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Analysis of heavy metals found in vegetables from some cultivated irrigated gardens in the Kano metropolis, Nigeria

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The use of industrial and domestic wastewaters for irrigation on vegetable gardens is a public health concern. Using atomic absorption spectrophotometry (AAS), concentrations of Cr, Co, Cu, Ni, Pb and Zn were determined in four different vegetables, including, spinach, okra, onions and tomatoes, grown in effluent irrigated fields at Sharada, Kwakwachi and Jakara in the Kano metropolis, Nigeria. Similar vegetable samples from another irrigated field at Thomas Dam, in the remote part of Kano, were used as control. Samples were collected during dry and rainy seasons. The mean level of metals obtained ranged widely from 0.28 mg/Kg Cr to 18.89 mg/Kg Zn. Samples from Jakara garden indicated highest mean levels of Co (1.14 ± 0.17 mg/Kg), Cu (7.50 ± 1.08 mg/Kg), Zn (18.89 ± 1.93 mg/Kg) and Cr (0.85 ± 0.10 mg/Kg) while those from Sharada indicated highest levels of Ni (2.02 ± 0.35 mg/Kg) and Pb (1.60 ± 0.53 mg/Kg). Comparison of results with the control showed significant levels (p<0.05) of all the metals analyzed in the vegetable samples obtained from the effluent irrigated gardens. However, the levels were within the National Agency for Food and Drug Administration and Control (NAFDAC) tolerable limits for metals in fresh vegetables.

Key words: Industrial effluents, irrigation, vegetables, metals, atomic absorption spectrophotometry (AAS), Kano.

INTRODUCTION

Irrigation is the artificial addition of water to soils in order to meet plants' needs to overcome drought limitations and improve the crops' yields. However, other factors such as soil and water quality and management practices are also important. Wastewater irrigation is known to contribute significantly to the heavy metal contents of soils (Mapanda et al., 2005; Devkota and Schmidt, 2000).

In Zimbabwe, Nyamangara and Mzezewa (1999) implicated land disposal of sewage and industrial effluents as the chief source of heavy metal enrichment of pasturelands and agricultural fields. Barrow and Webber (1972), Pike et al. (1975) pointed out the dangers of repeatedly treating soils with metallurgical slag because of the possible build up of elements to toxic concentrations. Juste (1974) observed that the spreading of some organic wastes (town refuse, domestic and industrial effluents etc) might contribute to increased levels of nonessential metals in soil, which could cause poor plant growth. Studies conducted by Kisku et al. (2000) in Kalipur, Bangladesh, on the uptake of Cu, Pb, Ni and Cd by *Brassica oleracea* from fields irrigated with industrial effluent indicated widespread contamination from heavy metals despite showing a healthy and gigantic external morphology. High levels of accumulation of heavy metals from soil by common garden vegetables have been reported by many environmental researchers (Boon and Soltanpour, 1992; De Pieri et al., 1997; Xiong, 1998). Therefore, heavy metal contamination of vegetables cannot be underestimated as these foodstuffs

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are important components of human diet.

Vegetables are rich sources of vitamins, minerals, and fibers, and also have beneficial anti-oxidative effects. However, intake of heavy metal-contaminated vegetables may pose a risk to the human health. This is because, heavy metals have the ability to accumulate in living organisms and at elevated levels they can be toxic. It has been reported that prolonged consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of the metals in the kidney and liver of humans causing disruption of biochemical leading numerous processes, to cardiovascular, nervous, kidney and bone diseases (Trichopoulos, 1997; Jarup, 2003).

Determination of the chemical composition of plants is one of the most frequently used methods of monitoring environmental pollution. Various plants have been used as bioindicators (Kasanen and Venetvaara, 1991). Several studies have been reported on the accumulation of environmental pollutants in plants. In Israel, for example lichen and higher plant species were exposed near industrial areas in order to detect the accumulation of heavy metals in these plants (Naveh et al., 1979). Tree barks and their leaves remain in the environment for a long period and are sensitive indicators of the environmental contamination with heavy metals, sulphur and fluorine (Ayodele and Ahmed, 2001). Batagarawa (2000), analyzed moss plant in Kano metropolis for heavy metals and reported high levels of lead, zinc and cadmium from industrial areas of Sharada, Bompai and Challawa. Nuhu (2000) also reported high levels of cadmium, manganese and lead in mango leaves obtained from industrial areas of Bompai, Challawa and Sharada in Kano metropolis.Kano is one of the highly populated cities in Nigeria. It lies within longitude 8° 32 E and latitude 11° 58 N, within a topographical drainage of River Jakara flowing north east. The vegetation of the area is the savannah type, with more grasses than hard wood trees. The average annual rainfall of the area is 817 mm and the temperature varies between 27 to 35 ℃ with a moderate relative humidity.

