

Bioaccumulation of heavy metals in frequently consumed leafy vegetable grown along Nigeria-Benin Seme Border, West Africa

¹Osundiya M. O., ^{2*}Ayejuyo O. O., ³R. A. Olowu, ¹Bamgboye O. A. and ¹Ogunlola A. O.

¹Department of Chemistry, Lagos State University, LASU post office, Lagos, Nigeria

²Department of Chemistry, University of Lagos, Akoka, Nigeria

³Department of Chemistry, University of the Western Cape, Private Bag X17 Bellville, South Africa

ABSTRACT

Vegetable growing along major highways with heavy vehicular movement has been a serious concern to food safety specialist in large cities. The contributions of heavy metals in selected vegetables through atmospheric deposition were quantified using atomic absorption spectrophotometer. The level of some heavy metal (.Pb, Cu, Fe, and Cr) were examined in the edible portion of *Telfiria occidentalis*, *Corchorus olitorius*, *Celocia argentea*, and *Thymus Vulgaries*, grown along Nigeria-Republic of Benin border Seme. The results showed that the levels of heavy metal ranged from $21.69 \pm 7.36 \mu\text{g/g}$ Cu to $172.87 \pm 62.05 \mu\text{g/g}$ Fe in *Telfaria occidentalis*, $21.74 \pm 13.00 \mu\text{g/g}$ Pb to $304.50 \pm 72.77 \mu\text{g/g}$ Fe in *Corchorus olitorius*, $16.75 \pm 10.54 \mu\text{g/g}$ Pb to $260.74 \pm 215.37 \mu\text{g/g}$ Fe in *Celocia argentea* and $23.53 \pm 3.52 \mu\text{g/g}$ Cu to $406.33 \pm 225.06 \mu\text{g/g}$ Fe in *Thymus Vulgaries* were recorded in site A. The value heavy metal contamination obtained from site B ranged from $18.91 \pm 11.98 \mu\text{g/g}$ Pb to $166.49 \pm 86.22 \mu\text{g/g}$ Fe in *Telfaria occidentalis*, $16.57 \pm 9.22 \mu\text{g/g}$ Pb to $292.36 \pm 196.33 \mu\text{g/g}$ Fe in *Corchorus olitorius*, $19.99 \pm 8.54 \mu\text{g/g}$ Pb to $354.03 \pm 302.80 \mu\text{g/g}$ Fe in *Celocia argentea* and $21.73 \pm 8.44 \mu\text{g/g}$ Pb to $388.20 \pm 226.39 \mu\text{g/g}$ Fe in *Thymus Vulgaries*. The order of contamination in the vegetable sample was $\text{Fe} > \text{Cr} > \text{Cu} > \text{Pb}$. The data were analyzed with *t*-test and ANOVA. There were no significant different between the ($p < .05$) between the level of heavy metal in vegetable at each sampling site. The high levels of metal in the sampled vegetable may be attributed to excessive application of fertilizers and other agro chemical, as well the use of waste water for washing the vegetables. The obtained results were higher than the threshold value of WHO, FEPA and China stipulated standards for mature plant tissue except for copper in all the analyzed vegetable. Therefore, the consumption of these vegetables as food may pose possible health hazards to human.

Keywords: *Telfaria occidentalis*, *Corchorus olitorius*, *Celocia argentea* and *Thymus Vulgaries*, fertilizer, bioaccumulation, leafy vegetable, heavy metal

