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Research Article

Levels and Field Accumulation Risk of Heavy Metals in Vegetables from Metal Recycling Companies

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Abstract

Background and Objective: Heavy metal pollution of the environment is an increasingly significant problem. This study was designed to investigate the potential health risks posed by metal recycling companies on vegetable crops. **Materials and Methods:** A total of 27 vegetable samples (*Talinum triangulae*, *Amaranthus hybridus* and *Solanecio bialfrae*) were collected around metal recycling companies at Ile-Ife and Ikirun, Osun state, Nigeria. Atomic absorption spectroscopy was used to determine the concentration of the metals. The data obtained were subjected to descriptive statistical analysis such as mean, standard deviation, t-test and one-way analysis of variance using SPSS. **Results:** Experimental results indicated that the concentrations of Ca, Cd, Cr, Cu, Fe, Mg, Mn and Zn in the vegetables were in the range 100.5-490.5, 0-2.8, 0-15.5, 4.5-135.5, 138.6-1081.2, 35.5-545.4, 5.2-545.2 and 40.4-961.1 mg kg⁻¹, respectively. The mean concentrations were in the order of Fe>Zn>Ca>Mn>Mg>Cu>Cr>Cd. Generally and relative to the control, vegetables from the sites were slightly enriched in Cu, Mn and Zn (Enrichment factor = 1.61-8.02) while *Talinum triangulae* was highly enriched in Mn (Enrichment factor = 28.21-28.81). Using SPSS, the results indicated that significant difference (p<0.05) exists between the levels of these metals and the control. The levels of Cd, Cr, Cu, Fe, Mn and Zn from the sites were also found to be greater than the FAO/WHO safe limits but within for the control. **Conclusion:** The high accumulation factors (AF>1) obtained for Zn in site A and Mn in site B signal the contamination of vegetables at these sites an indication that vegetables around metal recycling sites are contaminated to some extent and should not be consumed.

Key words: Baseline levels, enrichment factors, trace and heavy metals, metal recycling, atomic absorption spectrometer

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INTRODUCTION

Heavy metal pollution of the environment is an increasingly significant problem in the industrialized world. It occurs in the environment via several pathways, both natural and anthropogenic. The main sources of heavy metal pollution are mining industry, agriculture and automotive industry¹. Research has shown that the general public are exposed to a number of health problems due to indiscriminate dumping of urban waste matter, industrial waste, mineral exploitation, harmful agricultural practices, etc². Despite this proven fact, there is usually more emphasis on air and water since man and animal breath air and drink water directly. Hence human, animals and the environment are vulnerable to the effect of pollution from these sources unlike soil and vegetation pollution whose effects are more indirect³. Heavy metals are non-biodegradable and persistent environmental contaminants which may be deposited on the surfaces and then absorbed into the tissues of the vegetables. Plants take up heavy metals by absorbing them from deposits on the parts of the plant exposed to the polluted water or air⁴. Wastewater from mining industries, paint industries, chemical laboratories etc. often contain high concentrations of heavy metals⁵. These elements at concentration exceeding the physiological demand of vegetables, not only could administer toxic effects in them but also could enter the food chain, get biomagnified and pose a potential threat to human health. The toxic elements accumulated in organic matter in soils are taken up by growing plants. Intake of vegetables is an important path of heavy metal toxicity to human being. Crops and vegetables grown in soil contaminated with heavy metals have greater accumulation of heavy metals depending on the nature of vegetables and potential to accumulate or absorb heavy metals⁶. The biotoxic effects of heavy metals depend on the concentrations, oxidation states of heavy metals, kind of sources and mode of deposition. Dietary intake of heavy metals through contaminated vegetables may lead to various chronic diseases. Vegetable uptake of metals is one of the major pathways by which soil metals enter into food chain and is subsequently bio-accumulated to high concentrations causing serious risk to human health when plant based food stuffs are consumed. The health risks will depend on the chemical composition of the waste material, its physical characteristics, the vegetables cultivated and the consumption rate⁷.

