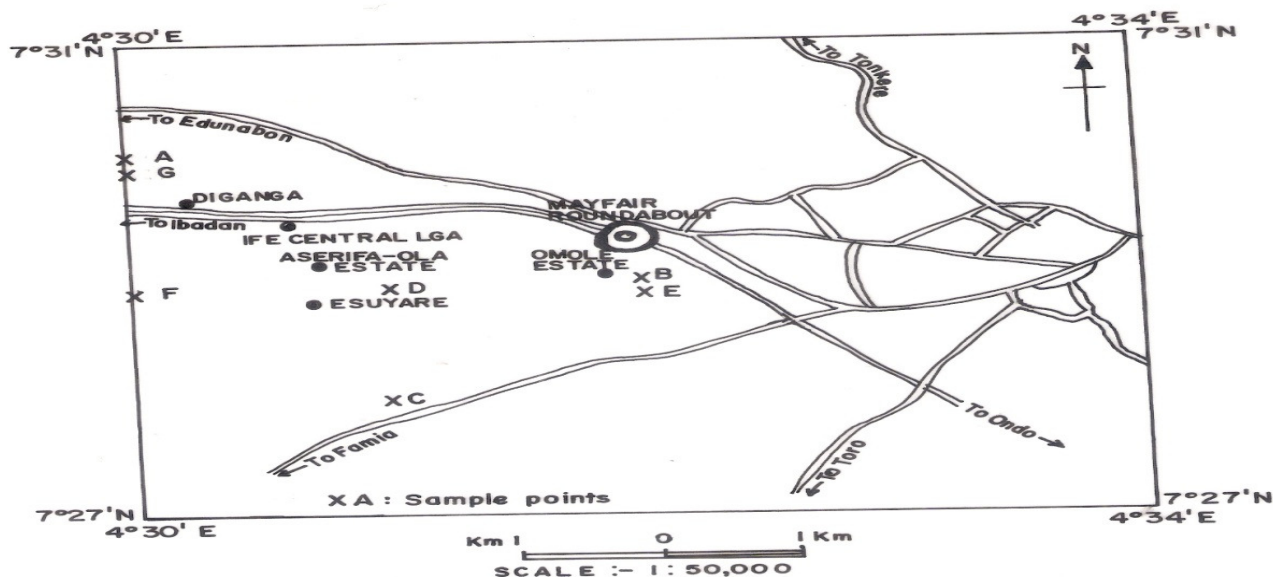


Figure 2. Map of the study area.

RESULTS

The results obtained from metal speciation of each farm land (Figure 2) and total digestion of the edible part of the vegetable (*A. hybridus*) on each plot for seven elements were presented in Table 2a to 2g. The total metal in the soil (TMS), total metal in vegetable (TMV) was determined by acid dissolution and vegetable uptake (VUP) was determined by speciation through the exchangeable and acid extractable ions stages. Table 3 is the summary of the seven metals determined in this study. The TMV was generally higher than VUP, except plot A for Mn, plot B for Zn, plot D for Cu and plot C for As but statistically not significant at 95 and 99% probability levels. The analysis of variance on metals on different plots showed that there is no significant difference between the concentrations of metals on the plots.

Generally, concentrations of Fe were the highest in all the plots in this study and cadmium and arsenic were almost the same in concentrations both in the soil and the vegetables. The metals' concentrations ranges in the soils and vegetables in µg/g are as follows; {Fe (12.540-20.915), Mn (1.727-2.506), Zn (0.717- 1.571), Cu (0.292-0.569), Pb (0.019-0.030) As (0.016-0.033) and Cd (0.015- 0.028)} µg/g : {Fe (7.359-11.205), Mn (0.964-1.580), Zn (0.542- 1.220), Cu (0.010- 0.272), Pb (0.015-0.085), As (0.012-0.019) and Cd (0.012- 0.018)} µg/g. The order of the decreasing level of concentration in µg/g of all the metals in the soil and vegetables in the plots is given below:

