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Assessment of cadmium concentrations in wastewater, soiland vegetable samples grown along Kubanni stream channels in Zaria, Kaduna State, Nigeria

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ABSTRACT

The concentration of cadmium was determined in wastewater, soil and vegetable (carrot, lettuce, onion, spinach, cabbage, tomato and okro) samples collected on seasonal basis from January, 2013 to September 2014 along Kubanni stream channels in Zaria. The results showed cadmium levels in wastewater were in the range of 1.01 – 2.02 mg/L for the year 2013 and 0.50 – 6.50 mg/L in 2014; 1.00 – 3.50 mg/Kg for the year 2013 and 1.31 – 7.15 mg/Kg in 2014 for the soil while the vegetables had concentrations in the range of 0.20 – 6.10 mg/Kg for the year 2013 and 0.60 – 5.60 mg/Kg in 2014. Statistical analysis revealed no significant difference in cadmium levels across the locations and seasons for wastewater, soil and vegetables analyzed. Pearson correlation showed moderate (r = 0.488) relationship between cadmium levels in wastewater for the year 2013 and 2014, negligible (r = 0.002) relationship for soils between these two years while low (r = 0.395) relationship was obtained for vegetables cultivated in 2013 and that of 2014 respectively. Cadmium concentrations obtained in this study was higher than Maximum Contaminant Levels set by Standard Organizations such as W.H.O. and F.A.O.

Keywords: Cadmium concentration, wastewater, Kubanni River, soil and vegetable.

INTRODUCTION

Cadmium is known to be carcinogenic and fatal, it is generally dangerous to living organism especially man because of its bioaccumulation nature, it accumulates in living tissues anytime it is taken up and stored faster than it is metabolized or excreted [1]. Cadmium is a dangerous element because it can be absorbed via the alimentary tract; penetrate through placenta during pregnancy and damage membranes and DNA [2]. Once in the human body, it may remain in the metabolism from 16 to 33 years and is connected to several health problems such as renal damages and abnormal urinary excretion of protein [3]. Cadmium contamination of agricultural soils from wastewater irrigation is of serious concern since it has implications on human health. A study carried out by [4] using water containing Cd and Pb added to irrigate cabbage, carrots and lettuce revealed that Cd and Pb concentrations increased with irrigation water concentrations significantly with p-value of Cd<0.0001 and Pb<0.05.

Modern agriculture is becoming nuisance to mankind. The insecticides, pesticides, chemical fertilizers especially nitrate and phosphate are used annually to boost agricultural production and these chemicals are leached down to the soil by rain and eventually end up to contaminate the ground water and stream waterways and River Kubanni is equally surrounded by these types of activities which are likely to pollute the waterway.The major causes of water pollution in most countries of the tropics can be linked to human activities such as sewage and refuse disposal, industrial effluents, agricultural activities, mining and quarrying activities. The most common source of water pollution in developing nations is domestic sewage and refuse. [5] is of the opinion that several chemical elements including cadmium have their origin in the composing high refuse dumps and that is similar to pollution pattern in the catchment area of Kubanni River. Several other studies have shown that a considerable number of elements are leached from refuse dumps during rainy season into ground water and stream [6].

Rivers are victims of the negative impacts of urbanization and industrialization, water bodies become contaminated with untreated solid and liquid wastes [7]. Different regulations put in place to protect the environment in Nigeria have not been effective in controlling the indiscriminate dumping of effluents into open water bodies and some of these rivers are being used for irrigation system. The effluents range from phosphate, nitrate, nitrite, sulphate, chlorides and heavy metals (Cd, Cr, Pb, Mn, Co, Fe, Cu, Zn) to name a few are received by the river making some of them unfit for farming activities and other uses. Cadmium levels in some of Nigerian rivers, soils and vegetables were in concentrations above acceptable level according to some researches [8].