Vegetables play important roles in human nutrition, most especially as sources of vitamin C, folic acid, minerals and

dietary fibre⁸. This study is of great concern because vegetables easily take up heavy metals which become accumulated in their edible parts⁹. The problem of heavy metals entering the food chain requires systematic assessments to make timely decisions to avoid severe health effects¹⁰. Such metals produce several clinical and physiological effects when they are consumed by humans. The heavy metal accumulation in the edible parts of some cultivated plants (*Brassica oleracea* var. *capitata*, *Portulaca oleracea*, *Vitis vinifera*, *Raphanus sativus*, *Phaseolus vulgaris* and *Vigna unguiculata* subsp. *unguiculata*) from a volcanic region in Southern Turkey was assessed by Saglam¹¹. Kumar and Seema¹² investigated the level of Cd, Pb, Zn, Cu, Cr and Ni in soil and edible portion of green leafy vegetables, grown in soil irrigated with wastewater and assessed the impact on health of residents of the study area. The authors suggested that regular monitoring of heavy metals in vegetables is essential to prevent excessive build-up of heavy metals in the food chain and that the use of wastewater for irrigation should be avoided. Trace metals analysis of soil and edible plant leaves from abandoned municipal waste dumpsite in Owerri, Nigeria was also assessed by Chizoruo *et al.*¹³. The authors affirmed that abandoned solid waste dumpsites contained significant concentrations of heavy metals which are absorbed and accumulated by plants. Benson *et al.*¹⁴ investigated and quantified trace metal concentrations in *Commelina africana* L. and Psammitic sandflats in Niger Delta, Nigeria. The authors stated that the order of trace metal concentrations in the *Commelina africana* L. samples is Zn>Ni>Cr>Pb>Cd and that the potential sources of metal loadings may be associated with anthropogenic activities such as petrochemical operations, fuel combustion and industrial wastes dump.

In the study area considered, there is high rate of consumption of vegetables due to its affordability and nutritional values. So there is need for regular investigation of the levels of pollution/contamination posed by these heavy metals as a result of this economically worthwhile activities or recycling process. Therefore, the aim of the present study is to determine the levels, enrichment and field accumulation factors of trace and heavy metals in edible plant samples (vegetables) around metal recycling companies and suggests the health risk associated with their consumption.

MATERIALS AND METHODS

Sample collection: Sampling was carried out in September, 2016 at the end of rainy season. The sites considered in this study were located at Ile-Ife and Ikirun, Osun state, Nigeria.

Osun state is within latitudes 7°30' N and longitudes 4°30' E in South-Western part of Nigeria. The state is landlocked and occupies 9,251 km². Twenty-seven samples were collected in all. Three samples of each of the vegetables were collected from each site. Identical samples were also collected behind the Conference Centre, Obafemi Awolowo University Ile-Ife as control (where no anthropogenic activity that could cause contamination takes place). The vegetable samples are the African spinach (*Amaranthus hybridus*), water leaf (*Talinum triangulæ*) and Bogoli leaf (*Solanecio bialfrae*). All glass wares were washed with distilled water followed by soaking in 10% nitric acid for few hour to avoid contamination. Stalk of the plants were carefully removed using nylon gloves and cleansed properly. The samples were freeze dried, labeled accordingly and kept separately. The same procedure was used for the identical samples used as control. Samples were preserved in the refrigerator.

Digestion procedure: A 0.5 g vegetable sample was weighed into a digestion flask. Ten mL of conc. HCL and HNO₃ (3:1) were added to it and heated to about 334°C for about 4 h on FOSS Tecator digester until the black colour decolorized or gave a clear solution. The solution was allowed to cool and filtered before making it upto 50 mL. Blank was also prepared in the same way but the sample was replaced with de-ionized water. Lanthanum is added to these solutions to prevent potential anionic interferences. The concentrations of heavy metals in the vegetables were determined using the atomic absorption spectrometer (Perkin Elmer 200A). Each of the samples was analyzed in triplicate for the various heavy metals determined to ensure precision and accuracy.

Enrichment and accumulation factors: The enrichment factor (EF) for each of the elements was determined by using crustal values and Fe as the reference element (Eq. 1). Thus, Eq. 1 indicates how enriched the samples are in heavy metals:

$$EF = \frac{\frac{X}{\text{Concentration of Fe (sample)}}}{\frac{Y}{\text{Concentration of Fe (reference)}}} \quad (1)$$

where, X is the concentration of the element in the sample, Y is the concentration of the element in the reference. The reference used in this research is the non-contaminating site (i.e., the control).

Since heavy metals translocate from soil to edible parts of the crops, the accumulation factors (AF) of each of the heavy metals was determined from the levels of these metals in the soil samples by the use of Eq. 2¹⁵:

$$AF = \frac{\text{Heavy metal concentration in food crops edible part}}{\text{Heavy metal concentration in the soil}} \quad (2)$$

Quality assurance and statistical analysis: Quality assurance was guaranteed through repeated measurements and the use of blanks for correction of background and other sources of error. Standards were prepared for the 6 elements determined and analyzed by the equipment used before running the samples. The high correlation coefficients (0.999172-0.999895) obtained in the calibration curves for the elements indicated proper calibration and the reliability of the results presented in this study.