INTRODUCTION

The main sources of our essential metals are food and water which are also the medium through which we come in contact with various toxic metals. Heavy metals are without difficulty accumulated in the edible parts of leafy vegetables, as compared to grain or fruit crops [1]. Vegetables take up heavy metals and accumulate them in their edible [2] and inedible parts in amount high enough to cause medical troubles both to animals and human beings consuming these metal-rich plants [3]. Heavy metals are ever-present because of their extreme use of their compounds in industrial applications and are very detrimental because of their non-biodegradable nature, long

biological half-lives and their potential to accumulate in different body parts. Most of the heavy metals are extremely toxic because of their solubility in water. Even low concentrations of heavy metals have harmful effects to man and animals because there is no good mechanism for their removal from the body [4,5] Additionally, the consumption of heavy metal-contaminated food can negatively deplete some essential nutrients in the body leading to decrease in intrauterine growth retardation, immunological deficiencies, disabilities associated with malnutrition, impaired psycho- social behaviour, and a high prevalence of upper gastrointestinal cancer[6]. It is known that serious systemic harms can develop as a result of increased accumulation of dietary heavy metals such as lead and cadmium in the human body[7]. Major contamination of seeds, plant products with toxic chemical elements due to contaminated soil and water has been observed as a result of release of these toxicants into the sea, rivers, and lakes as well as into irrigation channels. The practice of growing vegetables within and at the edges of cities is extremely aged and most of these cultivated lands are polluted with heavy metals via vehicular emissions, pesticides, fertilizers, industrial effluents and other anthropogenic activities[8-11] The yield of vegetable is reduced due to the presence of heavy metal in soil because metabolic processes of plants are disturbed [12,13] Generally, the concentrations of heavy metals are higher in soils than vegetables grown on the same soils. This indicates that only a small portion of soil heavy metals is transported to the vegetables and the root acts as a fence to the translocation of heavy metals within plant [14]. A convenient way of quantifying the relative differences of bioavailability of metals to plants is the transfer quotient. The higher transfer quotient of heavy metal indicates the stronger accumulation of the respective metal by that vegetable [7,15]. The transfer quotients for Cd and Cu were higher than other metals and Fe[15]. The outcome of heavy metals pollution differs from one vicinity to the other as the application of fertilizers and other human activities differ at each site. It has been reported that phosphate fertilizers are the major source of soil heavy metals contamination. This contamination is due to the presence of cadmium as an impurity in phosphate rocks. Because of the massive application of these fertilizers, the contamination of heavy metals in soil occurs [16] The majority of the heavy metals are the natural components of earth's crust and from there they are absorbed by plants and hence transferred to food chain. These metal concentrations differ from soil to soil. Metals concentration of vegetables mainly depends on the texture of soil or media on which they grow but this also depends on the type and nature of plant[17]. Other sources of heavy metals for plants are: traffic density, rainfall in atmospheric polluted areas, atmospheric dusts, use of oil or fossil fuels, for heating, plant protection agents and fertilizers which could be adsorbed through leaf blades[18-21]. These plant materials could also be polluted from various sources including trace metals as farmers wash them with waste water before bringing them into the market [22]. Distributions of heavy metals in plants are based upon availability and concentrations of heavy metals as well as particular plant species and its populations [23]. It has been reported by numerous researchers that some common vegetables are capable of accumulating high levels of metals from the soils [24, 25]. Certain species of Brassica (cabbage) are hyper-accumulators of heavy metals into their edible tissues [24]. The utilization of polluted water in the immediate surroundings of big cities for growing vegetables is a widespread practice in Nigeria. Even though this water is considered a rich source of organic matter and plant nutrients, it also contains sufficient amounts of soluble salts and metals like Fe, Mn, Cu, Zn, Pb, Ni, Sn, Hg, Cr, As and Al. When such water is employed for irrigation of crops for a long time, these heavy metals may accumulate in soil and may be toxic to the plants and also cause deterioration of soil [24, 26]. Various classes of vegetables are grown in many parts of Nigeria. In Lagos State, western part of Nigeria, vegetables are heavily cultivated and consumed as food. Lagos is the commercial hub and the industrial nerve center of Nigeria with an estimated population of more than 15 million people and environmental concerns are normally focused on Lagos State [4,5]. Conversely, to enhance the yield of these vegetables, application of fertilizers and manures are occasionally done to the soil. There are therefore, the possibilities of over applications of these fertilizers and manures. Thus, the uptake and storage of some heavy metal pollutants from these wastewater, fertilizers and manures by the vegetables are very likely since these heavy metals are soluble and mobile in ground water.