In many developing countries, it is a common practice to grow vegetables along banks of river passing through urban centres. Waters of such rivers have often been reported to be polluted by heavy metals like cadmium [9]. The extent of absorption of the elements by the plant depends on among other things, on the nature of the plant, chemical constituent of the pollutants, concentration of the element in the soil, pH and the interaction with other metals [10]. Kubanni River passes through SabonGari area of Zaria city with its high population density tends to generate waste like effluents from agricultural, domestic and industrial sources within its vicinity. Its proximity to Zaria town makes it receives agricultural and domestic wastes from nearby houses and the same river is being used for irrigation farming especially in the harmattan and dry seasons.

Study Area

Zaria city is in northern Nigeria on longitude 7˚42˙E and latitude 11˚03˙N, within the drainage of River Kubanni flowing to the south east direction through Ahmadu Bello University.The vegetation of the area is the savannah type with more grasses than hard wood trees. The average annual rainfall is 875mm and the temperature varies between 27 to 35˚C with a relative humidity [11]. The geology of the study area is composed mainly of fine grain gneisses and migmatite with some coarse-grained granitic outcrops in few places. The soil of the study area is mainly sandy-clay loam with poor infiltration because of the high clay content [12]. The entire vegetation and soils of the study area have been under great anthropogenic influences which have greatly modified the entire landscape [13]. Kubanni River is known for its human activities like farming, source of drinking water, washing and fishing. Some peasant farmers use its bank for farming throughout the year especially Sabon-gari area, here there is planting of vegetables of different varieties. This necessitates irrigated farming system to meet up with the demand for vegetables and promotes the use of wastewater, herbicides, fungicides, pesticides and fertilizers which are sources of pollutants [14]. High population of the area coupled with the amount of waste that is indiscriminately discharged into the body of Kubanni River makes it prone for contamination which necessitate the study on the nature of vegetables consumed by people from the area. This study is aimed at ascertaining the extent to which cadmium is accumulated in wastewater, soil and vegetables through man-made activities.

EXPERIMENTAL SECTION

Sampling

Wastewater samples from Kubanni stream were obtained from five different sampling points on a four month basis along the stream channels for the period of two years. Sampling was conducted in the harmattan, dry and rainy seasons. Wastewater samples were collected using composite sampling in a polyethylene plastic containers that were previously cleaned by washing in non-ionic detergent and then rinsed with tap water and soaked in 10% HNO_3 for 24 hours and finally rinsed with deionized water prior to usage [7]. During sampling, sample bottles used were rinsed with sampled water three times and then filled to the brim at a depth of one meter below the wastewater from each of the five designated sampling points. Wastewater sample bottles were labelled, stored in ice-blocked coolers and transported to the laboratory while in the laboratory, they were stored in the refrigerator at about 4 °C prior to the analysis [15].Soil samples were collected at three depths (0-5 cm, 5-10 cm and 10-15 cm) from both side of the river banks by using spiral auger of 2.5 cm diameter. Soil samples were randomly sampled and bulked together to form a composite sample from each designated point. They were then put in clean plastic bags, labelled and transported to the laboratory. The full grown vegetable of [spinach (*Amaranthushybridus*), lettuce (*Lactuca sativa*), cabbage (*Brassica oleracea*), carrot (*Daucuscarota),* okro (*Hibiscus esculentus*), onion (*Allium cepa*) and tomato (*Lycopersiconesculenetum*)] were randomly handpicked from various garden plots along Kubanni stream channels using hand-gloves, bulked together to form a composite sample, wrapped in big brown envelopes, labeled accordingly and transported to the laboratory.

