Assessment of Heavy Metals in Guinea Sorrel (*Hibiscus Sabdariffa*) Cultivated on Fadama Soils in Maiduguri, Nigeria.

Abstract:
Concentration values of heavy metals namely Aluminium (Al), Cobalt (Co), Iron (Fe), Lanthanum (La), Manganese (Mn), Chromium (Cr), Rubidium (Rb), Scandium (Sc), Samarium (Sm), Thorium(Th), Vanadium(V) and Zinc(Zn) were determined in Guinea Sorrel (*Hibiscus sabdariffa)* vegetables employing instrumental neutron activation analysis (INAA) technique. Heavy and trace metal in Guinea Sorrel vegetables obtained from fadama farming lands in Maiduguri, Nigeria were assessed with the aim to ascertained the health risk associated with their consumption by comparing the concentration values of the metal pollutants in the vegetables with the WHO/FAO recommended maximum permissible limit (MPL) for edible vegetables. The result obtained showed that the concentration values of Al ranged from 932 ± 18ppm to 3369 ± 54ppm, Co from 0 .12 ± 0.03ppm to 40 ± 4 ppm, La from 1.00 ± 0.03ppm to 38 ± 4 ppm, Manganese from 112 ± 0.4ppm to 176 ± 1 ppm, Rubidium from 4 ± 0.5ppm to 21 ± 1ppm, Sc from 0.10 ± 0.007ppm to 27 ± 1ppm Sm from 0.106 ± 0.004ppm to 17.2 ± 0.4 ppm, V from 1.10 ± 0.3ppm to 4 ± 1ppm and Zn from 17 ± 3ppm to 63 ± 4ppm, and Fe from 379 ± 33ppm to 2316 ± 65 ppm. The variation in concentration values of the metals determined in the samples with locations suggests that there might be effects of anthropogenic and or natural processes that contributed to the abundance of the trace and heavy metals in the soils on which the guinea sorrel were cultivated. The results also indicate that the concentration levels of Fe, Cr, Mn, and Co, in guinea sorrel samples from some of the sites were above the acceptable limits given by FAO/WHO for consumable vegetables.
Key Words: Assessment, metal pollutants, permissible limit, fadama soils

Introduction

There is an increasing trend in concentration of heavy metals in the environment which has attracted considerable attention amongst ecologists globally during the last decades and has also begun to cause concern in most of the major metropolitan cities. The Excessive accumulation of heavy metals in agricultural soils through the use of agrochemicals and by other sources may not only result in soil contamination but also lead to elevated heavy metal up-take by vegetables and thus affect food quality and safety [1].

In many developing countries it is a common practice to grow vegetables along banks of rivers passing through urban Centre of which waters of such rivers have often been reported to be polluted by heavy metals [2].

It is a known fact that Vegetables are important edible crops and are an essential part of the human diet and generally consumed because of their nutrition value [3], [4], [5] but take up heavy metals and accumulate them in their edible parts [6]).and studies have shown that the heavy metals are easily accumulated in the edible parts of leafy vegetables, as compared to grain or fruit crops [7], [8] and also the quantities accumulated can be high enough to cause clinical problems both to animals and human beings when they consume these metal-rich vegetable/plants [9]. The extent of absorption of the elements by the plant depends on among other things, the nature of the plant, and chemical constitution of the pollutant, concentration of the element in the soil, pH and the interaction with other metals [10].

The dumping of solid waste generated from domestic and cottage industries on farmlands along channels or streams that transcend urban Centre usually contaminates the soils and if plants are cultivated thereon can be a primary route of human exposure to metal toxicants [11] hence heavy metals in soils used for cultivation is viewed as an international problem because of the effects on ecosystem in most countries [12]. According to [13] the situation of heavy metal pollution is more worrisome in the developing countries where research efforts towards monitoring the environment has not been given the desired attention by the stakeholders.

Many studies have shown that municipal refuse may increase heavy metal contamination in soil and underground water [14], [15] which may have effects on the host soils, crops and human health [16]. Thus the environmental impacts of municipal refuse are greatly influenced by their heavy metal contents. In Nigeria the situation is no better by the activities of most industries and populace towards waste disposal and management which usually lead to increasing levels of pollution of the environments.