Study area

Jakara (JKR) and Kwakwachi (KKC) gardens are irrigation sites alongside Jakara river valley at Ahmaddiya and Sabon-gari areas respectively, while Sharada (SRD) garden is located in the middle of industries at Sharada industrial estate all in the Kano metropolis. In these three sites, farming activities are carried out throughout the year but with domestic and industrial wastewaters being used to treat the soils during dry seasons. Thomas (TMS) Dam is another irrigation site outside Kano metropolis where fresh water from the dam is being used to treat the soils during dry seasons.

The objectives of this study were to analyze the vegetable samples from the irrigation sites for heavy

metals and to compare results obtained with one another and with those of National Agency for Food and Drugs Administration and Control (NAFDAC) safe limits, while using vegetable (spinach, okra, onions and tomatoes) samples from Thomas Dam as control. The metals of interest include cobalt (Co), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). The results obtained from this study will be useful for assessing the metals contamination and as well as determining the need for remediation. The results would also provide information for background levels of metals in the vegetables in the study area.

MATERIALS AND METHODS

Analytical reagent (AnalaR) grade chemicals and distilled water were used throughout the study. All glassware and plastic containers used in this work were washed with detergent solution followed by 20%(v/v) nitric acid and then rinsed with tap water and finally with distilled water.

Sampling and sample treatment

The vegetables analyzed include spinach, okra, tomatoes and onions. Samples were collected twice in the year 2002 from three different farms in each site. The first round of sampling was carried out in May towards the end of the dry season while the second round was in September at the peak of the rainy season. Each sample was randomly handpicked, wrapped in a big brown envelope and labeled.

In the laboratory, each sample was washed with tap water and thereafter with distilled water and then dried in an oven at $80 \,^{\circ}\text{C}$ (Larry and Morgan, 1986). At the end of the drying, the oven was turned off and left overnight to enable the sample cool to room temperature. Each sample was grounded into a fine powder, sieved and finally stored in a 250 cm³ screw capped plastic jar appropriately labeled.

Digestion procedure

A 2.0 g of the sample was weighed out into a Kjaedahl flask mixed with 20 cm³ of concentrated sulphuric acid, concentrated perchloric acid and concentrated nitric acid in the ratio 1: 4: 40 by volume respectively and left to stand overnight. Thereafter, the flask was heated at 70 °C for about 40 min and then, the heat was increased to 120 °C. The mixture turned black after a while (Erwin and Ivo, 1992). The digestion was complete when the solution became clear and white fumes appeared. The digest was diluted with 20 cm³ of distilled water and boiled for 15 min. This was then allowed to cool, transferred into 100 cm³ volumetric flasks and diluted to the mark with distilled water. The sample solution was then filtered through a filter paper into a screw capped polyethylene bottle.

Instrumental analysis

An Alpha 4 model atomic absorption spectrophotometer (Chemtec Analytical, UK) equipped with photomultiplier tube detector and hollow cathode lamps was used for the determination of metal concentrations. Working standards were also prepared by further dilution of 1000 ppm stock solution of each of the metals and a calibration curve was constructed by plotting absorbance versus concentration. By interpolation, the concentrations of the metals in sample digests were determined.