This study is designed to examine the levels of heavy metals (Pb, Cu, Fe, and Cr) in edible portions of four different vegetables namely *Ocimum gratissimum*, *Telfairia occidentalis*, *Corchorus olitorius*, *Colosia argentea* grown along Lagos Seme border and ascertain the suitability or otherwise of the vegetables for human consumption.

MATERIALS AND METHODS

Sampling and pre treatment

Two sites were selected on the highways. Nigeria-Seme border is a dual carriage way. Sampling periods were designed such that peak hours were covered. Four different vegetables were selected and collected randomly such that those grown very close to the highways at a distance of 5 meters from the highway designated as Site A and

those grown in the interiors 200 meters away from the main road designated as site B. The samples were collected from the two sides of the road (i.e. Nigeria to Benin Republic, Benin Republic to Nigeria). Edible portions of the fresh of *Thymus vulgaris*, *Telfaria occidentals*, *Corchorus olitorius* and *Celosia argentea* were collected randomly from the farm land and they were carefully and thoroughly washed with distilled water to eliminate suspended particles. The vegetable samples were collected using a sharp plastic knife into new, clean polyethylene bags. The collected samples were transported to the laboratory and drained

Analytical procedure for heavy metal Determination

Samples for analysis were dried using the oven dry method at 105°C for 24 h [27,28] to obtain the moisture content. The dried vegetable sample were powdered with a stainless steel blender and passed through a 2 mm size sieve. About 2.0 g of each sample was weighed and digested in a mixture of 10 ml of concentrated HCl, 5ml concentrated, H₂SO₄ and 15 ml of concentrated HNO₃ in a beaker under a fume hood. The content of the flask was mixed and heated at 150°C for 45 min on a hot plate. The mixture was heated constantly until a dense fume evolved. This was further heated strongly for about half an hour. The resulting solution was cooled and filtered through Whatman 42 filter paper before making up to marking in 50 ml volumetric flask with distilled water.

Determination of heavy metal

The determination of heavy metals was achieved by atomic absorption spectrophotometer (AAS), using a Varian Spectra atomic absorption spectrophotometer, Buck Scientific 210 GVP model. All determination was done in five times and a spike sample was used to verify the accuracy of the procedure

RESULTS AND DISCUSSION

The levels of heavy metal investigated in the leafy vegetable study were based on dry weight and the results are presented in Tables 1 to 3. The values are given as mean \pm std. The results are means of six replicates. The concentrations of lead (Pb) and copper (Cu) were observed to be the lowest for all the samples collected from both sites while the level of iron (Fe) and chromium (Cr) were the highest. Due to the influence of heavy metal on the nutritive values of agricultural material as well as their negative effect on human beings maximum permissible level of toxic metal in human food were set by National International bodies [21,27,28]. For this reason an ever more important feature of food quality must be to control the concentrations of heavy metals in food [25, 29]. The result of the analysis revealed that the level of Pb in all the sample from both sites were between 16.57 $\mu\text{g/g}$ in *Celocia argentea* (*shoko*) and 24.07 $\mu\text{g/g}$ in *Thymus Vulgaries* (*curry*) with a range of 9.00-35.99 and 16.99-39.98 $\mu\text{g/g}$ respectively. The highest level of Pb in site A was observed in *Thymus Vulgaries*, *Telfcirea occidentals* and *Corchorus olitorius* in that order in the leafy vegetable. Highest concentration was observed from *Thymus Vulgaries*, *Celocia argentea* and *Telfcirea occidentals* in site B.