Statistical analysis: The data obtained were subjected to descriptive statistical analysis such as mean, standard deviation, t-test and one-way analysis of variance (at 0.05 level of significance) using Statistical Packages for Social Sciences (SPSS) software (version 17.0 for Windows, SPSS Inc., Chicago, IL).

RESULTS AND DISCUSSION

The descriptive statistics indicating the levels of heavy metals in the samples is shown in Table 1, while Table 2 depicts the comparison of the observed levels with literatures and FAO/WHO's safe limits for these heavy metals in vegetables. The mean enrichment factors of vegetables for the sites and the accumulation factors (AF) of each of the heavy metals are shown in Table 3 and 4, respectively. The mean concentrations were in the order of Fe>Zn>Ca>Mn>Mg>Cu>Cr>Cd. Some of the values were below the detection limits. The frequency distribution of these trace and heavy metals in the samples is as shown in Fig. 1.

The results showed that the levels of Cd, Cr, Cu, Fe, Mn and Zn from metal recycling sites were found greater than FAO/WHO¹⁸ safe limits but were within for the control. The mean concentrations (mg kg⁻¹) of Cu, Fe and Zn in vegetables from the observed sites were considerably higher than the levels reported for vegetables (African spinach) in Central North-Western Nigeria, Eastern district and Middle district of Saudi-Arabia^{16,17}. In some cases, the Cd and Cr levels of the control and Ile-Ife site were below the detection limits (Table 2). However, it should be noted that most of these

Table 1: Descriptive statistics of the levels of heavy metals (mg kg^{-1}) in vegetables from the sites and control (n = 3)

Location	Sample ID	Vegetables	Elements (mg kg^{-1})									
			Ca	Cu	Cr	Cd	Fe	Mg	Mn	Zn		
Ile-Ife	A	Water leaf	Range	179.4-220.0	121.2-126.9	0-68	0.6-1.3	503.0-552.6	60.9-109.9	309.9-314.7	315.5-387.0	
			Mean $\pm$ SD	199.7 $\pm$ 20.3	123.0 $\pm$ 1.8	BDL	0.9 $\pm$ 0.3	528.8 $\pm$ 25.8	85.4 $\pm$ 25.5	302.3 $\pm$ 12.4	327.2 $\pm$ 11.6	
	B	A. Spinach	Range	179.9-260.9	107.7-110.1	0-14.9	0.6-2.8	745.2-1081.2	35.5-142.4	243.5-291.9	751.0-783.8	
			Mean $\pm$ SD	220.4 $\pm$ 40.5	108.9 $\pm$ 1.2	BDL	1.7 $\pm$ 0.9	968.2 $\pm$ 123.0	88.9 $\pm$ 53.5	267.7 $\pm$ 24.2	767.0 $\pm$ 16.2	
	C	Bologi leaf	Range	389.3-440.9	37.2-47.4	0-13.3	0-0.9	609.1-637.0	46.0-103.5	115.1-180.1	93.6-259.2	
			Mean $\pm$ SD	414.6 $\pm$ 25.3	42.3 $\pm$ 5.1	-	BDL	623.1 $\pm$ 14.0	74.7 $\pm$ 40.6	152.5 $\pm$ 27.6	176.4 $\pm$ 9.1	
Ikirun	A	Water leaf	Range	179.8-220.6	123.3-139.5	3.1-7.1	1.5-1.9	692.6-994.3	52.9-107.9	519.6-545.0	302.8-519.7	
			Mean $\pm$ SD	200.2 $\pm$ 20.4	131.4 $\pm$ 8.1	5.2 $\pm$ 1.9	1.7 $\pm$ 0.2	843.4 $\pm$ 151.3	80.4 $\pm$ 27.5	532.3 $\pm$ 12.7	491.2 $\pm$ 13.3	
	B	A. Spinach	Range	189.7-240.9	167.4-179.6	6.7-15.5	0.7-1.9	692.6-994.3	512.9-545.4	475.0-545.2	927.2-961.1	
			Mean $\pm$ SD	215.3 $\pm$ 25.6	173.0 $\pm$ 5.6	11.1 $\pm$ 6.2	1.3 $\pm$ 0.6	752.9 $\pm$ 24.4	534.1 $\pm$ 11.3	510.1 $\pm$ 35.1	944.4 $\pm$ 17.2	
	C	Bologi leaf	Range	430.1-490.5	146.32-149.5	12.5-14.5	BDL	619.3-625.3	101.5-102.3	140.1-145.3	251.9-270.3	
			Mean $\pm$ SD	460.4 $\pm$ 30.3	147.9 $\pm$ 1.6	13.5 $\pm$ 1.0	-	622.8 $\pm$ 3.5	101.9 $\pm$ 0.4	142.7 $\pm$ 2.6	266.0 $\pm$ 14.1	
Control	A	Water leaf	Range	140.6-150.6	8.9-10.9	BDL	BDL	259.1-267.4	150.3-152.5	5.2-5.8	49.0-53.8	
			Mean $\pm$ SD	150.0 $\pm$ 0.6	9.9 $\pm$ 1.0	-	-	263.0 $\pm$ 4.9	151.4 $\pm$ 1.1	5.5 $\pm$ 0.3	51.1 $\pm$ 2.4	
	B	A. Spinach	Range	180.9-200.5	7.5-8.9	BDL	BDL	150.9-152.2	101.5-102.3	5.4-5.8	50.3-52.2	
			Mean $\pm$ SD	190.7 $\pm$ 9.8	8.2 $\pm$ 0.7	-	-	151.3 $\pm$ 0.9	101.9 $\pm$ 0.4	5.6 $\pm$ 0.2	51.4 $\pm$ 1.1	
	C	Bologi leaf	Range	100.5-140.5	4.5-7.6	BDL	BDL	138.6-148.6	140.1-142.3	6.0-10.5	40.4-44.5	
			Mean $\pm$ SD	120.5 $\pm$ 7.6	6.0 $\pm$ 1.5	-	-	142.4 $\pm$ 4.2	141.2 $\pm$ 1.1	8.3 $\pm$ 2.3	42.4 $\pm$ 2.1	