Compling site	Metals							
Sampling site	Со	Cr	Cu	Ni	Pb	Zn		
Spinach								
SRD	0.68±0.29 ^a	0.60±0.12 ^b	0.69±0.12 ^b	2.02±0.35 ^a	1.60±0.53 ^a	6.63±0.64 ^c		
KKC	0.69±0.06 ^a	0.53±0.09 ^b	0.75±0.11 ^b	1.39±0.10 ^b	1.47±0.10 ^a	8.37±0.67 ^b		
JKR	0.73±0.26 ^a	0.85±0.15 ^ª	1.02±0.25 ^a	1.68±0.13 ^b	0.97±0.05 ^b	10.81±1.49 ^a		
TMS	0.24±0.09 ^b	0.19±0.03 ^c	0.33±0.15 ^c	B.D.L.	B.D.L.	1.69±0.49 ^d		
			Okra					
SRD	0.94±0.21 ^ª	0.64±0.08 ^a	4.24±0.86 ^b	1.13±0.08 ^ª	1.10±0.04 ^a	3.26±0.38 ^c		
KKC	0.82±0.12 ^b	0.69±0.08 ^a	6.11±0.67 ^a	0.88±0.06 ^b	1.00±0.03 ^ª	4.23±0.56 ^b		
JKR	0.97±0.18 ^a	0.74±0.07 ^a	6.74±0.70 ^a	1.10±0.23 ^a	0.71±0.04 ^b	5.55±0.64 ^a		
TMS	0.24±0.16 ^c	0.18±0.03 ^b	2.42±0.31 ^c	B.D.L.	B.D.L.	1.32±0.21 ^d		
			Onion					
SRD	0.77±0.25 ^b	0.64±0.07 ^a	4.77±1.00 ^b	0.99±0.02 ^b	0.95±0.05 ^a	11.78±1.00 ^c		
KKC	0.86±0.21 ^b	0.51±0.12 ^b	6.81±0.85 ^a	0.54±0.04 ^c	0.78±0.03 ^b	15.48±0.83 ^b		
JKR	1.14±0.17 ^a	0.59±0.06 ^a	7.50±1.08 ^a	1.70±0.01 ^a	0.64±0.04 ^b	18.89±1.93 ^ª		
TMS	0.17±0.05 ^c	0.33±0.07 ^c	3.16±0.42 ^c	B.D.L	B.D.L	4.79±0.49 ^d		
Tomato								
SRD	0.55±0.17 ^b	0.49±0.11 ^b	0.74±0.21 ^b	1.20±0.11 ^a	1.56±0.18 ^b	1.55±0.19 ^b		
KKC	0.64±0.13 ^b	0.45±0.04 ^b	1.05±0.21 ^ª	1.01±0.06 ^a	1.44±0.11 ^b	1.79±0.36 ^b		
JKR	0.75±0.16 ^ª	0.58±0.03 ^a	1.11±0.20 ^a	1.05±0.07 ^a	1.79±0.12 ^ª	2.54±0.22 ^a		
TMS	0.13±0.09 ^d	0.16±0.05 ^c	0.51±0.15 [°]	B.D.L	B.D.L	0.67±0.22 ^c		

Table 1A. Average levels of heavy metals (mg/Kg) in vegetables in the dry season.

Values are mean \pm SD of three samples of each vegetable, analyzed individually in triplicate. Mean values in the same column followed by the same superscript letters are not significantly different (*p*<0.05). B.D.L: Below detection limit.

Statistical analysis

All analysis was performed in triplicates. Results were expressed by means of \pm SD. Statistical significance was established using one way analysis of variance (ANOVA). Means were separated according to Duncan's multiple range analysis (p < 0.05) using software SPSS 16.0.

RESULTS AND DISCUSSION

The mean concentrations of Co, Cr, Cu, Ni, Pb and Zn in different vegetable samples from the three effluent irrigated sites and the control are listed in Tables 1A and B. The results generally show significant levels (p < 0.05) of metals in vegetable samples obtained from the effluent irrigated gardens (JKR, KKC and SRD) compared with those obtained from the control (TMS) garden. The high concentrations of heavy metals observed in the vegetable samples from the effluent irrigated gardens might be related to the concentrations of the metals in the soil (Al Jassir et al., 2005; Akinola and Ekiyoyo, 2006). Also from the results, general reductions in metal levels were observed in vegetables sampled during the rainy season when compared with those sampled during dry season.

This may be due to the fact that during the rainy season, the gardens were not irrigated with the wastewater. There is also the possibility of rainwater leaching away parts of the metals that have accumulated in the soil, thus reducing the quantity of these metals available to plants in the soil.

However, there are a few cases in the control site where negative values were recorded for percentage loss of metal in rainy season samples over those of the dry season, thus indicating an increase in metal levels in the rainy season samples over those of the dry season (Table 2). This may be attributed to the possibility of the runoffs from the surrounding land containing metal salts being washed into the control site.

Generally, the mean concentration range of Cu in all vegetables analyzed was 0.30 to 7.50 mg/Kg, with the highest concentration recorded for Jakara onions and the lowest for spinach from the control site. The maximum value recorded is below the National Agency for Food and Drug Administration and Control's (NAFDAC) maximum tolerable Cu concentration of 40 mg/Kg in fresh vegetables (Figure 1). Ni was below detectable level in the control samples while the highest level of 2.02 mg/Kg was obtained in SRD spinach. Also Pb was below the