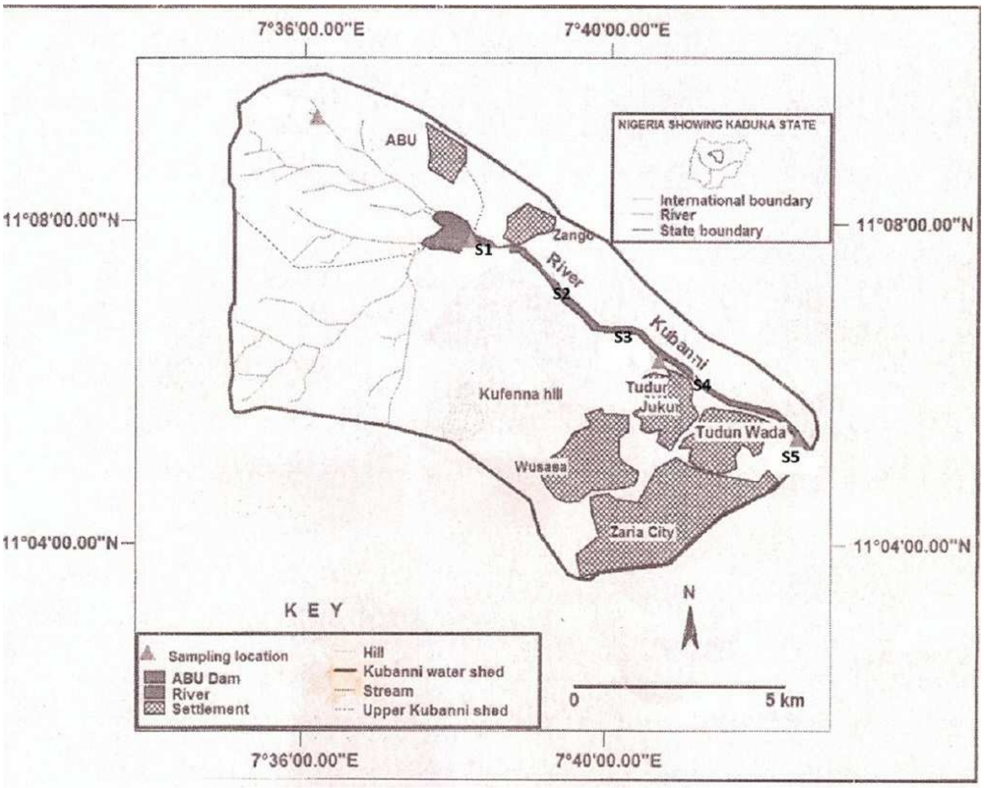

Figure 1 :- Map of sampling Sites

Sample Treatment

Wastewaters used for cadmium determinations were acidified at the points of sampling with 5 cm^3 of concentrated HNO_3as to avoid microbial activities on the wastewaters which might reduce the concentrations of intended cadmium before analysis and they were kept in a refrigerator prior to analysis [15]. Soil samples were air-dried, crushed and passed through 2 mm mesh sieve. The soil samples were then put in clean plastic bags, sealed and labelled accordingly [16]. Each vegetable samples were washed with tap water, followed by deionized water, air dried in the laboratory, grounded to powder and sieved using 250 µm sieve [17].

Digestion of Wastewater Samples for Cadmium Determination

1000 cm^3 of each wastewater sample was transferred into a beaker and 50 cm^3 concentrated HNO_3 were added. The beaker with the content was placed on a sand bath and evaporated down to about 20 cm^3. The beakers were cooled and another 5 cm^3 concentrated HNO_3 were added to each beaker. The beakers were covered with watch glasses and returned to the sand bath. The heating was continued and then small portion of HNO_3 was added onto each beaker until the solutions appeared light colour and clear. The beakers wall and watch glasses were washed with deionized-water and the samples were filtered to remove any insoluble materials that could clog the atomizer. Each sample volume was made up to 100 cm^3 with deionized water [7]. Determination of Cd in the wastewater sample was done at 229 nm wavelengths using Alpha-4 Model Atomic Absorption Spectrophotometer (AAS) [18].

Determination of Cadmium in Soil Samples

Two grams of each soil sample was weighed into acid-washed glass beakers. Soil samples were digested by the addition of 20 cm^3 of aqua-regia (mixture of HCl and HNO_3 in ratio 3:1) to each soil sample and 10 cm^3 of 30 % H_2O_2 were added in small portion to avoid any possible overflow leading to loss of material from the beaker. The beakers were covered with the watch glasses and heated on a water bath for 2 hours at 90 ºC. The beakers wall and watch-glasses were washed with deionized water and the samples were filtered out to separate the insoluble solid from the supernatant liquid. Soilsamples volume was made up to 100 cm^3 by adding deionized water to the mark levels. It was then analyzed for Cd at 229 nm wavelengths using Alpha-4 Model Atomic Absorption Spectrophotometer (AAS) [18].

