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## Comparative Assessment of Heavy Metals Concentration in the Soil in the Vicinity of Tannery Industries, Kumbotso Old Dump Site and River Challawa Confluence, at Challawa Industrial Estate, Kano State, Nigeria

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### **Abstract:**

*The objective of this research work was to compare the concentration of heavy metals (Ni, Zn, Cu, Cr, Co, Cd, Pb) in the soil samples from the vicinities of four tanneries (Mahaza, Fata, Mario, GLT); Kumbotso old dump site; River Challawa confluence and Yan-sama town at Challawa industrial estate, Kano state Nigeria using atomic absorption spectrophotometry (AAS). The results obtained in the soil ranged between (29.45-14.10 $\mu\text{g g}^{-1}$ ) Ni, (18.50-9.70 $\mu\text{g g}^{-1}$ ) Zn, (37.85-25.74 $\mu\text{g g}^{-1}$ ) Cu, (56.95-25.00 $\mu\text{g g}^{-1}$ ) Cr, (14.10-9.00 $\mu\text{g g}^{-1}$ ) Co, (21.65-11.65 $\mu\text{g g}^{-1}$ ) Cd, (17.45-9.85 $\mu\text{g g}^{-1}$ ) Pb. Soil samples from Kumbotso old dump site recorded the highest means values of both Ni and Cr which might be attributed to the facts that all the tanneries around the area dumped their waste directly. The levels of the all determined metals are relatively lower in the soil samples from the control site (Cu exclusive), suggesting the possible mobility of the metals from the point source to the neighbouring environment either through leaching or runoffs or both. The levels of some of the metals in both areas were higher than the FEPA and WHO permissible limits. Therefore, people living around the area and the consumption of agricultural products grown within the area are prompt to heavy metal contamination as the time of this research work unless an urgent step is taken by the relevant agencies.*

**Keywords:** pollution, heavy metals, soil, Challawa.

### **1. Introduction**

Pollution is one of the most important problems around the world in which thousands of millions of world inhabitants suffer health problems related to industrial, (effluents, sewage, oil spillage etc), agricultural and atmospheric pollutants. Industrial wastes and effluents are being discharged randomly on the soil, into canals, rivers, along road sides or in the vicinity of industry without any treatment in Nigeria and other parts of the world. They pollute productive soils, natural water system as well as ground water (Abul-Kashem and Balram, 1998). Heavy metals are extremely persistent in the environment. They are non-biodegradable and thermodegradable and therefore readily accumulate to toxic level (Akguc et al, 2008). Heavy metals can accumulate in soil at toxic level due to long term application of waste-water. The contamination of vegetables with metals due to the soil and atmospheric contamination poses a threat to their quality and safety (El-Fadel et al, 1997). Industrial effluent discharged from textiles and tannery contains a higher amount of metals especially chromium, copper and cadmium (Deepali, and Gangwar, 2010). Other sources of the metals are mines, foundries, smelters and coal-burning power plants, combustion by product and vehicles emission. Among the key issues in environmental research on heavy metals is their mobility in ecosystem and transfers into the food chains (Steinners et al, 1997, 2000; Donisa et al., 2000). Human exposure to heavy metals occurs primarily through inhalation of air and ingestion of food and water. (Jimoh and Mohammed, 2012). The soil, a main part of the terrestrial ecosystem, is a habitat for a great number of organisms but at the same time, the most endangered component of the environment, which open to influence of different varieties of pollutants arising from human activities. The accumulation of heavy metals in agricultural soils is of increasing concern due to the food safety issues and potential health risks not only on crop plants but also on human health as well as its detrimental effects on soil ecosystems (Weigert, 1991) The use of dump site as farm land is a common practice in urban and sub urban centers in Nigeria because of the fact that decayed and composed wastes enhance soil fertility (Ogunyemi et al, 2003).

Soil may become contaminated by the accumulation of heavy metals and metalloids through emission from readily expanding industrial area, mine, tailing, disposal of high metal waste, leaded gasoline and plant land application of fertilizers, animals manure sewage disposal, pesticides, waste-water irrigation, coal combustion residues, spillage of petrochemicals and atmospheric deposition (Khan et al, 2008; Zhang et al, 2010).