Table1: Mean levels ($\mu\text{g/g}$) of Pb, Cu, Fe and Cr in some leafy vegetables in site A grown along the Nigeria- Seme Highway

Site A	Pb ($\mu\text{g/g}$)		Cu ($\mu\text{g/g}$)		Fe ($\mu\text{g/g}$)		Cr ($\mu\text{g/g}$)	
	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range
Ugwu	22.32 \pm 11.38	11.50- 41.47	21.69 \pm 7.36	15.44-35.44	172.87 \pm 62.05	104.99-259.94	37.328 \pm 20.21	17.20-68.87
Ewedu	21.74 \pm 13.00	10.01- 42.49	22.76 \pm 9.69	12.54-38.68	304.50 \pm 72.77	114.94-518.17	51.09 \pm 40.18	28.54-131.96
Shoko	16.75 \pm 10.54	9.00-35.99	20.95 \pm 12.08	2.45-32.09	260.74 \pm 215.37	79.96-574.77	101.22 \pm 100.15	27.53-259.22
Churry	24.07 \pm 8.21	16.99-39.98	23.53 \pm 3.52	18.44-27.13	406.33 \pm 225.06	169.87-734.13	111.95 \pm 72.88	41.99-182.28

Table 2: Mean levels ($\mu\text{g/g}$) of Pb, Cu, Fe and Cr in some leafy vegetables in site B grown along the Nigeria-Seme Highway

Site B	Pb ($\mu\text{g/g}$)		Cu ($\mu\text{g/g}$)		Fe ($\mu\text{g/g}$)		Cr ($\mu\text{g/g}$)	
	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range	Mean \pm SD	Range
Ugwu	18.91 \pm 11.98	10.14-28.64	21.09 \pm 7.43	10.14-28.64	166.49 \pm 86.22	69.97-279.9	67.75 \pm 52.68	27.09-166.91
Ewedu	16.57 \pm 9.22	6.50-30.48	20.73 \pm 5.05	14.44-28.64	292.36 \pm 196.33	114.93-534.71	47.56 \pm 18.95	33.39-83.55
Shoko	19.99 \pm 8.54	10.99-35.49	20.11 \pm 7.51	10.41-27.95	354.03 \pm 302.80	69.96-754.77	90.75 \pm 90.76	33.13-267.27
Churry	21.73 \pm 8.44	13.99-37.89	22.15 \pm 3.51	16.24-25.15	388.20 \pm 226.39	159.76-715.16	111.56 \pm 74.23	38.55-192.11

Table 3 Comparison of mean concentration in leafy vegetables from site A and B with recommended standards

SITE A	Pb (µg/g)	Cu (µg/g)	Fe (µg/g)	Cr (µg/g)
	Mean±SD	Mean±SD	Mean±SD	Mean±SD
<i>Telfeiria occidentals</i> (Ugwu)	22.32±11.38	21.69 ± 7.36	172.87 ±62.05	37.328±20.21
<i>Corchorus olitorius</i> (Ewedu)	21.74±13.00	22.76 ±9.69	304.50±72.77	51.09±40.18
<i>Celocia argentea</i> (Shoko)	16.75±10.54	20.95±12.08	260.74±215.37	101.22± 100.15
<i>Thymus Vulgaries</i> (Churry)	24.07±8.21	23.53±3.52	406.33±225.06	111.95±72.88
SITE B				
<i>Telfeiria occidentals</i> (Ugwu)	18.91±11.98	21.09 ± 7.43	166.49 ± 86.22	67.75 ± 52.68
<i>Corchorus olitorius</i> (Ewedu)	16.57± 9.22	20.73±5.05	292.36±196.33	47.56±18.95
<i>Celocia argentea</i> (Shoko)	19.99±8.54	20.11±7.51	354.03±302.80	90.75±90.76
<i>Thymus Vulgaries</i> (Churry)	21.73±8.44	22.15±3.51	388.20±226.39	111.56±74.23
Recommended maximum limit for vegetables	0.30	73.3	425	2.30