Digestion of Vegetable Samples for Cadmium Determination

Three grams of the dry sample of each vegetable sample was ashed using Muffle furnace that was set at 450 °C until a constant weight was obtained. On cooling, the ash was transferred to a decomposition flasks and 1cm^3 of concentrated HNO_3 was added. The content was refluxed on a hot plate for 40 minutes and on cooling 20 cm^3 of deionized water was added, boiled for 3minutes and filtered. 10 cm^3 of 2M HNO_3 was added to the resulting solutions in a 100 cm^3 volumetric flask. They were made up to the mark with deionized water, cadmium was determined at 229 nm wavelengths using Alpha-4 Model Atomic Absorption Spectrophotometer (AAS) [18].

RESULTS AND DISCUSSION

The results of cadmium in wastewater, soil and vegetables analyzed were expressed in form of bar-charts using Microsoft Excel (Window 7 Professional), the results obtained were subjected to one way Analysis of Variances (ANOVA) and Pearson Product Moment Correlations (PPMC) using Statistical Package for the Social Sciences (SPSS) 20.0 versionsoftware. Null hypothesis was adopted and this was set at 95% Confidence Mean level to check if there is significant difference in the concentrations of cadmium analyzed. Statistical decision for Pearson Correlation Coefficients (r) were taken as follows;

(i) If $0.05 \leq r \leq 0.20$ there is negligible relationship
(ii) If $0.21 \leq r \leq 0.40$ there is low relationship
(iii) If $0.41 \leq r \leq 0.60$ there is moderate relationship
(iv) If $0.61 \leq r \leq 0.80$ there is substantial relationship
(v) If $0.81 \leq r \leq 1.00$ there is very high relationship [19]

Figure 2 shows cadmium concentrations in wastewater from Kubanni stream channels. Concentrations range of 1.01 – 2.02 mg/L was obtained in the year 2013. Highest level was observed at Tundun-wada (2.02 mg/L) during harmattan season followed by 2.01 mg/L at Industrial area along Jos road in the dry season and 1.95 mg/L at Sabon-gari also in the dry season. Least level was noticed at Sabon-gari in rainy season with concentration of 1.01 mg/L. High level of cadmium during harmattan season might be attributed to harmattan-dusts as reported by [20]. In the year 2014, cadmium range level of 0.50 – 6.50 mg/L was recorded. Highest concentration of the cadmium was found at Industrial area along Jos road (6.50 mg/L) during harmattan season followed by 5.49 mg/L during dry season from the same sampling location. Unguwa-fulani also showed high level of cadmium (3.70 mg/L) during harmattan season while the least level was observed at Kwangila (0.50 mg/L) during rainy season. High concentration of cadmium in harmattan might be related to similar reason given above as harmattan-dusts from the area are rich in cadmium according to [20]. Comparing 2013 and 2014 results for cadmium level in wastewater, there was gradual increase from 2013 (1.20 – 2.20 mg/L) to 2014 (0.79 – 6.50 mg/L) which might be as a result of excessive application of fertilizers, herbicides, fungicides and other chemicals in 2014as suggested by [14]. All the sampling sites analyzed hadcadmium level above the [21] threshold limitof 0.10 mg/L (Figure 2). The results reported by [22] (1.00 – 3.58 mg/L) was less than 1.01 – 2.20 mg/L for cadmium level in the year 2013 from this study but greater than that of year 2014 (0.50 – 6.50 mg/L) results.