Materials and Methods

This work covers a study area that lies between latitude $11^{o}\ 48^{'}$ N to 11^{0} 52'N and longitude $13^{o}\ 06^{'}$ E to 13^{0} 14'E at an altitude of 345m above sea level Figure 1. The area of study is known for its long period of dryness, with Sudan type of climate, Savanna or Tropical grassland vegetation and light annual rainfall.

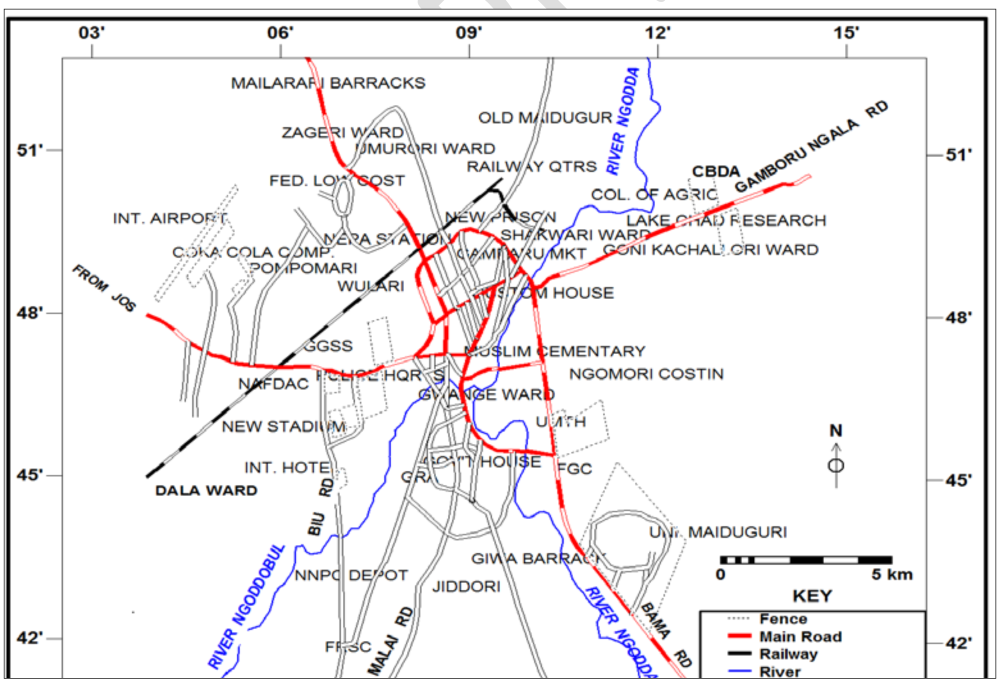

Figure1: Maiduguri Township Map Showing River Ngadda.
Source: Ministry of Land and Survey.

Sample Collection

Fresh Guinea Sorrel (*Hibiscus sabdariffa)* vegetables samples were collected directly on six different farmlands (sampled sites) along the bank of rive Ngadda and Alau dam and labeled with the identification codes (D1, D2, D3, D4, D5, D6) Figure 2. The locations points for the collection of samples were obtained using Global Positioning System (GPS) by taking the ordinates. Samples from the study area were collected in a pre-designed manner such that on each farmland in the specified area, samples were collected at different locations of the farm and homogenized to constitute a sampled site.

Figure 2: Guinea Sorrel Sampled Sites Along River Ngadda and Alau dam

Sample Preparation

The fresh vegetable samples collected were put in a clean black polyethylene bags and were adequately labeled for easy identification during the laboratory exercise. The samples were taken to herbarium laboratory in Biology Department of Ahmadu Bello University, Zaria for identification. After identification, they were taken to laboratory where they were thoroughly washed with running tap water and properly rinsed with double distilled water to remove any airborne particulates. The vegetables were then air dried and oven dried at $60^{o}C$ temperature for not less than eight hours and then grounded and sieved to required particle size using a sieve that were pre-cleaned. The sample was put in a sample bottle, labeled and caped. The samples were then taken to Centre for Energy Research Training (CERT) Ahmadu Bello University, Zaria for further preparation and analysis.

Sample Preparation for Neutron Activation Analysis

Instrumental Neutron Activation Analysis (INAA) techniques which is a sensitive method for accurate determination of elemental concentration in materials was used in this study employing Nigeria Research Reactor-1 (NIRR-1) facility located at Center for Energy Research, Ahmadu Bello University Zaria, Kaduna State of Nigeria. The detail and function of NIRR-1 is seen in the work of [17], [18].