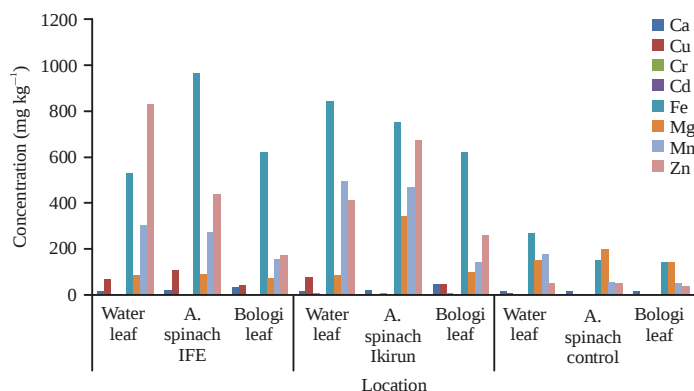
Fig. 1: Mean concentration (mg kg^{-1}) of heavy metals in vegetables

Table 2: Comparison of results obtained with literature and FAO/WHO safe limits

Elements	Results in this study (mg kg^{-1})		Central North Western Nigeria (mg kg^{-1}) ¹⁶	Eastern district Saudi-Arabia (mg kg^{-1}) ¹⁷	Middle district Saudi-Arabia (mg kg^{-1}) ¹⁷	FAO/WHO Safe limits (mg kg^{-1}) ¹⁸
	Site	Control				
Ca	179.4-490.5	100.5-200.5	-	-	-	1000.00
Cu	37.2-179.2	4.5-10.9	0.33-0.63	-	14.07 ± 0.44	73.00
Cr	0.0-15.5	BDL	-	-	-	1.30
Cd	0.0-1.9	BDL	BDL	4.02 ± 0.16	4.13 ± 0.14	0.20
Fe	503.0-1081.2	138.6-267.4	0.214-0.334	156.40 ± 9.82	94.70 ± 3.34	425.00
Mg	101.5-152.5	35.5-545.5	-	-	-	400.00
Mn	115.1-545.2	5.2-10.5	-	26.53 ± 0.35	25.13 ± 0.57	6.60
Zn	93.6-961.0	39.5-53.8	0.22-0.37	35.54 ± 1.09	30.18 ± 0.78	99.40

BDL: Below the detection limit, Mean $\pm$ SD

Table 3: Mean enrichment factors (EF) of the elements in the vegetables

Location	Sample ID	Description	Elements						
			Ca	Cu	Cr	Cd	Mg	Mn	Zn
Ile-Ife	A	Water leaf	0.66	6.28	-	-	0.28	27.30	3.16
	B	A. Spinach	0.18	2.05	-	-	0.13	8.570	2.34
	C	Bologi leaf	0.64	1.61	-	-	0.12	4.190	0.94
Ikirun	A	Water leaf	0.41	4.21	-	-	0.10	17.37	2.98
	B	A. Spinach	0.22	4.25	-	-	1.05	18.30	5.01
	C	Bologi leaf	0.87	5.62	-	-	0.16	3.930	1.43