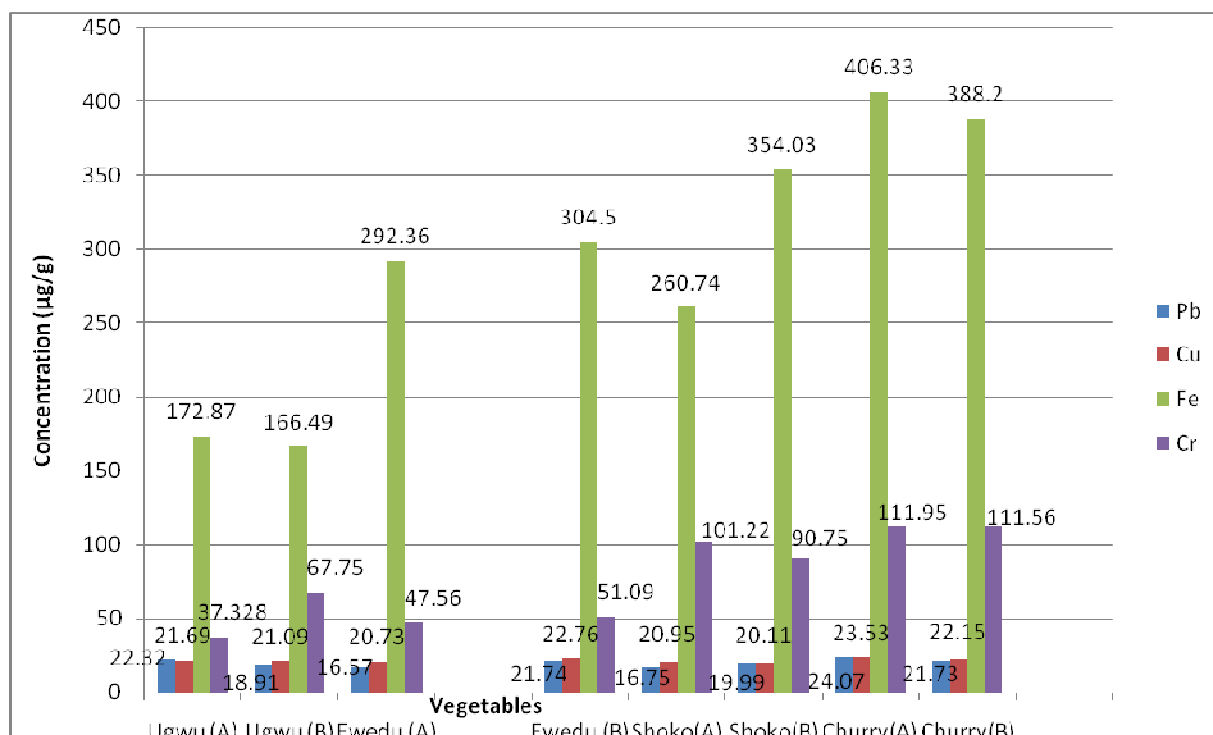


Figure 1. Bar chart showing the comparison in heavy metal concentration from site A and B

Lead (Pb) has been reported to be a serious cumulative body poison which penetrates into the body system via food air and water respectively and cannot be detached by washing the vegetables[22, 30]. The high levels of Pb in some of these leafy vegetables may be attributed to pollutants in irrigation water, farm soil or vehicular emission from heavy traffic on the road as lead is present in the fuel as an anti-knocking agent [31]. The level of Pb reported for the leafy vegetable in this study is lower than those reported and higher than the WHO, FEPA and China standard recommended limits of 0.3 µg/g and 0.2 µg/g reported for some leafy vegetables [25,27, 32, 33]. This is an indication of high pollution load of Pb in the vegetable from the studied area . Copper is an important micronutrient which acts as a biocatalyst, required for body pigmentation in addition to iron, maintaining a healthy central nervous system, prevents anemia and interrelated with the function of Zn and Fe in the body [34]. Most plants contain certain amount of copper which is inadequate for normal development and is regularly guaranteed through artificial or organic fertilizers application [33]. It has been reported that copper toxicity induces iron deficiency, lipid peroxidation and membranes destruction [35]. In this present study, the concentration of Cu in all the analyzed sample from the sampling sites varied between 21.09 and 23.53 µg/g with *Telfeiria occidentals* from site B having lower concentration and *Thymus Vulgaries* from site A recording the highest value. The results in this work which may be attributed majorly to atmospheric deposition were observed to be higher than other earlier reports [21, 25] lower than what was reported for some cultivated leafy vegetables in Ethiopia[36].