The concentration of these metals in the environment varies considerably depending on the soil concentration and proximity to the source of emission (Kenneth and Harvey, 1997). Soil is a vital resource for sustaining two human needs of quality food supply and quality environment (Opaluwa et al, 2012).

Plant grown on a land polluted with municipal, domestic or a land polluted with Municipal domestic or industrial wastes can absorb heavy metals in form of mobile ions present in the soil through their roots or through foliar absorption. These absorbed metals get bioaccumulated in the roots, stem and leaves of plants (Fatoki, 2000). Prevention of soil pollution and its harmful effects however requires some basic knowledge about the soil (Coskun et al, 2006). Depending on their origin, trace elements exist in different minerals form and chemical compounds and in different combinations with minerals and organic components of soil and sediments which may vary according to various conditions e.g. pH, temperature, microbiological activity, oxidation state etc (Babatunde et al., 2014).

The objective of this research work was to compare the concentration of heavy metals (Ni, Zn, Cu, Cr, Co, Cd, Pb) in the soil samples from the vicinities of four tanneries (Mahaza, Fata, Mario, GLT); Kumbotso old dump site; River Challawa confluence and Yan-sama town at Challawa industrial estate, Kano state Nigeria.

## 2. Material and Methods

Analytical (AnalaR) grade reagents and de-ionized water were used for the experiment. All glassware and plastic containers used were washed with liquid soap, rinsed with water, soaked in 10% (v/v) nitric acid for 24 hrs, cleaned thoroughly with distilled water and dried.

### 2.1. Study Area

Challawa Industrial Estate Kano, northern Nigeria is bounded by latitude range of 11052.65"N–11054.29"N and longitude range of 8027.52E'–8028.853'E at an average elevation of about 430 m above the mean sea level. The study site is characterized by a gentle slope trending in N-S direction. All the industries located in the area discharge their effluents into Challawa River located at about 2.0 km downstream from the cluster of the industries. The area which falls between the industrial site and the river is about 6.0 km<sup>2</sup>. It mainly constitutes cultivated portions and few village settlements.

### 2.2. Sampling Procedure

Soil samples were collected from the vicinities of the four tanneries industrial sites, Kumbotso old dump-site, River Challawa confluence and Yan-sama town at Challawa industrial estate, Kano state Nigeria in November, 2012 by 3:45pm, and a total of twenty one soil samples were collected. Three soil samples (10m apart) each were collected in the vicinity of Mahaza tannery, Mario tannery, Fata tannery and GLT tannery Kumbotso old dump-site, river Challawa confluence (points where the tanneries' effluents mix with river Challawa). Also, three soils were sampled as a control from Yan-sama town. The samples were collected using treated polythene bag and sampling was done by excavating micro pit and collection was started from the lower site of surface horizon to avoid contamination.

S/No	Sample code	Key
1	A	Soil in the vicinity of Mahaza tannery
2	B	Soil in the vicinity of Fata tannery
3	C	Soil in the vicinity of Mario tannery
4	D	Soil in the vicinity of GLT tannery
5	E	Soil from river Challawa confluence
6	F	Soil from Kumbotso old-dump site
7	G	Soil from Yan-sama town

Table 1: Coding of soil samples

### 2.3. Sample Pre-Treatment

The collected soil samples were thoroughly mixed; air dried in a clean room to avoid contamination and grounded using mortar and pestle to pass through 2 mm sieve.

### 2.4. Sample Digestion

2.0g of the soil sample was weighed into a beaker; 15cm<sup>3</sup> HNO<sub>3</sub> (70% V/V, S.G:1.42) was added and then brought to boiling on a hot plate in a fume cupboard. Most of the acid mixture was allowed to evaporate and the residue cooled. 15cm<sup>3</sup> HNO<sub>3</sub> and 5.0cm<sup>3</sup> HClO<sub>4</sub> (70%V/V, S.G:1.66) were again added and the resulting mixture evaporated to dryness. The residue thus, obtained was allowed to cool and 12.50cm<sup>3</sup> of (1-5) HCl was added and then heated to dryness. After cooling, small amount of de-ionized water was added to the residue and the mixture was filtered using whatman (540) filter paper and made to 100cm<sup>3</sup> in a standard volumetric flask using

de-ionized water. This solution was transferred into a treated plastic bottle for AAS (“AA-6800) analysis; Triplicate digestion of samples and blank were carried out to ensure precision.