Soil: Fe> Mn> Zn> Cu> Pb> As ≥ Cd Table 3

Vegetable: Fe> Mn> Zn> Cu> Pb> As ≥ Cd Table 3

DISCUSSION

The extent of absorption of elements by plants depend on the nature of the plants, chemical constitution of the pollutants, concentration of the elements in the soil, pH and interaction with other elements in the soil (Zurera et al., 1989). The chemical forms of heavy metals are directly related to their solubility in the soil and these control its bioavailability or mobility (Xian, 1989). The soluble forms of heavy metals have high relation to the uptake by plants (Miller and Mcfree, 1983). The exchangeable and acid extractable fractions bound to organic matters are mobile fractions that are easily bioavailable to plants stages 1 and 4. The risk assessor generally can categorize metal bioavailability and uptake based on soil pH and organic matter. It may be difficult to achieve a pH = 2 (for acid extractable fractions) in the environment because the soil was not acidic (the pH ranges from 7.1 to 8.3), but in places where there is heavy industrial presence or gas flaring, it is possible, therefore, the concentration of metals at this stage will be much lower in the environment than what was obtained for the calculation of plant uptake in this study. The theoretical values obtained for metals available for plant uptake (VUP) were lower than the total metal in vegetable (TMV) for all the elements except plot A for Mn, plot B for Zn, plot D for Cu and plot C for As reasons for this are not understood at the moment.

Plants/vegetable get their nutrients from available elements in the soil (as shown sum total of metals

Table 2a. Concentration of Mn in soil and Vegetable in µg/g.

SITE	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5	TMS	TMV	VUP (1 and 4)
PLOT A	0.754±0.003	0.535±0.003	0.435±0.003	0.221±0.003	0.559±0.003	2.506±0.195	0.964±0.073	0.976±0.377
PLOT B	0.684±0.003	0.410±0.003	0.314±0.003	0.523±0.003	0.535±0.003	2.468±0.140	1.580±0.240	1.208±0.112
PLOT C	0.520±0.003	0.509±0.003	0.434±0.003	0.354±0.003	0.319±0.003	2.138±0.090	1.570±0.144	0.875±0.117
PLOT G	0.704±0.003	0.570±0.003	0.433±0.004	0.409±0.003	0.352±0.003	2.469±0.142	1.192±0.079	1.114±0.209
PLOT E	0.631±0.003	0.473±0.003	0.390±0.003	0.311±0.003	0.182±0.003	1.988±0.169	1.233±0.122	0.943±0.226
PLOT F**	0.531±0.003	0.389±0.003	0.511±0.003	0.322±0.003	0.252±0.003	2.006±0.120	1.073±0.054	0.853±0.147
PLOT D**	0.315±0.003	0.473±0.003	0.326±0.004	0.376±0.003	0.236±0.003	1.727±0.087	1.085±0.098	0.692±0.043

** - controls, TMS - Total metal in soil by digestion, TMV- Total metal in vegetable by digestion, VUP- Total metal available for vegetable uptake.

Table 2b. Concentration of Zn in soil and Vegetable in µg/g.

SITE	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5	TMS	TMV	VUP (1 and 4)
PLOT A	0.396±0.004	0.396±0.004	0.207±0.004	0.125±0.004	0.316±0.004	1.438±0.120	0.682±0.042	0.520±0.192
PLOT B	0.409±0.004	0.409±0.004	0.108±0.004	0.315±0.004	0.332±0.004	1.571±0.123	0.542±0.009	0.723±0.066
PLOT C	0.205±0.004	0.136±0.004	0.179±0.004	0.121±0.004	0.215±0.004	0.854±0.042	0.737±0.059	0.325±0.059
PLOT G	0.384±0.004	0.325±0.004	0.148±0.067	0.199±0.004	0.215±0.004	1.269±0.097	0.734±0.056	0.582±0.131
PLOT E	0.262±0.004	0.307±0.004	0.068±0.001	0.121±0.004	0.111±0.004	0.868±0.104	1.220±0.252	0.382±0.099
PLOT F**	0.319±0.004	0.201±0.004	0.070±0.002	0.126±0.004	0.123±0.012	0.838±0.096	0.547±0.019	0.444±0.136
PLOT D**	0.121±0.004	0.306±0.004	0.060±0.002	0.120±0.008	0.111±0.004	0.717±0.094	0.666±0.039	0.241±0.001

** - controls, TMS - Total Metal in soil by digestion, TMV- Total metal in vegetable by digestion, VUP- Total metal available for vegetable uptake.