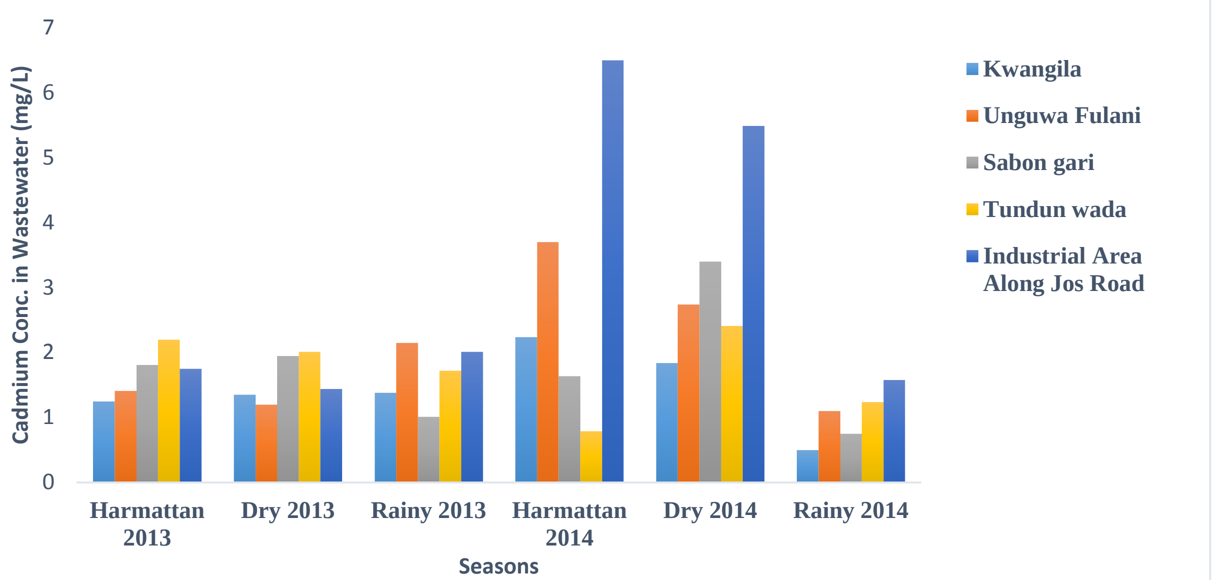

Fig. 2: Cadmium Concentrations in Wastewater from Kubanni Stream Channels, Zaria

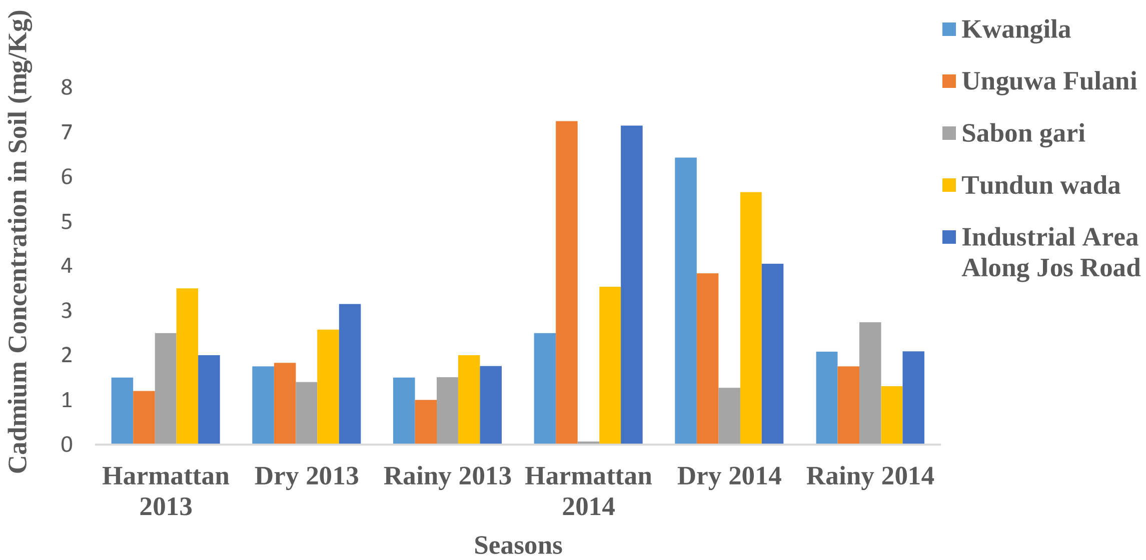

Fig. 3: Cadmium Concentrations in Soil from Kubanni Stream Channels, Zaria

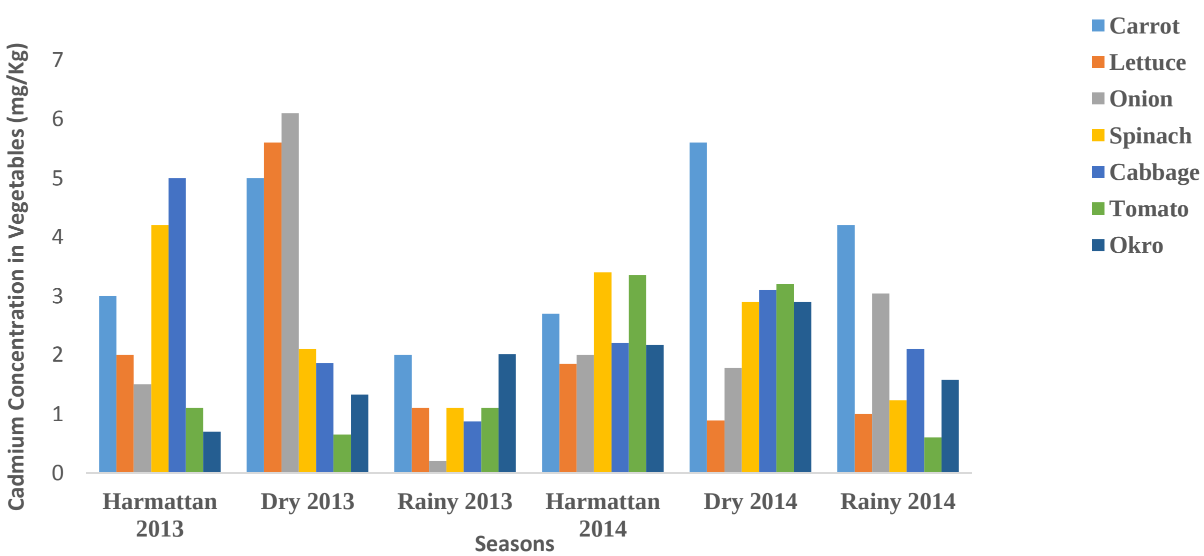

Fig. 4: Cadmium Levels in Vegetables from Kubanni Stream Channels, Zaria

Table 1:- Analysis of Variance for Cadmium in Wastewater, Soil and Vegetable (Seasons & Locations)

	Wastewater			Soil		Vegetable	
Parameter	cadmium across locations	cadmium across seasons	cadmium across locations	cadmium across seasons	cadmium among vegetables	cadmium across seasons	cadmium among wastewater, soil and vegetable
Signif.	0.184	0.965	0.281	0.981	0.220	0.983	0.000

Table 2:- Summary of Pearson Product Moment Correlation for Cadmium in Wastewater, Soil & Vegetable

Variables	*N*	$\bar{x}$	SD	r	df	Signif.
Cadmium 2013 (W)	15	1.644	0.376	0.488	13	0.065
Cadmium 2014 (W)	15	2.395	1.747			
Cadmium 2013 (S)	15	2.012	0.709	0.002	13	0.994
Cadmium 2014(S)	15	3.449	2.255			
Cadmium 2013 (V)	21	13.820	4.434	0.395	19	0.077
Cadmium 2014 (V)	21	6.550	4.394			