Iron (Fe) is an important mineral. It is needed to help our red blood cells deliver oxygen to the rest of the body. Iron is essential for many proteins and enzymes that maintain good health, transporting oxygen in the blood to all parts of the body as well as essential for proper functioning of the liver. The concentration of iron (Fe) in the samples analyzed varied between 166.49 and 406.33 $\mu\text{g/g}$ with the lowest observed in *Corchorus olitorius* (Ewedu) *Telfairia occidentals* (Ugwu) and *Celocia argentea* (shoko) in both sites. *Thymus Vulgaries* (Churry) plant contained higher amount of Fe with a value of 388.20 and 406 $\mu\text{g/g}$ in site A and B respectively. Furthermore the value of Fe in both site was found to be lower than what was reported for some leafy vegetables obtained in some agricultural farmlands in Ethiopia as well as the recommended maximum limit for vegetable [32, 33, 36]. It has been reported that high level above the permissible level may lead to leaves chlorosis due to iron toxicity whereas in human it can cause vomiting, upper abdominal pain, pallor, cyanosis, diarrhea, dizziness, shock, haemochromatosis, diabetes, diseases of liver, lungs and kidney, haepatoma and cardinomyopathy [36, 37]. Chromium is a trace element that is important in the body. It is able to stabilize blood sugar levels, which could prevent diabetes, by using insulin efficiently. It also aids the breakdown of fats in the body and is said to increase the good cholesterol in the body while lowering the bad cholesterol. Cr in all the tested samples varied between 37.33-111.95 $\mu\text{g/g}$ with *Telfairia occidentals* (Ugwu) having the lowest and *Thymus Vulgaries* (Churry) having the highest. The result in this study showed that the level of chromium in all the vegetable were above the recommended maximum limit for vegetable indicating that the consumption of this vegetable grown along this highway may have deleterious effect on human when consumed [33, 38]. The side effects from taking high doses of chromium include irregular heartbeat, upset stomach, itching and flushing. As far as non-essential elements are concern, chromium can cause ulceration, kidney and liver damage.

The variations in the concentrations of the heavy metals in the sampled from both site vegetables may be attributed to the heavy metals concentrations of soil, air and irrigation water of their production sites and also to the adsorption of heavy metals from aerial depositions during transportation and marketing. It can be shown from the obtained data that concentrations of all the heavy metals in vegetables were recorded maximum at the sampling site A located very close to the highway with heavy traffic load. In all the vegetable samples the concentrations of heavy metal were above the maximum permissible level for vegetables except copper which is below the recommended maximum limit. The accumulation of these heavy metal can be ascribed to air deposition and the order of contamination in the sampling sites was $\text{Fe} > \text{Cr} > \text{Cu} > \text{Pb}$. The elevated levels of the metals in the vegetables could be ascribed to excessive usage of fertilizers and other agro-chemicals, as well as the incessant use of waste water in irrigating the soils as well as high traffic load in the area.

Statistical test of significance using the Student t-test and analysis of variance (ANOVA), (Table 4) showed no significant differences at 95% level of confidence in the concentration of the heavy metals (Pb, Cu, Fe and Cr) in vegetables is obtained from the sampling sites.