Table 2c. Concentration of copper in µg/g.

SITE	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5	TMS	TMV	VUP (1 and 4)
PLOT A	0.087±0.002	0.104±0.002	0.0620±0.002	0.053±0.002	0.090±0.002	0.396±0.021	0.245±0.016	0.140±0.024
PLOT B	0.091±0.002	0.093± 0.002	0.0510± 0.002	0.033±0.024	0.083±0.002	0.351±0.027	0.235±0.015	0.124±0.041
PLOT C	0.093±0.002	0.069±0.002	0.0680±0.002	0.053±0.002	0.092±0.001	0.375±0.017	0.272±0.024	0.146±0.028
PLOT G	0.081±0.002	0.088±0.002	0.237±0.297	0.069±0.002	0.095±0.002	0.569±0.069	0.205±0.019	0.150±0.008
PLOT E	0.081±0.002	0.087±0.008	0.067±0.002	0.054±0.001	0.053±0.002	0.342±0.015	0.010±0.025	0.135±0.019
PLOT F**	0.088±0.008	0.070±0.002	0.049±0.036	0.061±0.002	0.062±0.010	0.330±0.014	0.183±0.002	0.149±0.019
PLOT D**	0.022±0.018	0.093±0.002	0.060±0.002	0.065±0.002	0.052±0.003	0.292±0.025	0.234±0.015	0.087±0.030

** - controls, TMS - Total metal in soil by digestion, TMV- Total metal in vegetable by digestion, VUP- Total metal available for vegetable uptake.

Table 2d. Concentration of Arsenic in µg/g.

SITE	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5	TMS	TMV	VUP (1 and 4)
PLOT A	0.007±0.001	0.005±0.001	0.005±0.001	0.003±0.001	0.005±0.001	0.025±0.001	0.012±0.001	0.010±0.003
PLOT B	0.010±0.001	0.004±0.001	0.005±0.001	0.005±0.001	0.005±0.001	0.029±0.002	0.019±0.003	0.015±0.003
PLOT C	0.009±0.0010	0.008±0.001	0.006±0.001	0.006±0.001	0.004±0.0010	0.033±0.002	0.014±0.001	0.015±0.002
PLOT G	0.005±0.001	0.004±0.001	0.006±0.0010	0.002±0.001	0.003±0.001	0.020±0.001	0.013±0.001	0.007±0.002
PLOT E	0.006±0.001	0.003±0.001	0.006±0.001	0.004±0.002	0.003±0.001	0.022±0.001	0.014±0.001	0.009±0.002
PLOT F**	0.004±0.001	0.002±0.001	0.005±0.001	0.004±0.001	0.003±0.001	0.018±0.001	0.014±0.001	0.008±0.001
PLOT D**	0.004±0.001	0.003±0.001	0.004±0.001	0.003±0.001	0.002±0.001	0.016±0.001	0.016±0.001	0.007±0.001

** - controls, TMS - Total metal in soil by digestion, TMV- Total metal in vegetable by digestion, VUP- Total metal available for vegetable uptake.

Table 2e. Concentration of Lead in µg/g.