(W)= Wastewater, (S)= Soil, (V)= Vegetable

Figure 3 shows cadmium concentrations in soil from Kubanni stream channels. The concentrations determined were in the range of 1.00 – 3.50 mg/Kg for the year 2013. Highest level of 3.50 mg/Kg was found during the harmattan season at Tundun-wada followed by 3.15 mg/Kg at Industrial area along Jos road during dry season and closely followed by 2.58 mg/Kg during dry season at Tundun-wada sampling site while the least level was observed at Unguwa-fulani (1.00 mg/Kg) during rainy season. Generally, cadmium level was low in rainy season as indicated in figure 3 which might be due to dilution effect as suggested by [23]. High concentrations of cadmium from these locations (Tundun-wada and Industrial area along Jos road) might be as a result of industrial effluent being discharged from nearby industries while that of Tundun-wada might due to nearness to refuse dumping sites as suggested by [24]. In the year 2014, cadmium had concentrations in the range of 1.31 – 7.15 mg/Kg. Highest level of 7.15 mg/Kg were found at Industrial area along Jos road and Unguwa-fulani during harmattan season followed by 5.66 mg/Kg as determined during dry season at Tundun-wada sampling site while the least level was recorded at Tundun-wada but in rainy season with concentration of 1.31 mg/Kg. Comparing the results of the year 2013 and 2014, they had concentrations in the range of 0.10 – 7.22 mg/Kg. There was gradual increase in cadmium level from harmattan season 2013 (1.20 – 3.50 mg/Kg) to 2014 (1.31 – 7.15 mg/Kg). Also, increment was noticed from dry season 2013 (1.40 – 3.15 mg/Kg) to dry season 2014 (1.27 – 6.43 mg/Kg). These elevated levels of cadmium during harmattan and dry seasons might be related to deposition of harmattan-dusts, excessive use of wastewater for irrigationand fertilizers application as suggested by [25]. Other worker with high level of cadmium in superphosphate fertilizer was [14] as they reported concentrations of 1.24 – 3.17 mg/Kg. Results obtained in this study exceeded the maximum allowable limit for cadmium in soil (3.0 mg/Kg) by [21] and this indicates that the soils used for farming in the sampling locations are polluted with cadmium metal and this is in agreement with the reported values by [26] (2.3 – 5.3 mg/Kg).

Figure 4 shows cadmium levels in vegetables obtained from Kubanni stream channels. In the year 2013, the concentrations determined were in the range of 0.20 – 6.10 mg/Kg. Highest level was found in onions (6.10 mg/Kg) that was planted during dry-season followed by lettuce (5.60 mg/Kg) in the same season. High concentration was also observed in cabbage (5.0 mg/Kg) during harmattan season while the least level of 0.21 mg/Kg was noticed in rainy-season. High accumulation of cadmium during harmattan and dry seasons might be as a result of harmattan-dusts, excessive use of wastewater and application of superphosphate fertilizers to irrigate the farmlands as suggested by [8] and [14]. Least concentration for cadmium was noticed in rainy-season (0.20 – 2.01 mg/Kg) and this might be as a result of dilution effect as suggested by [23]. In the year 2014, cadmium levels in the range of 0.60 – 5.60 mg/Kg was obtained. Highest level was found in carrot (5.60 mg/Kg) in dry season followed by 4.20 mg/Kg also in carrot but in rainy season. High levels were also observed in spinach (3.40 mg/Kg) and tomato (3.35 mg/Kg) both in harmattan season. Similar cadmium levels were noticed in spinach (2.90 mg/Kg), cabbage (3.10 mg/Kg) and tomato (3.20 mg/Kg) in dry season (Figure 4). Comparing results of the year 2013 and 2014, there was gradual increase in cadmium level from rainy season 2013 (0.21 – 2.01 mg/Kg) to that of year 2014 (0.60 – 4.20 mg/Kg). High levels were observed in both harmattan (1.50 – 5.00 mg/Kg) and dry (0.65 – 6.10 mg/Kg) seasons of both years. Okro showed least accumulation of 0.61 – 2.05 mg/Kg throughout the period of analyses while carrot had highest accumulation (2.00 – 5.60 mg/Kg) among the vegetables analyzed. Results obtained for cadmium in this study was higher than maximum permissible limit set by [21] (0.10 mg/Kg). The cadmium levels in this study were below the concentrations obtained by other workers including[27](0.01 – 12.86 mg/Kg), [28] as they reported 6.79 mg/Kg in spinach and 24.30 mg/kg in radish however, it was less to reported concentrations by [8] (0.11 – 1.67 mg/Kg).