Compling site	Metal						
Sampling site	Со	Cr	Cu	Ni	Pb	Zn	
Spinach							
SRD	0.60±0.04 ^a	0.45±0.06 ^b	0.53±0.16 ^b	1.39±0.06 ^a	1.03±0.02 ^ª	5.29±0.94 ^c	
KKC	0.54±0.19 ^a	0.34±0.03 ^c	0.54±0.15 ^b	0.99±0.16 ^b	0.91±0.11 ^ª	6.86±0.94 ^b	
JKR	0.61±0.13 ^a	0.60±0.11 ^a	0.66±0.21 ^a	1.07±0.20 ^b	0.65±0.12 ^b	8.18±0.47 ^a	
TMS	0.22±0.08 ^c	0.18±0.03 ^d	0.30±0.07 ^c	B.D.L.	B.D.L.	1.59 0.72 ^d	
Okra							
SBD	0 82+0 13 ^a	0.38+0.11 ^a	3 54+0 58 ^b	0 85+0 13 ^a	0 66+0 02ª	2 47+0 57 ^c	
KKC	0.72+0.15 ^b	0 40+0 09 ^a	4 97+0 60 ^a	0.67+0.6 ^b	0.67+0.02 ^a	3 29+0 36 ^b	
JKR	0.76 ± 0.21^{b}	0.43 ± 0.07^{a}	5.45 ± 0.32^{a}	$0.57\pm0.08^{\circ}$	0.53 ± 0.02^{b}	4.51 ± 0.53^{a}	
TMS	0.18±0.09 ^c	0.16±0.06 ^b	2.44±0.40 ^c	B.D.L.	B.D.L.	1.22±0.47 ^d	
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000	o o t i o o t ^b			0 7 0 · 0 00 ³	0.74.0.003		
SRD	$0.64\pm0.31^{\circ}$	$0.51 \pm 0.09^{\circ}$	$4.20\pm0.65^{\circ}$	$0.73\pm0.06^{\circ}$	$0.74\pm0.02^{\circ}$	10.33±0.95°	
KKC	0.72±0.08b	$0.43\pm0.05^{\circ}$	5.83±0.61	0.41 ± 0.10^{2}	$0.59\pm0.02^{\circ}$	13.79±1.16 [±]	
JKR	0.93±0.08 [°]	$0.44\pm0.08^{\circ}$	6.12±0.51°	0.45±0.04°	$0.53\pm0.02^{\circ}$	15.75±0.65°	
TMS	0.18±0.09°	0.29±0.06°	3.23±0.06°	B.D.L.	B.D.L.	4.60±0.57°	
Tomato							
SRD	0.46±0.05 ^b	0.34±0.04 ^a	0.63±0.10 ^b	0.85±0.15 ^a	1.05±0.13 ^ª	1.30±0.36 ^b	
KKC	0.54±0.24 ^b	0.34±0.09 ^a	0.84±0.19 ^a	0.78±0.16 ^b	0.95±0.11 ^ª	1.55±0.49 ^b	
JKR	0.63±0.05 ^a	0.35±0.07 ^a	0.87±0.19 ^a	0.75±0.06 ^b	0.48±0.12 ^b	1.84±0.71a	
TMS	0.12±0.17 ^c	0.18±0.02 ^b	0.45±0.11 [°]	B.D.L.	B.D.L.	0.71±0.31 [°]	

 Table 1B. Average levels of heavy metals (mg/Kg) in vegetables in the rainy season.

Values are mean \pm SD of three samples of each vegetable, analyzed individually in triplicate. Mean values in the same column followed by the same superscript letters are not significantly different (p>0.05) B.D.L: Below detection limit.

detectable level in control samples while SRD spinach recorded the highest level of 1.60 mg/Kg. The highest values obtained for Pb and Ni are below the NAFDAC safe limits for these metals (2.00 and 2.70 mg/Kg, respectively) in fresh vegetables.

The mean concentration range for Co was found to be 0.12 to 1.14 mg/Kg with the highest concentration recorded in JKR onions and the lowest in tomato from control site. The mean concentration range for Cr was found to be 0.16 to 0.85 mg/Kg with the highest concentration recorded in JKR spinach and the lowest in the okra from control site. The results indicated the mean concentration range of Zn to be 0.67 to 18.89 mg/Kg with the highest concentration found in JKR onions and the lowest in tomatoes from the control site. However, the highest value obtained is still below the NAFDAC safe limit of Zn (50 mg/Kg) in fresh vegetables. The results obtained in this study are comparable with some literature values of similar studies reported previously (Onianwa et al., 2001; Erwin and Ivo, 1992; Pennington et al., 1995).