**3. Result and Discussion**

The means concentrations of heavy metals in the soils are shown in Figure 1.0. The levels of the metals in the soil are recorded in ranges. Ni ranged from  $29.45 \pm 2.05 \mu\text{g g}^{-1}$  to  $14.10 \pm 1.62 \mu\text{g g}^{-1}$ ; Zn ranged from  $18.50 \pm 1.30 \mu\text{g g}^{-1}$  to  $9.70 \pm 0.65 \mu\text{g g}^{-1}$ ; Cu ranged from  $37.85 \pm 5.15 \mu\text{g g}^{-1}$  to  $24.75 \pm 0.213 \mu\text{g g}^{-1}$ ; Cr ranged from  $56.95 \pm 3.85 \mu\text{g g}^{-1}$  to  $25.00 \pm 2.0 \mu\text{g g}^{-1}$ ; Co ranged from  $14.10 \pm 0.195 \mu\text{g g}^{-1}$  to  $9.00 \pm 0.90 \mu\text{g g}^{-1}$ ; Cd ranged from  $21.65 \pm 4.65 \mu\text{g g}^{-1}$  to  $11.65 \pm 2.25 \mu\text{g g}^{-1}$ ; Pb ranged from  $17.45 \pm 1.80 \mu\text{g g}^{-1}$  to  $9.8 \pm 1.05 \mu\text{g g}^{-1}$  respectively. The results showed that some heavy metals like Cr, Cu and Ni were present in considerable amount in the soil.

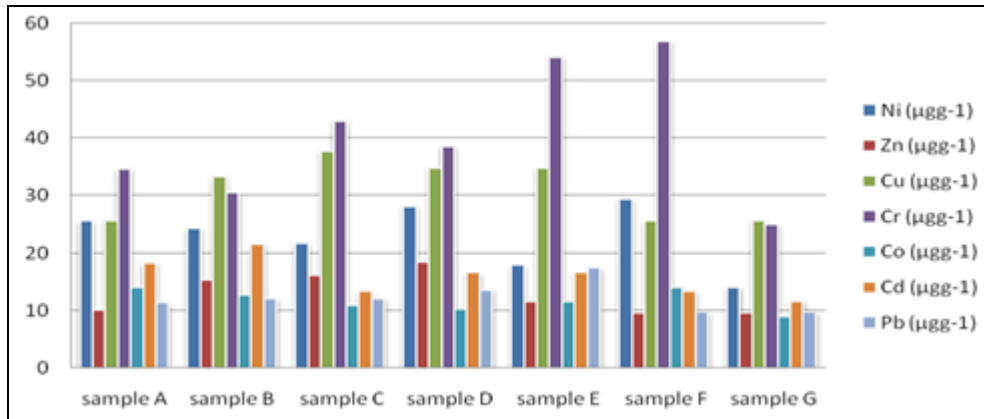


Figure 1: The means concentration of heavy metals in the collected samples of various sites.

