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DETERMINATION OF HEAVY METAL CONCENTRATIONS IN SOIL AND VEGETABLES IRRIGATED WITH WASTE WATER IN CHANCHAGA AREA OF MINNA, NIGERIA

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ABSTRACT

The concentrations of the heavy metals Pb, Cd, Cr and Cu in soil and edible parts of spinach, jute mallow and tomato were determined in vegetable farms located in Chanchaga area of Minna, Nigeria, in which the farms are irrigated with domestic waste water. The aim of the study was to assess the levels of these metals in the vegetables viz-a-viz their suitability for human consumption based on established permissive limits. Composite samples of soil and vegetables were collected from ten farms in the area and also from two farms not irrigated with waste water (as control). Samples were digested in triplicates using a mixture of concentrated nitric and perchloric acids (3:1), followed by metal determination using Flame Atomic Absorption Spectrophotometer. The mean and range of metal concentrations (µg/g dry weight) in soil samples were Pb 16.9±16.1(5.2 – 55.9), Cd 0.4±0.2(0.2 – 0.7), Cr 6.2±4.5(1.7 – 15.8) and Cu 11.8±6.8(6.5 – 28.1), respectively, while that of vegetables were Pb 6.3±3.4(0.4 – 19.2), Cd 0.9±0.4(0.1 – 2.4), Cr 5.2±2.2(1.1 – 13.1) and Cu 15.5±5.8(4.8 – 36.8) respectively. The soil-plant Transfer Factor (TF) values showed that the order of uptake of metals by vegetables was Cd > Cu > Cr > Pb. The concentrations of the heavy metals in the three vegetables were generally higher than the WHO/FAO maximum permissive limits. This calls for concern, especially in the case of Pb and Cd which are highly toxic and of no known biological use.

KEYWORDS: heavy metals, soil, vegetables, waste water, permissive limits

INTRODUCTION

Some heavy metals are required in trace amounts by living organisms, some are essential for certain metabolic activities while others are essential components of enzymes and pigments in living systems (Chou *et al.*, 2000). Chromium is required for normal carbohydrate, lipid and nucleic acid metabolism, while small amount of nickel is required to maintain good health in animals (Macrae *et al.*, 1997). Cobalt is essential for nitrogen fixation by rhizobium in legume noodles and also a component of vitamin B_{12} (Macrae *et al.*, 1999). Iron is an essential component of respiratory pigments, such as haemoglobin of vertebrate blood, the red erythrocruorin found in many annelids and mollusks, and the green chlorocruorin of certain polycheate worms (Falk, 1984). Copper is found to be essential in haemoglobin formation, production of RNA, cholesterol utilization, among others, while zinc is essential for protein synthesis, carbon dioxide transport and sexual function. Others such as lead, arsenic, mercury and cadmium have no known beneficial importance in living organism (Adeniyi, 1996).

Toxicity of heavy metals arises when concentration is above certain safe limits, which vary from metal to metal, in which case they are not metabolized by the body and accumulate in the soft tissues (Prasad, 2004). All toxic metals can endanger human health on slight exposure; the critical organs they affect in the body differ from one metal to the other (Welz, 1985).

Heavy metals occur as natural constituents of the earth crust and are present is soils mostly in minimal, insignificant eco-toxicological concentrations (Nriagu, 1990). They are however introduced into the ecosystem by anthropogenic activities such as mining, metal works, agricultural activities, combustion of fossil fuels, manufacture and use of materials containing heavy metals as well as the disposal of wastes (Chou *et al.*, 2000). As a result of urbanization and increasing anthropogenic activities, the heavy metal pollution of soil, water and atmosphere represents a growing environmental problem affecting food quality and human health in cities (Nriagu, 1990). Consumption of vegetables is one of the pathways by which heavy metals enter the food chain. The presence of heavy metals in fertilizers and waste waters contribute to additional sources of metal pollution for cultivated vegetables (Yusuf *et al.*, 2002).
The aim of this study is to assess the levels of the heavy metals Pb, Cd, Cr and Cu in soil and edible parts of three commonly consumed vegetables; spinach, jute mallow and tomato in some vegetable farms irrigated with

waste water in Chanchaga area of Minna, a city in the north-central region of Nigeria, *viz-a-viz* the suitability of the vegetables for human consumption, based on established permissive limits.