Table 4. Duncan's one way analysis of variance the heavy metal concentration in the analyzed vegetables

	Pb ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)
Site A	0.300 ^a	0.647 ^a	0.52 ^a	0.879 ^a
Site B	0.407 ^a	0.602 ^a	0.120 ^a	0.132 ^a

Table 5 Correlations of variation between the heavy metal in the sludge sample

		Pb ($\mu\text{g/g}$)	Cu ($\mu\text{g/g}$)	Fe ($\mu\text{g/g}$)	Cr ($\mu\text{g/g}$)
Pb ($\mu\text{g/g}$)	Pearson Correlation	1	.227	0.597 ^{**}	0.531 ^{**}
	Sig. (2-tailed)		.121	.000	.000
	N	48	48	48	48
Cu ($\mu\text{g/g}$)	Pearson Correlation	0.227	1	.185	.256
	Sig. (2-tailed)	0.121		0.208	.079
	N	48	48	48	48
Fe ($\mu\text{g/g}$)	Pearson Correlation	.597 ^{**}	.185	1	.672 ^{**}
	Sig. (2-tailed)	0.000	.208		0.000
	N	48	48	48	48
Cr ($\mu\text{g/g}$)	Pearson Correlation	0.531 ^{**}	.256	0.672 ^{**}	1
	Sig. (2-tailed)	0.000	0.079	0.000	
	N	48	48	48	48

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

Pearson correlation coefficient analysis (Table 5) at 99% level of confidence showed a positive strong correlation between Pb and Fe, Pb and Cr as well as Fe and Cr in the vegetables sampled with r value of 0.597, 0.531 and 0.672 respectively. This shows that there is a common source of these metals in the study vegetables.

CONCLUSION

The results obtained in this study on concentration of heavy metals in some leafy vegetables compared well with earlier reports. Generally, the levels of heavy metals were observed to be higher than the recommended limit for vegetable except copper that exhibited lower values than recommended standards. It is worth noting that consumption of these vegetables from this studied area as food may constitute possible health hazards to humans at the time of the study. The elevated level of heavy metal in the vegetable may be attributed to excessive usage of fertilizers, manures as well as crop irrigation with all sort of polluted water hence farmer should be educated on this problem to shun the practice by exploring good farm practices. Furthermore, the results obtained in this study would go a long way in fortifying the scanty baseline data for the assessment of the distribution of heavy metals in leafy vegetables.