Analysis of variance was conducted to establish difference in cadmium levels among the sampling locations in the year 2013 and 2014 for wastewater as shown in Table 1. It shows that $p = 0.184 > 0.050$ means there is no significant difference in cadmium levels across the sampling locations as observed from their mean. Cadmium concentrations were also examined across the seasons to establish their differences in wastewater. The result reveals $p = 0.965 > 0.050$ this means that there is no significant difference in cadmium concentration across the seasons.This might be due to sampling areas falling within the same vicinity thereby their soil geological formations are similar (fine grain gneisses and migmatite) irrespective of change in seasons as suggested by [29]. From the same ANOVA Table 1 above, $p = 0.281 > 0.050$ shows there is no significant difference in cadmium levels across the sampling sites for soil as their mean are relatively close. Also, Table 1 indicates $p = 0.981 > 0.050$ means no significant difference in cadmium concentrations across the seasons for soil. Their mean values are close to one another and may be attributed to anthropogenic activites in the sampling sites as suggested by [13].From the same ANOVA Table 1, $p = 0.220 > 0.050$ shows there is no significant difference in cadmium concentrations among various vegetables analyzed. Table 1 also indicates $p = 0.983 > 0.050$ this means that there is no significant difference in cadmium levels across the seasons for vegetables analyzed. Analysis of variance in Table 1 elaborates on the difference existing among the cadmium concentrations in wastewater, soil and vegetables of sampling locations and shows, $p = 0.000 < 0.050$ this means that there is significant difference incadmium levels when its concentration in wastewater, soil and vegetable of the sampling sites were comparedwith one another indicating each constituent has different concentration range of cadmium within it.

Pearson Product Moment Correlation (PPMC) was conducted to establish the relationship between cadmium levels in wastewater, soil and vegetables for the year 2013 and 2014 as presented in Table 2. Statistical analysis showed the mean with standard deviation of 1.643±0.376 for 2013 while 2.395±1.747 for 2014 in wastewater. Statistical analysis also revealed Pearson correlation $(r) = 0.488$, degree of freedom $(df) = 13$ and $p = 0.065 > 0.050$ this means that there is moderate relationship between cadmium levels in wastewater for the year 2013 and 2014 respectively.Table 2 also shows PPMC for cadmium concentrations in soil between the year 2013 and 2014. Statistical data showed mean with standard deviation level for cadmium to be 2.012±0.709 in the year 2013 while 3.449±2.255 was obtained in the year 2014 with the degree of freedom $(df) = 13$, Pearson correlation $(r) = 0.002$ and $p = 0.994 > 0.050$ indicates that there is negligible relationship between cadmium level in soil for 2013 to that of 2014. In addition, statistical data showed the mean with standard deviation level of 13.820±4.434 in the year 2013 while 6.550±4.394 was obtained in the year 2014 for vegetable analyzed. Statistical analysis indicated that Pearson correlation $(r) = 0.395$, degree of freedom $(df) = 19$ and $p = 0.077 > 0.050$ this means that there is low relationship between cadmium level in vegetables between the year 2013 and 2014 respectively.

CONCLUSION

The levels of cadmium analyzed across the various sampling sites for wastewaterwere found in the order of: Industrial area along Jos road > Unguwa-fulani > Sabon-gari > Tundun-wada > Kwangila while vegetables were in the order of: spinach > onion > carrot > lettuce > cabbage > tomato > okro. In conclusion, it can be deduced that cadmium showed high levels throughout the seasons though low concentrations were obtained in the rainy season indicating vegetables consumed in the studied areas are contaminated with cadmium metals. There is need to find means of removing this heavy metal (cadmium) which make these vegetables partially unsuitable for human consumption by stop using wastewater to irrigate the farmland in the area and stop indiscriminate discharge of refuse into the body of Kubanni River by providing appropriate dumpsites within the vicinity for this purpose.

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