MATERIALS AND METHODS

Composite samples of soils and vegetables were collected from 10 vegetable farms irrigated with waste water (F1 – F10) and also from 2 other farms not irrigated with waste water (C1 & C2) (as control) from Chanchaga area of Minna, Nigeria. Samples were collected in January 2011. Soil samples were collected with a stainless steel hand-trowel within 0 – 20cm depths. The sub-samples were collected along independent zig-zag paths to randomness. The trowel was carefully cleaned after each sampling exercise, to avoid cross-contamination (Mapanda *et al.*, 2007). The soil samples were air-dried for seven days to avoid microbial degradations. Prior to analysis, samples were re-dried in the oven at 110°C for about 3 hours and crush in a porcelain mortar and sieved through a 2mm plastic sieve to obtain fine soil particles. One gram (1 g) of the oven-dried and sieved composite soil samples from each of the farms (in triplicates) were first moistened with a few drops of water (to prevent sputtering) followed by the addition of 10cm^3 concentrated nitric acid (HNO_3). The mixture was slowly evaporated over a period of 1hour on a hot plate. The solid residue obtained was digested with 20cm^3 of a 3:1 mixture of concentrated nitric acid (HNO_3) and perchloric acid ($HClO_4$) for 10minutes at room temperature before heating was continued. The temperature of the hot plate was slowly raised over a period of 1hour until the fumes of $HClO_4$ start to escape and heating was continued until a clear solution was obtained. The mixture was allowed to cool to room temperature. The cooled mixture was then filtered using Whatman No. 1 filter paper into 100cm^3 volumetric flask and make up to mark with distilled water. The digests were stored in polythene bottles till analysis (Fatoki, 1996).

Vegetable samples were collected with gloved hands to avoid contamination. Samples of spinach (*Amarantus hybridus*) and jute mallow (*Corchorus olitorius*) were collected by randomly picking up some mature bottom leaves from the matured plants until a sizable bundle was gathered. Ripe fruits of tomato (*Lycopersicon esculentum*) were collected by randomly plucking the fruits from the plants (Mapanda *et al.*, 2007). The vegetable samples were washed with distilled water and air-dried for 24hours. The samples were then oven-dried at 90°C for 24hours before grinding. 1g of the thoroughly mixed dry matter from each of the farms (in triplicates) was weighed into 50cm^3 beaker followed by addition of 10cm^3 mixture of analytical grade concentrated acids HNO_3 and $HClO_4$ in the ratio 1:1 (Yusuf *et al.*, 2002). The beakers containing the samples were covered with watch glasses and left overnight. The digestion was performed at a temperature of about 96°C until about 4cm^{3}was left in the beaker. Then a further 10cm^3 of the mixture of acids was added and the mixture was allowed to evaporate to a volume of about 4cm^3. After cooling, the solution was filtered and made up to a final volume of 50cm^3 with distilled water (Yusuf *et al.*, 2002).

For quality assurance of methods, a recovery study was carried out by spiking 1g of five different soil samples each with 1cm^3 of standard solutions of the metals Pb, Cd, Cr and Cu. Furthermore, reference samples of soil and plant were analysed, under similar conditions. Recovery test gave % recoveries > 95% while in the analysis of reference materials, t-test results (at 95% Confidence Interval) show that statistically, there exists no significant difference between certified and obtained values.

Metal concentrations in working standards and digests were determined using Flame Atomic Absorption Spectrophotometer (Perkin Elmer AANALYST 200). Air-acetylene flame was used. The instrumental settings and operational conditions were in accordance with the manufacturer's specifications. Calibrations were performed in the range of analysis using analytical grade standard metal solutions. Blanks were also determined to ascertain the contribution of reagents to metal levels. Instrument calibration and blank determination were carried out at intervals of ten samples. The results obtained were subjected to statistical analysis.

RESULTS AND DISCUSSION

The mean concentrations of the heavy metals (µg/g dry weight) are given in Table 1 – 5. The concentrations of the metals were generally higher in samples from farms irrigated with waste water (F1 – F10) than in samples from the control farms (C1 & C2) (Tables 1 – 4). These differences are statistically significant, $p<0.005$, and shows some levels of pollution by these metals in farms irrigated with waste water. There existed positive correlations between concentrations of metals in soil, suggesting similar sources of metal enrichment which could be linked to the waste water application.