REFERENCES

- [1] F. Mapanda, Mangwayana, E. N., Nyamangara, J., Giller, K. E. *Agric, Ecosystem and Environment*, **2005**, 107, 151–156. doi:10.1016/j.foodchem.2008.04.049.
- [2] T.E. Bahemuka, Mubofu, E. B., *Food Chemistry*, **1991**, 66, 63–66.
- [3] M. G. M. Alam., Snow, E. T. Tanaka, A., *Science of the Total Environment*, **2003**, 308, 83–96
- [4] R.A. Olowu., Onwordi, C.T., Denloye, A.A. Osundiya, M.O Adebayo, N.O.. Owolabi, M.S Tovide, O.O., Moronkola B.A, Omoyeni O.A., Ajuwon O.R., *Research. J of. Environmental and. Earth Sciences.*, **2012**, 4, 237-243
- [5] R.A. Olowu, Ayejuyo, O.O., Adejoro, I.A., Adewuyi, G.O.. Yusuf, K.A, Onwordi C.T., Osundiya, M O. (2010). *E- Journal of Chemistry.*, **2010**, 2, 526-530.
- [6] L. Jarup, *B. Medical Bulletin*, **2003**, 68: 167-182.
- [7] S. F. Khan, R. Shahbaz, S. Aziz Khan M., Sadique. M. *World Applied Sciences Journal* **2009**, 6 (12), 1602-1606.
- [8] M. S. Jassir, Shaker, A., Khaliq, M.A., *Bulletin of Environmental Contamination and Toxicology*, **2005**, 75, 1020-1027.
- [9] E. L. Akubugwo, K. U. Osuocha, Nwaogu L. A., Chinyere G. C. *Advances in Applied Science Research*, **2013**, 4(4):190-195
- [10] D. U. Ekaete, U. D. Akpabio, I. E. Udo, *Asian Journal of Plant Science and Research*, **2013**, 3(4):116-122
- [11] R. K.Rattan, S.P. Datta, P.K. Chhonkar, K. Suribabu. A.K. Singh, *Agr. Ecosys. And Environ.*, **2005**, 109: 310-322.
- [12] J. R. Sanders, J.R., S.P. McGarth, T. Adams, *Environ. Poll.*, **1987**, 44: 193-210.
- [13] F. Al-Qurainy, A. Abdel-Megeed, *World App. Sci. J.* **2009**, 6 (7): 987-998.
- [14] V. Sunitha, B. Muralidhara, M. Ramakrishna, *Advances in Applied Science Research*, **2013**, 4(3):5-9
- [15] Cui, Y.L., R.H. Zhu, R.H. Zhi, D.Y. Chen, Y.Z. Huang, Y. Qiu China, *Environmental. International.*, **2004**, 30: 785-791.
- [16] Zhou, Q., Y. Wu, X. Xiong, *Chin. J. Appl. Ecol.*, **1994** 5: 428-441
- [17] P. Kovacheva, Djingova R., Kuleff I, *Phyto. Bal.* **2000**, 6: 91-102.
- [18] A. Lozak, Soltyk K, Ostapczuk P, Fijalek Z, *Science of the Total Environment*. **2002**, 289: 33-40.
- [19] O. P. Sobukola, Awonorin S. O, Idowu M. A., Bamiro, F. O.. *International. J. of Fd Sci. Tech*, **2008**. 43(2): 237-242
- [20] O. M. Atrouse, Oran S. A, Al-Abbadi, S. Y. *International Journal of Food Science Technology*. **2004**, 39: 413-417.
- [21] A. Lozak, Soltyk, K, Ostapczuk P, Fijalek Z. *Science of the Total Environment*. **2002**, 289: 33-40.
- [22] U. Divrikli, Saracoglu, S., Soylak, M., Elci L. *Fresenius Environ. Bull.* **2003**, 12: 1123-1125.
- [23] W. F. Punz, Sieghardt, H. *Environ. Exp. Bot.*, **1993**, 33(1): 85-98
- [24] E. I. Uwah, Ndahi, N. P. Abdulrahman F. I., Ogugbuaja, V. O. *J. of Environ Chem. and Ecotoxicol.* **2010**, 3(10), 264-271.
- [25] Xiong, Z.T. *Bull. Environ. Contam. Toxicol.*, **1998**, 60: 285-291.

-
- [26] S. Khan, S. Farooq, R. Shahbaz, S. Aziz Khan M., and Sadique. M. *World Applied Sciences Journal*, **2009**, 6(12), 1602-1606.
- [27] Official Method of Analysis. Association of Official Analytical Chemists, AOAC, Arlington, **1990**.
- [28] American Public Health Association (APHA). Standard Methods for the Examination of Water and Wastewater. 16th Ed. APHA. New York, **1992**, pp. 75 –86.
- [29] M.A. Radwan, Salama, A. K. *Food Chemistry. Toxicology*, **2006** 44: 1273-1278.
- [30] M. S. Jassir, Shaker, A., Khaliq, M.A., *Bulletin of Environ. Contam. and Toxicol*, **2005**, 75, 1020-1027.
- [31] M.O. Atayese, Eigbadon, A.I. Oluwa K.A. Adesodun J.K. *African Crop Science Journal*, **2009**, 16, 225 – 235.
- [32] Federal Environmental Protection Agency (**1991**) Guideline and standards for Environmental Pollution Control in Nigeria. FEPA, Lagos.
- [33] F. Itanna *Ethiopian J. Health Dev.* **2002** 16 (3) 295-302.
- [34] I. O. Akinyele, Osibanjo, O., *Food Chem.* **1982**, 8: 247- 251.
- [35] M.I. Zaidi, Asrar A, Mansoor, A, Farooqui M.A. *J. Appl. Sci.* **2005** 5(4): 708-711.
- [36] P. C. Prabu. *EJEAFCH*, **2009**, 8 (9), 818-827.
- [37] D. J. Ferner *Med. J* **2001**, 2: 1-5
- [38] E. T. Tyokumbur, Okorie *Biol. Trace Elem. Res.*, **2011**, 140, 215-224.