SITE	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5	TMS	TMV	VUP (1 and 4)
PLOT A	0.006±0.001	0.0080±0.001	0.0040±0.001	0.0050±0.001	0.0070±0.001	0.0300±0.002	0.0150±0.001	0.0110±0.001
PLOT B	0.007±0.001	0.0060±0.001	0.0040±0.001	0.0040±0.001	0.0060±0.001	0.0270±0.001	0.0170±0.001	0.0110±0.002
PLOT C	0.007±0.001	0.0040±0.001	0.0030±0.001	0.0030±0.001	0.0060±0.001	0.0230±0.002	0.0853±0.032	0.0100±0.003
PLOT G	0.006±0.001	0.006±0.001	0.003±0.001	0.004±0.001	0.006±0.001	0.025±0.001	0.017±0.001	0.010±0.001
PLOT E	0.005±0.001	0.006±0.001	0.003±0.001	0.004±0.001	0.004±0.004	0.023±0.001	0.015±0.001	0.009±0.001
PLOT F**	0.006±0.001	0.004±0.001	0.005±0.001	0.001±0.001	0.004±0.001	0.020±0.002	0.014±0.001	0.008±0.004
PLOT D**	0.003±0.001	0.006±0.001	0.004±0.001	0.003±0.001	0.003±0.001	0.019±0.001	0.014±0.001	0.006±0.001

** - controls, TMS- Total metal in soil by digestion, TMV- Total metal in vegetable by digestion, VUP- Total metal available for vegetable uptake.

Table 2f. Concentration of Cadmium in µg/g.

SITE	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5	TMS	TMV	VUP (1 and 4)
PLOT A	0.007±0.001	0.004±0.001	0.005±0.001	0.003±0.003	0.002±0.001	0.021±0.002	0.012±0.001	0.010±0.003
PLOT B	0.010±0.001	0.001±0.001	0.005±0.001	0.005±0.001	0.004±0.001	0.028±0.003	0.018±0.003	0.015±0.003
PLOT C	0.009±0.001	0.004±0.001	0.006±0.001	0.006±0.001	0.003±0.001	0.028±0.002	0.016±0.001	0.015±0.002
PLOT G	0.005±0.001	0.003±0.001	0.006±0.001	0.002±0.001	0.003±0.001	0.019±0.002	0.017±0.001	0.007±0.002
PLOT E	0.009±0.001	0.003±0.001	0.006±0.001	0.006±0.001	0.003±0.001	0.027±0.003	0.015±0.001	0.015±0.002
PLOT F**	0.004±0.001	0.002±0.001	0.005±0.001	0.004±0.001	0.002±0.001	0.017±0.001	0.014±0.001	0.008±0.001
PLOT D**	0.004±0.001	0.002±0.001	0.004±0.001	0.003±0.001	0.002±0.001	0.015±0.001	0.015±0.001	0.007±0.001

** - controls, TMS - Total metal in soil by digestion, TMV- Total metal in vegetable by digestion, VUP- Total metal available for vegetable uptake.

Table 2g. Concentration of Iron in µg/g.

SITE	STAGE 1	STAGE 2	STAGE 3	STAGE 4	STAGE 5	TMS	TMV	VUP (1 and 4)
PLOT A	5.137±0.006	5.135±0.006	2.193±0.006	2.787±0.165	5.665±0.080	20.915±1.575	10.018±0.505	7.923±1.662
PLOT B	4.779±0.006	4.035±0.006	1.858±0.006	1.344±0.138	3.146±0.006	15.160±1.440	10.364±0.579	6.122±2.429
PLOT C	5.618±0.006	2.114±0.006	1.645±0.188	1.928±0.006	3.222±0.006	14.525±1.630	10.509±0.999	7.545±2.609
PLOT G	4.839±0.006	4.109±0.063	1.645±0.186	5.971±0.005	1.938±0.320	18.502±1.867	11.205±0.825	10.809±0.800
PLOT E	4.115±0.006	3.941±0.018	2.112±0.006	1.182±0.006	1.524±0.006	12.873±1.369	9.249±0.818	5.296±2.074
PLOT F**	5.133±0.006	2.973±0.006	2.063±0.006	1.809±0.144	2.435±0.381	14.413±1.332	7.3593±0.246	6.942±2.350
PLOT D**	2.143±0.006	4.084±0.006	2.348±0.006	1.974±0.006	1.993±0.006	12.540±0.893	8.659±0.477	4.116±0.119

** - controls, TMS - Total metal in soil by digestion, TMV- Total metal in vegetable by digestion, VUP- Total metal available for vegetable uptake.