Generally, the other of accumulation of metals in soil was Pb > Cu > Cr > Cd while that of vegetables was Cu > Pb > Cr > Cd (Table 5). Spinach accumulated more metals, followed by jute mallow and then tomato. This is in agreement with some earlier reports that leafy vegetables have greater potential for accumulating heavy metals in their edible parts than grains and fruit crops, due to their higher transpiration rate (Mapanda *et al.*, 2007). It is pertinent to note also that spinach has broader leaves than jute mallow, while the edible part of tomato analysed was the fruit.

The soil-plant Transfer Factor (TF) qualifies the relative differences in bioavailability of metals to plant and is a function of both soil and plant properties. The TF of metals was calculated using the equation:

$$TF = \frac{concentration\ of\ metal\ in\ vegetables}{concentration\ of\ metal\ in\ soil}$$

Higher transfer factors reflect relatively poor retention in soils or greater efficiency of plants to uptake metals (Kachenko and Singh, 2006). The TF values showed that the order of uptake of metals by vegetables is Cd > Cu > Cr > Pb. Cd had the highest TF for all the vegetables. This is due to its high mobility (Prasad, 2004). Spinach generally had the highest TF values for all the metals followed by jute mallow and tomato, due to their relative transpiration rate (Kisku *et al.*, 2000)

CONCLUSION

It is evident from this study that the waste water used for irrigating the vegetable farms contributed to their heavy metals burden. The concentrations of the heavy metals in soil samples were generally lower than the WHO/FAO maximum permissive limits (Table 5). On the other hand, the concentrations of the heavy metals in the three vegetables were generally higher than the WHO/FAO maximum permissive limits, except for Cu. The higher concentrations of Pb, Cd and Cr in the vegetables could be detrimental to human health and calls for concern especially in the case of Pb and Cd which are highly toxic and of no known biological use. The treatment of the waste water before use for irrigation purpose is recommended.

Table 1: Mean Concentrations (μg/g dry weight) of Pb in Farm Soil and Edible Part of Vegetable

Sample	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	C1	C2
Soil	35.1 ±5.3	12.8 ±2.1	8.3 ±1.9	5.8 ±1.1	5.2 ±1.1	7.2 ±0.7	8.1 ±0.2	5.6 ±1.6	25.4 ±1.4	55.9 ±5.7	2.8 ±1.1	4.2 ±1.2
Spinach	4.1 ±0.3	7.5 ±2.1	9.6 ±1.9	12.7 ±1.5	11.5 ±1.5	6.5 ±2.5	1.8 ±1.7	14.7 ±1.7	19.2 ±1.8	10.9 ±1.8	3.4 ±2.1	4.1 ±1.4
Jute Mallow	0.4 ±0.1	2.6 ±0.2	5.6 ±1.5	8.3 ±1.1	1.3 ±1.1	6.7 ±2.3	5.2 ±2.3	13.5 ±1.2	4.8 ±1.2	4.1 ±1.1	0.4 ±0.1	1.4 ±0.6
Tomato	1.6 ±0.4	1.4 ±0.3	4.5 ±1.7	5.7 ±2.9	4.4 ±1.2	2.8 ±1.3	3.2 ±1.1	7.7 ±2.5	2.3 ±1.2	3.6 ±1.7	1.4 ±0.2	1.1 ±0.5

F1, F2,……F10 = Ten randomly selected vegetable farms C1 & C2 = control farms

Table 2: Mean Concentrations (μg/g dry weight) of Cd in Farm Soil and Edible Part of Vegetable

Sample	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	C1	C2
Soil	0.7 ±0.2	ND	0.4 ±0.2	0.3 ±0.2	0.6 ±0.1	0.4 ±0.1	0.3 ±0.1	0.4 ±0.3	0.2 ±0.1	0.5 ±0.3	0.4 ±0.1	0.2 ±0.1
Spinach	1.3 ±0.2	1.1 ±0.1	1.5 ±0.7	1.2 ±0.4	1.8 ±0.6	2.4 ±1.4	2.2 ±1.2	1.6 ±0.3	0.8 ±0.2	1.8 ±0.5	0.4 ±0.1	0.2 ±0.1
Jute Mallow	0.2 ±0.1	0.5 ±0.2	0.3 ±0.1	0.6 ±0.2	0.6 ±0.1	0.7 ±0.3	1.3 ±0.2	0.8 ±0.5	ND	0.9 ±0.2	0.2 ±0.1	0.3 ±0.1
Tomato	0.3 ±0.1	0.4 ±0.1	0.3 ±0.1	ND	0.7 ±0.2	0.5 ±0.1	0.9 ±0.3	0.6 ±0.2	0.1 ±0.1	0.2 ±0.1	ND	0.2 ±0.1