Conventional method of sample preparation of vegetable samples for irradiation was used as provided by [17] adopted after which the samples were then put in an irradiation vial. The vial was then capped and sealed. Standard Reference Material (SRM) NIST 1573a which is a direct representative of the vegetable sample was put in the same type of vial with that of the sample.

Sample Analysis

The samples and standard of known quantities of the elements in question were irradiated simultaneously in identical positions, followed by measuring the induced intensities of both the standard and the sample in a well-known geometrical position. For data processing, the gamma-ray spectrum analysis software WINSPAN, 2004 used by [19] based on the practice of using the activity induced at time after irradiation for time *t* and given by equation

$$A_t = \frac{\varepsilon \sigma_Q \rho W_Q \varphi}{M_Q} = N_A\left(1 - e^{-\lambda t_i}\right) ds^{-1} \qquad (1)$$

A_t is activity of element Q at the end of radiation (ds^{-1}), σ_Q is neutron capture cross section of element (cm^2), ρ is fractional abundance of particular isotope of element Q, M_Q is atomic weight of element Q to be measured , N_A is Avogadro's number (mol^{-1}) , λ is decay constant of induced radionuclide (s^{-1}), t_i is irradiation time (s), φ is the flux of neutron used in irradiation ($m^{-2}s^{-1}$) and W_Q is weight of element Q irradiated.

The sample and standard parameters were then related as in equation

$$\frac{A_{sam}}{A_{std}} = \frac{\phi\omega\epsilon I N_A\left(1 - e^{-\lambda t_{irr}}\right)sam\left(e^{-\lambda t_d}\right)sam\left(1 - e^{-\lambda t_c}\right)sam}{\phi\omega\epsilon I N_A\left(1 - e^{-\lambda t_{irr}}\right)std\left(e^{-\lambda t_d}\right)std\left(1 - e^{-\lambda t_c}\right)std} \qquad (2)$$

where A_{sam} is activity of the unknown sample, A_{std} is activity of the standard. The standard is irradiated and counted under similar conditions as the sample, therefore common parameters in equation (2) cancelled out then the mass of the element in the sample relative to the standard comparator is calculated using equation

$$\frac{A_{sam}}{A_{std}} = \frac{m_{sam}}{m_{std}} \frac{\left(e^{-\lambda t_d}\right)}{\left(e^{-\lambda t_d}\right)} \frac{sam}{std} \qquad (3)$$

m_{sam} = mass of element in the sample, m_{std} = mass of element in standard, λ = decay constant for the isotope.

Results

Table 1 present concentration values of the various elements determined in amaranthus vegetables and the values were graphically represented in Figures 3-5 accordingly.

Table 1 Concentrations of Elements determined in Guinea Sorrel Samples from Different sites by INAA technique.

Sampled Site	Al	Fe	Mn	Br	Co	Cr	La	Rb	Sc	Sm	Th	V	Zn
D1	3369±054	1027±53	176±1.0	21±2.0	29±4.00	2.6±0.3	2.5±0.10	21±1	27±1.00	0.36±0.01	1.04±0.06	4±1.00	36±3.0
D2	1851±20	2316±65	121.4±0.50	12.1±1,5	40±4.00	8.6±0.3	38±4.00	14±1	21±1.00	BDL	81±5.00	2.82±0.41	63±4
D3	932±018	707±47	6±1.00	10±1.0	0.15±0.03	BDL	1.24±0.03	6±1.00	0.15±0.01	0.149±0.00	BDL	1.5±0.4	26±3
D4	1068±16	395±40	161.9±0.3	10±1.0	0.12±0.03	11.3±0.4	1.1±0.03	4±1	0.1±0.01	BDL	0.133±0.005	0.24±0.04	27.7±2.3
D5	1293±14	14490±130	173±1.0	3.6±0.6	1.0±0.3	BDL	5241±267	BDL	17.2±0.400	36±5	2.0±0.3	21±3	21±3
D6	1057±62	379±33	112.2±0.40	13±1.0	BDL	3.9±0.3	1.00±0.03	5.4±0.6	0.099±0.006	0.106±0.004	BDL	BDL	17±3

BDL: Below Detection Limit
All concentrations are in ppm

Daily Intake of Metals (DIM)

In order to quantify the level of exposure from consumption of the vegetable investigated, an index referred to as daily intake of metals (DIM) was calculated according to the expression:

$$DIM = \frac{M*C*I}{W} \qquad (4)$$

where M is the metal concentration in the vegetable (mg/kg), C is the conversion factor, I was the estimated quantity of vegetable taken on daily basis, and W is the average weight of a human being. The conversion factor (from fresh to dry weight of vegetable) of 0.085 was adopted from [20]; the average weights of an adult and a child were approximated to be 55.9 and 32.7 kg respectively, while the average quantities of vegetable taken on daily basis by adults and children were 0.345 and 0.232 kg/person/day respectively based on reports of [21] and [22].