EF<1: Not enriched, 1-10: Slightly enriched, 10+: Enriched

Table 4: Accumulation factors (AF) of the metals in the vegetables

Elements	Site A			Site B			Control		
	A	B	C	A	B	C	A	B	C
Cu	0.47	0.42	0.16	0.43	0.56	0.48	0.30	0.25	0.18
Fe	0.50	0.93	0.59	0.86	0.77	0.64	0.61	0.92	0.87
Mn	0.86	0.77	0.45	1.60	1.64	0.45	0.03	0.04	0.04
Zn	2.33	1.24	0.49	0.95	1.31	0.50	0.12	0.12	0.10

AF>1: Accumulation

elements are also needed in trace amount but could become toxic and detrimental to health when they are in excess. Mn in particular is essential for photosynthesis and its availability depends on the pH of the soil¹⁹. It was reported that Mn availability in plants can only be harmful when it reaches approximately 1000 mg kg^{-1} ²⁰ which is above the values

reported in this study. The high enrichment factors for Cu, Mn and Zn are worthy to be noted and studied since bioaccumulation of these metals (higher than the maximum permissible limits) could be toxic or detrimental to health. Similar trend was also observed for other heavy metals observed in this study (Table 2). Using SPSS (version 17.0 for

Table 5: Summary for enrichment factors (EF) of heavy metals in vegetables

Elements	Comment
Cu, Mn, Zn	Slightly enriched
Ca, Cd, Cr, Mg	Not enriched
Mn in water leaves from the sites and in African spinach(site B)	Highly enriched
EF<1: Not enriched, EF between 1 and 10: Slightly enriched, EF>10: Enriched	

Windows), the ANOVA result indicated that significant differences exist (at $p < 0.05$) in the levels of these elements among the three vegetables. In most cases, the results of t-test indicated that significant differences exist between the levels of Ca, Fe, Mn and Mg ($t = 1.4 \times 10^{-6}$ -0.027 at 0.05 level) in the sites and control. No significant difference occurred in the concentrations of Cd and Cr ($t > 0.05$). Also relative to the control, the levels of Cu and Zn in Bologi leaves differ significantly ($t = 7 \times 10^{-4}$). Vegetables from the sites were slightly enriched in Cu (EF = 1.61-6.28) and Zn (EF = 1.43-5.01) while water leaves were highly enriched in Mn (EF=17.37-27.30) followed by African spinach and Bologi leaves. This could be as a result of the variation in the rate of absorption or translocation of these metals by the plants, production capacity of each plant, distance from the source or exhaust and climatic factors. This is an indication that these metals are easily absorbed or translocated by water leaf than the two other vegetables. This result agreed with Al Jassir *et al.*^[21], who reported that leafy vegetables accumulate higher metal content than others. Table 5 is the summary of the enrichment factors presented on Table 3.

The enrichment factor of Fe could not be obtained since it was used as a reference otherwise it would have being as enriched as Zn since significant differences existed between the levels of Fe in the sites and control ($t < 0.05$). The accumulation factors of Zn were high (Table 4) for samples A and B (water leaf and African spinach) as well as Mn in site B for the two samples. The accumulation factors were less than 1 for other heavy metals.

Therefore, to address the potential health risks posed by metal recycling companies on crops, the government should formulate safety policies and measures for these companies. The safety policies should conform to international practices and ethical standards. New legislations and bills should be passed and approved stating the penalties and fines for environmental contamination by metal recycling companies. Moreover, environmental impact assessment (EIA) must be carried out periodically to monitor the levels of heavy metals in plant, air, soil and water samples.

CONCLUSION

The levels of Ca, Cu, Cd, Cr, Fe, Mg, Mn and Zn in vegetable samples have been studied using atomic absorption spectrometer. The results gave the baseline levels of heavy metals in three edible plant samples around metal recycling sites using t-test, the concentrations were significantly higher than the control ($t < 0.05$). The results showed that the levels of Cd, Cr, Cu, Fe, Mn and Zn from the sites were found greater than FAO/WHO safe limits but were within for the control. These 3 vegetables were slightly enriched in Zn, Cu and Mn. The vegetables from the sites were highly enriched in Mn in the order, water leaf>African spinach>Bogoli leaf. High accumulation factors (AF>1) was also obtained for Zn in site A and Mn in site B. The results from this work also indicated that environmental impact assessment must be carried out periodically to monitor the levels of these heavy metals, not only in plant samples but also in the air, soil and water samples.

SIGNIFICANCE STATEMENT

This study provides the baseline levels of the observed heavy metals in vegetables from Nigerian metal recycling sites and established the potential health risks associated with the consumption of such edible crops.

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