ND = Not Detectable

Table 3: Mean Concentrations (µg/g dry weight) of Cr in Farm Soil and Edible Part of Vegetable

Sample	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	C1	C2
Soil	10.2 ±3.3	8.5 ±0.9	2.5 ±0.2	3.9 ±0.1	3.6 ±1.2	6.6 ±1.5	2.4 ±1.2	15.8 ±2.9	1.7 ±0.5	6.8 ±1.1	1.9 ±1.1	2.1 ±1.2
Spinach	4.4 ±1.1	5.8 ±1.6	7.8 ±1.3	7.9 ±1.6	8.3 ±1.3	5.3 ±1.2	7.1 ±2.5	6.9 ±1.4	13.1 ±2.7	7.8 ±1.6	4.2 ±1.1	1.7 ±1.1
Jute Mallow	1.9 ±1.2	6.9 ±1.5	6.7 ±1.8	6.5 v1.3	5.6 ±1.1	3.9 ±1.1	1.2 ±0.2	3.8 ±1.2	4.8 ±1.2	3.5 ±1.5	2.9 ±1.4	2.2 ±1.2
Tomato	3.2 ±1.2	2.4 ±1.1	3.7 ±1.4	6.2 ±1.7	4.7 ±1.3	4.5 ±2.1	1.1 ±0.1	2.6 ±1.1	3.5 ±1.5	4.2 ±1.2	1.2 ±0.2	1.4 ±0.7

Table 4: Mean Concentrations (µg/g dry weight) of Cu in Farm Soil and Edible Part of Vegetable

Sample	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	C1	C2
Soil	14.6 ±5.4	6.5 ±2.1	9.9 ±2.3	7.1 ±0.3	8.9 ±1.1	12.8 ±2.4	11.4 ±2.1	8.8 ±2.2	9.5 ±2.1	28.1 ±4.1	5.4 ±2.3	4.2 ±1.4
Spinach	17.5 ±2.1	27.6 ±3.2	14.1 ±2.4	17.6 ±2.3	19.7 ±5.5	33.2 ±2.5	19.1 ±2.6	16.9 ±2.4	13.9 ±5.3	18.2 ±4.2	9.4 ±1.2	7.4 ±2.3
Jute Mallow	16.9 ±2.4	36.8 ±3.7	16.9 ±2.6	14.9 ±3.2	15.3 ±1.5	14.3 ±2.1	17.1 ±1.5	13.4 ±2.2	15.7 ±2.1	13.5 ±2.3	7.2 ±1.2	7.4 ±2.2
Tomato	13.5 ±3.1	10.9 ±2.3	11.6 ±2.4	5.6 ±2.7	16.7 ±3.4	7.5 ±1.8	5.7 ±1.6	8.9 ±2.1	4.8 ±1.5	6.2 ±1.4	8.2 ±1.1	5.5 ±1.7

Table 5: Mean and Range (µg/g dry weight) of Metal Concentrations in Soil and Vegetables from all Farms in the Study Site

	Pb	Cd	Cr	Cu
Soil	16.9±16.1 (5.2 – 55.9)	0.4±0.2 (0.2 – 0.7)	6.2±4.5 (1.7 – 15.8)	11.8±6.8 (6.5 – 28.1)
Spinach	9.9±4.8 (4.1 – 19.2)	1.6±0.5 (0.8 – 2.4)	7.4±2.8 (4.4 – 13.1)	19.8±6.1 (13.9 – 33.2)
Jute Mallow	5.3±4.1 (0.4 – 13.5)	0.6±0.3 (0.2 – 1.3)	4.5±1.8 (1.2 – 6.9)	17.5±7.4 (13.4 – 36.8)
Tomato	3.7±2.0 (1.4 – 7.7)	0.4±0.3 (0.1 – 0.9)	3.6±1.6 (1.1 – 6.2)	9.1±3.8 (4.8 – 16.7)
WHO/FAO(soil)	100	3	400	100
WHO/FAO(Veg.)	0.3	0.2	2.3	40

Table 6: Mean of Soil-Plant transfer Factor (TF) of Vegetables

Vegetable	TF(Pb)	TF(Cd)	TF(Cr)	TF(Cu)
Spinach	0.59	4.00	1.19	1.68
Jute Mallow	0.31	1.50	0.73	1.48
Tomato	0.22	1.00	0.58	0.77
Mean TF Value	0.37	2.17	0.83	1.31

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