The best way to estimate the health risk of any pollutant is to determine the level of exposure to that pollutant and the route(s) of exposure to a particular tissue or organ. In this study, the daily intake of metals (DIM) was used as the exposure index. Evaluation of DIM based on the stated assumptions revealed a minimum of 1.2×10^{-3} mg and a maximum of 836.7×10^{-3} mg for adults, while the children had a minimum of 1.4×10^{-3} mg and a maximum of 961.9×10^{-3} mg. It is obvious from the results that all the daily intakes of metal in guinea sorrel for all the elements for children were higher than the corresponding values for adults. The implication of these results is that children tend to take in more metals than adults, and this could be due to tenderness of children's body tissues. Again, the metals with relatively high DIM values (eg: Al = 0.837 mg, Fe = 0.464 mg for adults and Al = 0.962 mg, Fe = 0.533 mg for children) are mainly major elements with high natural abundances.

Discussion

Figure 3 presents the graph of the concentrations of Aluminium (Al), Iron (Fe) and manganese (Mn) determined in Guinea sorrel samples obtained at six different sites along the bank of river Ngadda and Alau dam. It can be observed from the graph that the concentrations of Aluminium were higest in all the samples obtained at the six different sites followed by iron and the least is manganese. The natural abundance ocncentrations of these elements could have been responsibe for the values. However, the concetratrations of Fe in amaranthus was above MPL given by FAO/WHO.

Figure 4 showed the graphical representation of the concentrations of Bromine (Br), Lanthanum (La), Rubidium (Rb), Cobalt (Co) Chromium (Cr) and Zinc (Zn). It is obvious from the graph that basically Zn > Co > La > Br > Rb > Cr in most of the sites.