Table 3. Summary of results showing the concentration of the metals in the soil, total metal in the vegetable and the corresponding vegetable uptake.

Site	Metals											
	Mn			Zn			Cu			As		
	MAS	VUP	TMV	MAS	VUP	TMV	MAS	VUP	TMV	MAS	VUP	TMV
A	2.506±0.195	0.976±0.377	0.964±0.073	1.438±0.120	0.520±0.192	0.682±0.042	0.396±0.021	0.140 ±0.024	0.245±0.016	0.025 ±0.001	0.010 ±0.003	0.012±0.001
B	2.468±0.140	1.208±0.112	1.580±0.240	1.571±0.123	0.723±0.066	0.542±0.009	0.351±0.027	0.124 ±0.041	0.235±0.015	0.029 ±0.002	0.015 ±0.003	0.019±0.003
C	2.138±0.090	0.875±0.117	1.570±0.144	0.854±0.042	0.325±0.059	0.737±0.059	0.375±0.017	0.146 ±0.028	0.272±0.024	0.033 ±0.002	0.015 ±0.002	0.014±0.001
G	2.469±0.142	1.114±0.209	1.192±0.079	1.269±0.097	0.582±0.131	0.734±0.056	0.569±0.069	0.150 ±0.008	0.205±0.019	0.020 ±0.001	0.007 ±0.002	0.013±0.001
E	1.988±0.190	0.943±0.226	1.233±0.122	0.868±0.104	0.382±0.099	1.220±0.252	0.342 ±0.015	0.135 ±0.019	0.010 ±0.025	0.022 ±0.001	0.009 ±0.002	0.014±0.001
F**	1.727±0.087	0.692±0.043	1.085±0.098	0.717±0.094	0.241±0.001	0.666±0.039	0.292 ±0.025	0.087 ±0.030	0.234±0.015	0.016 ±0.001	0.007 ±0.001	0.016±0.001
D**	2.006±0.120	0.853±0.147	1.073±0.054	0.838±0.096	0.444±0.136	0.547±0.019	0.330 ±0.014	0.149 ±0.019	0.183±0.002	0.018 ±0.001	0.008 ±0.001	0.014±0.001

Site	Pb			Cd			Fe		
	MAS	VUP	TMV	MAS	VUP	TMV	MAS	VUP	TMV
	A	0.030 ±0.002	0.011±0.001	0.015±0.001	0.021 ±0.002	0.010 ±0.003	0.012±0.001	20.915 ±1.575	7.923 ±1.662
B	0.027±0.001	0.011±0.002	0.017±0.001	0.028 ±0.003	0.015 ±0.003	0.018±0.003	15.160 ±1.440	6.122 ±2.429	10.364±0.579
C	0.023±0.002	0.010±0.003	0.085±0.032	0.028 ±0.002	0.015 ±0.002	0.016±0.001	14.525 ±1.630	7.545 ±2.609	10.509±0.999
G	0.025 ±0.001	0.010 ±0.001	0.017±0.001	0.019 ±0.002	0.007 ±0.002	0.017±0.001	18.502 ±1.867	10.809±0.800	11.205±0.825
E	0.023 ±0.001	0.009 ±0.001	0.015±0.001	0.027 ±0.003	0.015 ±0.002	0.015±0.001	12.873 ±1.369	5.296 ±2.074	9.249±0.818
F**	0.019 ±0.001	0.006 ±0.001	0.014±0.001	0.015 ±0.001	0.007 ±0.001	0.015±0.001	12.540 ±0.893	4.116 ±0.119	8.659±0.477
D**	0.020 ±0.002	0.008 ±0.004	0.014±0.001	0.017 ±0.001	0.008 ±0.001	0.014±0.001	14.413±1.332	6.942 ±2.350	7.359±0.246

MAS: Metals available in soil, VUP: vegetable uptake, TMV: total metal in vegetable.