Consequently, from the results, the general trend for the mean levels of metals analyzed in all vegetables sampled from the three effluent irrigated sites as well as the control for both dry and rainy seasons showed that for the concentrations of Cu and Zn, JKR > KKC > SRD > Control; for Co and Cr concentrations, JKR> SRD> KKC > Control; for Ni concentration, SRD> JKR > KKC > Control, and for Pb concentrations, SRD > KKC > JKR > Control (Figure 1). These sequences indicated that the metal contents of the vegetables are higher in areas being treated with wastewater. The observation is in good agreement with other studies elsewhere (Sharma et al., 2006; Sawidis et al., 2001) which suggested that uptake of metals by plants is proportional to their concentrations and availabilities in soils. Dasuki (2000) had earlier reported high levels of Cr (1.5 to 3.8 mg/Kg) in effluents from Sharada and Challawa industrial estates while Batagarawa (2000) had also reported high levels of Cu (1.74 to 11.54 mg/Kg), Pb (10.38 to 154.64 mg/Kg), and Zn (11.40 to 87.34 mg/Kg) in the samples of moss plant from Bompai and Sharada industrial estates in Kano metropolis.

The trend also shows that JKR garden recorded highest mean concentrations in four out of six metals analyzed (Co, Cu, Zn and Cr), while SRD garden recorded highest concentrations in two metals (Ni and Pb). Hence, the trend for the level of contamination by

Matala	SRD	KKC	JKR	Control	Mean ± % loss		
Metals	Vegetables						
Spinach							
Co	11.77	19.40	16.44	8.33	13.99±4.91		
Cr	25.00	35.84	29.41	5.26	23.88±13.19		
Cu	23.19	28.00	35.29	9.09	23.89±11.05		
Ni	31.19	28.78	36.31	B.D.L.	32.09±3.84		
Pb	35.63	38.10	32.10	B.D.L.	35.28±3.02		
Zn	24.23	18.04	24.33	5.92	18.13±8.66		
Okra							
Со	12.77	12.20	21.65	4.17	12.70±7.14		
Cr	40.63	42.03	41.89	11.11	33.92±15.22		
Cu	16.51	18.65	19.14	-0.83	13.37±9.53		
Ni	24.78	28.41	21.24	B.D.L.	24.81±3.59		
Pb	40.00	33.00	45.19	B.D.L.	39.40±6.12		
Zn	21.27	22.22	18.74	7.58	17.45±6.74		
Tomato							
Со	16.36	15.63	16.00	7.69	13.92±4.16		
Cr	30.61	24.44	39.65	-12.50	20.55±22.90		
Cu	14.86	20.00	21.62	11.76	17.06±4.56		
Ni	29.17	22.77	28.57	B.D.L	26.84±3.54		
Pb	33.97	35.42	39.24	B.D.L	36.21±2.72		
Zn	16.12	13.41	27.56	-5.97	10.96±5.25		
Onion							
Со	16.88	16.28	18.42	-5.88	11.43±11.57		
Cr	20.31	15.69	25.42	12.12	18.39±5.77		
Cu	11.77	14.39	18.40	-2.22	10.59±8.96		
Ni	26.26	24.07	35.71	B.D.L	28.68±6.19		
Pb	22.10	24.36	17.19	B.D.L	21.22±3.67		
Zn	12.31	10.92	16.62	3.97	10.96±5.25		

Table 2. Percentage loss of heavy metals in vegetables in rainy season compared with levels in dry season.

metals in the irrigation gardens is JKR > SRD > KKC > control (Figure 1). The high mean levels of Pb and Ni in SRD samples could be attributed to industrial emissions (Yilmaz and Zengin, 2004) while the high level of Pb in KKC could be attributed to automobile emissions as a result of its proximity to the road side in addition to the possible high levels of metal in contaminated wastewater being used for irrigation. The close relationship between lead concentrations and traffic intensity has been demonstrated in detail by many authors (Li et al., 2001; Viard et al., 2004). Furthermore, the relative high levels of Zn, Cu, Co and Cr in JKR and KKC samples may be attributed to the contaminated Jakara stream (Ogbalor, 1991; Dasuki, 2000) used for treating soils at the two sites, as many industrial and domestic waste waters are discharged into it.

Conclusion

This study further confirms the increased danger of growing vegetables on soils irrigated with contaminated industrial and domestic wastewaters. However, the levels of the metals are currently within the NAFDAC safe limits guidelines. But, if the practice of treating the soils in the irrigation gardens with contaminated waters is not controlled, it may lead to health hazard on the part of consumers of the vegetables on the long term. Therefore, there is the need to continually monitor, control and take necessary policy decisions so as to limit and ultimately prevent these avoidable problems. However, in the mean time, farmers from the study areas are hereby encouraged to use well water for irrigation in their gardens instead of contaminated streams.



Figure 1. Variation of total mean levels of metals in relation to the garden sites.

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