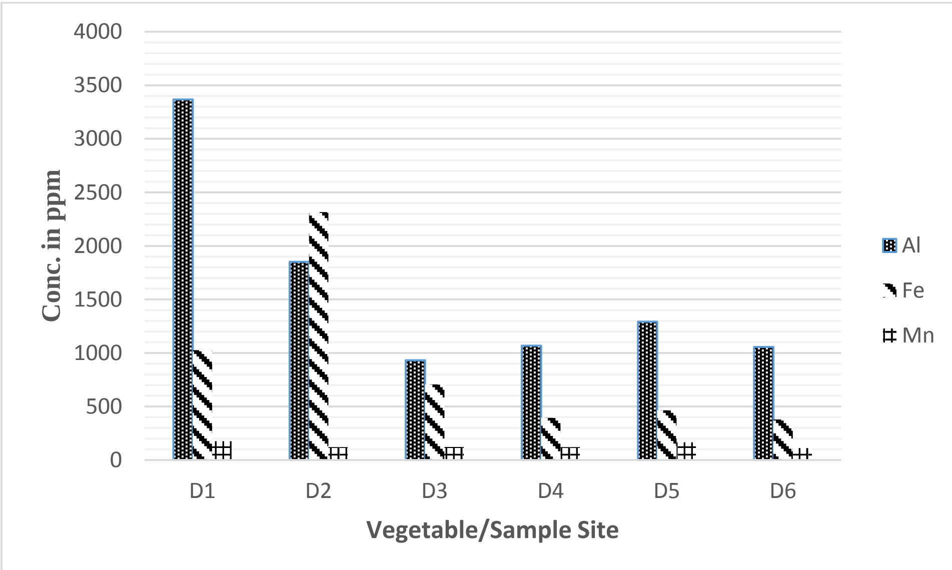

Figure 3: Concentrations of Elements Determined in Guinea Sorrel

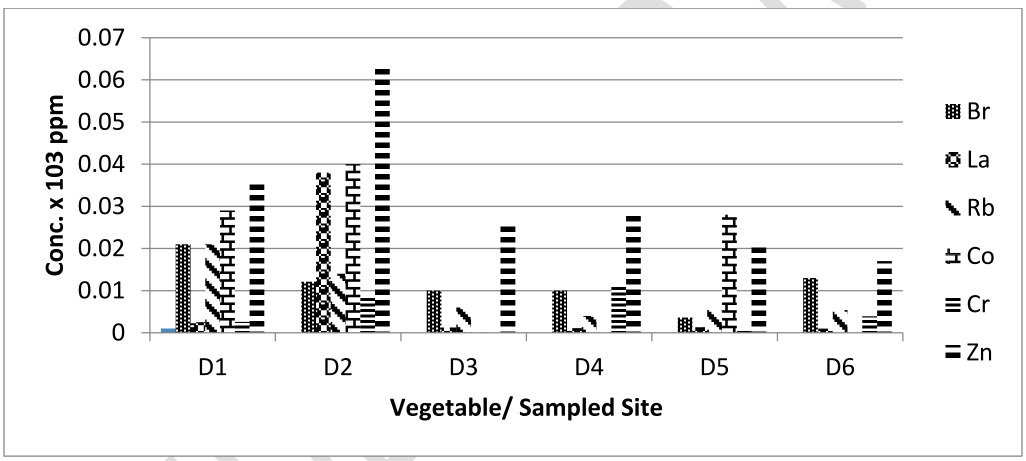

Figure 4: Concentrations of Elements Determined in Guinea Sorrel

Figure 4 showed the concentrations of Bromine (Br), Lanthanum (La), Rubidium (Rb), Cobalt (Co), Chromium (Cr) and Zinc (Zn). The maximum concentrations of all the elements were found to be at sampled site D2 which represent a location area around Custom Bridge adjacent to Custom area market which was a hub of activities on a daily basis. The maximum concentrations of cobalt 29 ppm Chromium 11.3 ppm, and Zinc 63 ppm exceed the safe limit recommended by FAO/WHO (2005) of 1. 0 – 2.00 ppm, 0.8- 0.85 ppm and 5.00 ppm respectively.

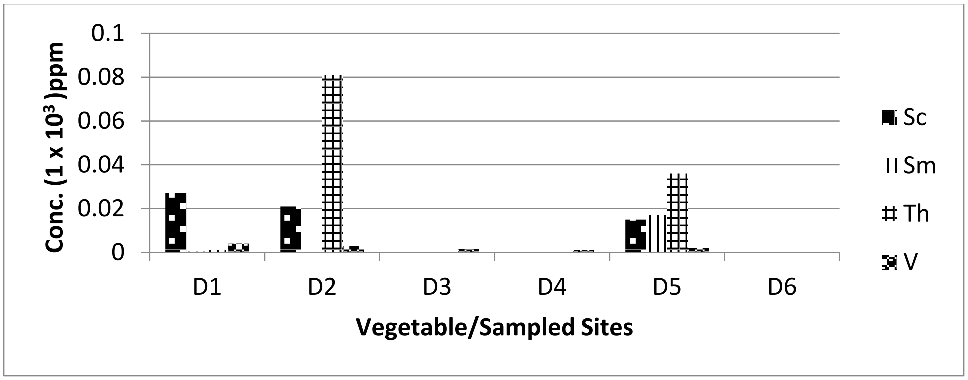

Figure 5: Concentrations of Elements Determined in Guinea Sorrel

Figure 5 showed the concentrations of Scandium, Samarium, Thorium, and Vanadium determined in the samples obtained at different sites of the study area. Scandium had a maximum concentration of at sampled site D1, Samarium at sampled site D5, Thorium at sampled site D2 and Vanadium 4 ppm at sampled site D1,

Conclusion

Generally, the concentration values of the various elements determined in Guinea sorrel samples showed that at sampled sites D1 and D2, the concentrations of Cr, Mn and Cr exceed the acceptable limit recommended by FAO/WHO. For sampled site D3, Mn and Zn concentrations exceed the FAO and WHO recommended acceptable limits while Cr concentrations was below detection limit. Sampled sites D5 was the reflection of sampled sites D3 where Mn and Zn concentrations exceed the recommended acceptable limits stated by FAO/WHO. For sampled sites D6, the concentrations of Cr, Mn, and Zn exceed the maximum recommended acceptable limit of concentration in vegetables by FAO/WHO.

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