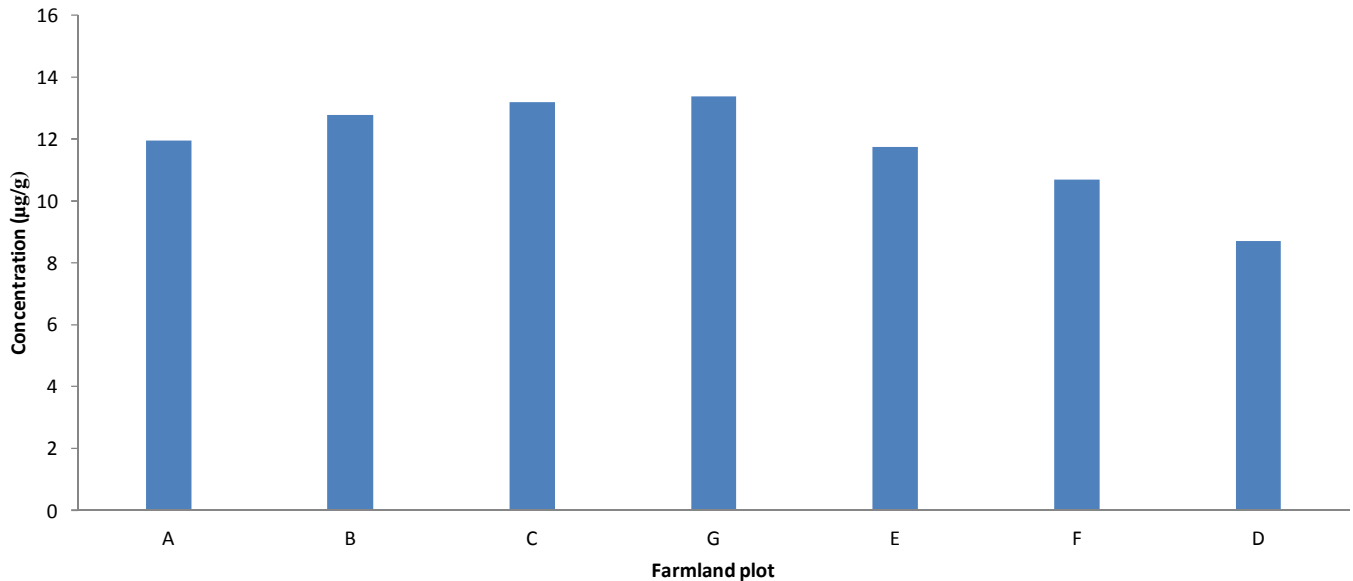


Figure 3. Metal load of the farmlands.

present on each plot, (Figure 3), therefore, it is expected that the total concentration of metals found in the vegetable (TMV) should not be higher than those available in the soil for plant uptake (VUP). Thus, other sources of pollution and contamination might have been responsible for this elevation in concentrations such as atmospheric deposition, vehicular emission during their production, transportation and marketing (Sharma et al., 2009) and polluted water used for irrigation. Aerial deposition on leaf surfaces and metal accumulation on the hairy and rough surfaces 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 (Marschner, 1995).

Atmospheric deposition had been attributed to the increase in the heavy metals in vegetables sold in the market at Riyadh city in Saudi Arabia (Jassir et al., 2005). A similar report was given by Sharma et al. (2008 a, b) in Varanasi, India. In many African countries vegetables are grown along river banks flowing through city centres and these waters are usually contaminated with heavy metals as a results of industrial, natural (such as weathering) and other anthropogenic activities (Suruchi and Pankaj, 2011). Waste waters from these sources used for irrigation could be a source of contamination to these vegetables.

The order of decreasing of the metals in soil and vegetable (Table 3) supported the claim that the elements in the vegetables were largely from the soil.

From this study, it was noted that for most metals analyzed, the metal concentration were within the permissible range or level in the plants most especially in

the edible part of the plants, this results supported the findings of (Akubugwo et al 2007), this vegetable contained low level of toxicants. The concentration of iron (Fe) is generally high in all the plots but less than 20.0 µg/g of WHO (2005) of metals in medicinal plants. The value obtained in this study was more than the recommended maximum concentration of trace metals in water for crop production FAO (1985 and 1995) of 5.0 mg/L. The permissible level of zinc (Zn) is 60.0 µg/g, but the tables show a less concentration in all the plots with no exception. Lead (Pb) value is much lower as expected because of the reduction in the use of leaded gasoline compared with WHO/FAO (2007) limit of 5.0 µg/g. The Cadmium (Cd) values were below the recommended value of 0.2 µg/g (Table 4). All the plots show low level of cadmium concentration, a development that is much more preferable because of the harmful effect of the metal. In the case of Manganese (Mn) the permissible level has not yet been ascertain but Sheded et al. (2006) put the value within 44.6 to 339 µg/g. From these results, the values were lower than Sheded's value. In all the plots the concentration of Copper (Cu) were below the permissible value of 3.0 µg/g, although they have varying concentration from plot to plot. Copper concentrations were relatively low, the mean levels of copper ranged from 0.010 to 0.272 µg/g, this is within the limit set by FAO/WHO (2007) for metals in vegetables. The levels of copper found in the vegetables did not pose any contamination or health risk to consumers. Azcue et al. (1988) reported mean copper concentrations in the range of 0.17 to 0.95 mg.kg⁻¹ for some vegetable food from Paraiba do sul River valley, Brazil.

Arsenic (As) is very poisonous and so has a generally

Table 4. Guideline for safe limits of heavy metals in plants/vegetables.

Plant standard ($\mu\text{g/g}$)	Cd	Cu	Pb	Zn	Mn	Fe	As
Indian standard (Awashthi 2000)	1.5	30.0	2.5	50.0	-	-	-
WHO/FAO (2007)	0.2	40.0	5.0	60.0	-	-	-
European Union Standards (EU 2006)	0.2	-	0.30	-	-	-	-
This study(range)	0.012- 0.018	0.010- 0.272	0.015-0.085	0.542- 1.220	0.964-1.580	7.359-11.205	0.012-0.019

Source: (Anita et al., 2010).

low values for all the concentration in the various sites as its permissible range is between 0.09 to 0.5 $\mu\text{g/g}$. The paired sample T-test results between TMV and VUP showed no significant difference both at 95 and 99% confidence level for all the metals. Meaning that, concentrations of TMV and VUP for each metal in all the plots are the same statistically.

Heavy metals at low concentration have damaging effects in man and animals because there is no good mechanism for their elimination from the body. Although, the concentration levels of these metals were found within the permissible level of FAO/WHO (1985, 2007). The interactive and accumulative effects need to be considered. The farmlands along the road sides Plots A, B, C, G and E, (11.944, 12.775, 13.203, 13.383 and 11.756 $\mu\text{g/g}$), had more metal load than the controls Plots F and D (10.689 and 8.704 $\mu\text{g/g}$) as shown in Figure 3. It could be said that the 'wears and tears' of vehicular parts and their emission played significant role in elevating the metals in the vegetables apart from atmospheric deposition.

Conclusion

The metals available for plants uptake in the soil are the exchangeable and the acid extractable fractions, which is largely dependent on soil pH and the amount of organic matter. The total metal concentrations found in the vegetables are more than the uptake from the soil indicating other sources of pollution were responsible for the increase. The order of decrease of metal concentration in the vegetables followed the order of decrease of the metals in the soil, showing that the major source of these metals in the vegetables were the soils on which they were planted. The concentrations of the metals analyzed in this study falls within FAO/WHO permissible limit. However, metals bioaccumulates in vital organs of the body and have no good mechanism for elimination. The build-up over time and cumulative effects may result in health related problems. Therefore, there should be a continuous monitoring of these, and similar sites to ensure that the concentrations of the metals in

the soil and vegetables do not rise above the acceptable limits.

ACKNOWLEDGEMENT

The authors acknowledge the assistance of Adeyemi Mayowa and Bode Owoeye in the field and laboratory work.

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