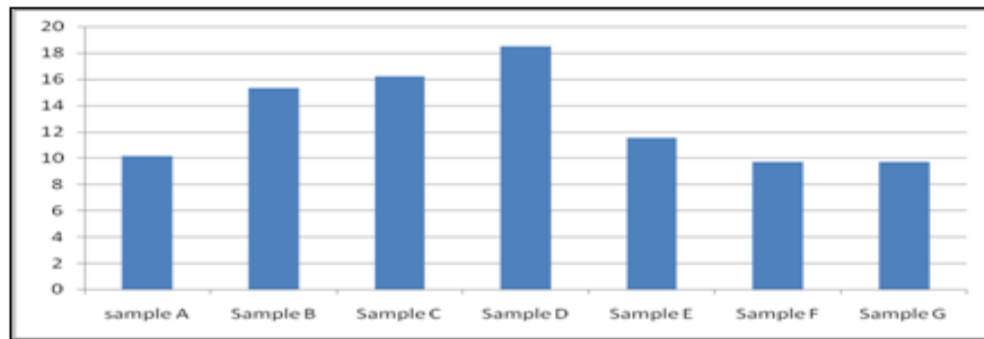


Figure 2: Variation of means Ni concentration from the various sampling sites

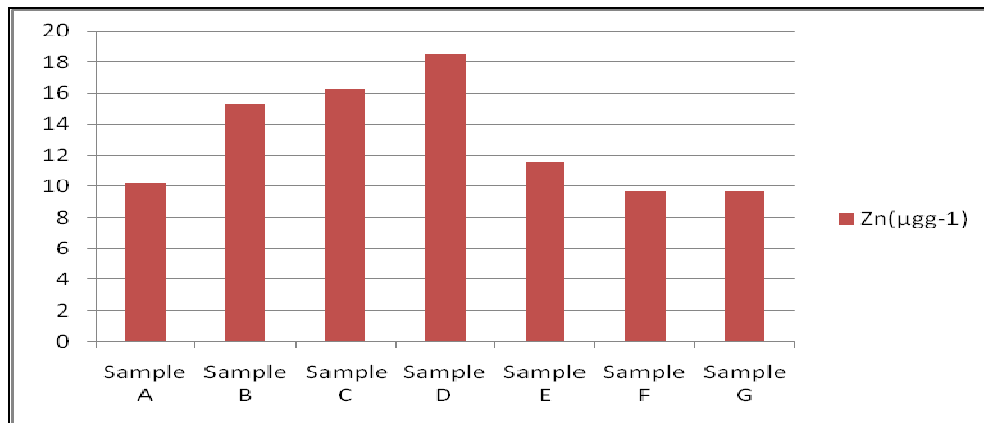


Figure 3: Variation of means Zn concentration from the various sampling sites

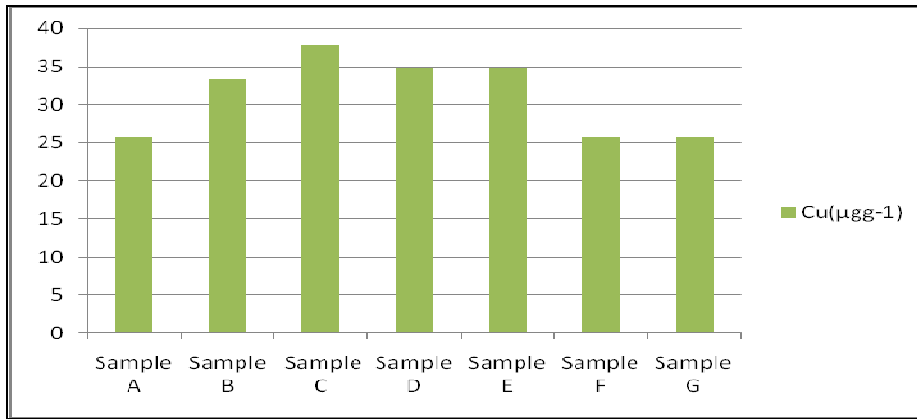


Figure 4: Variation of means Cu concentration from the various sampling sites

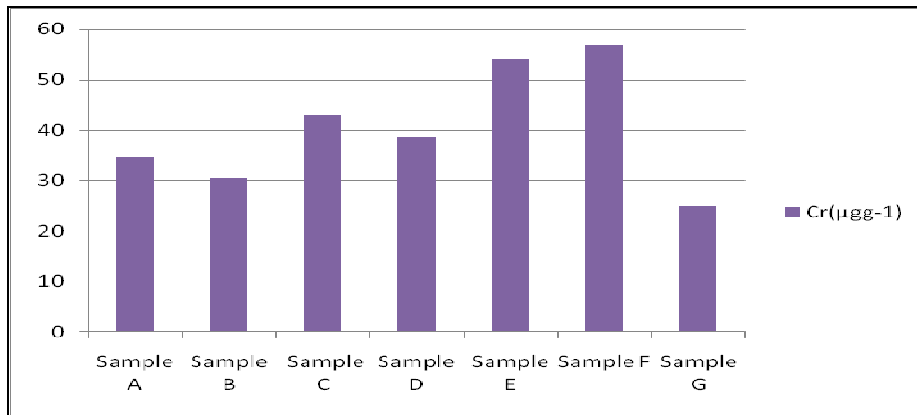


Figure 5: Variation of means Cr concentration from the various sampling sites

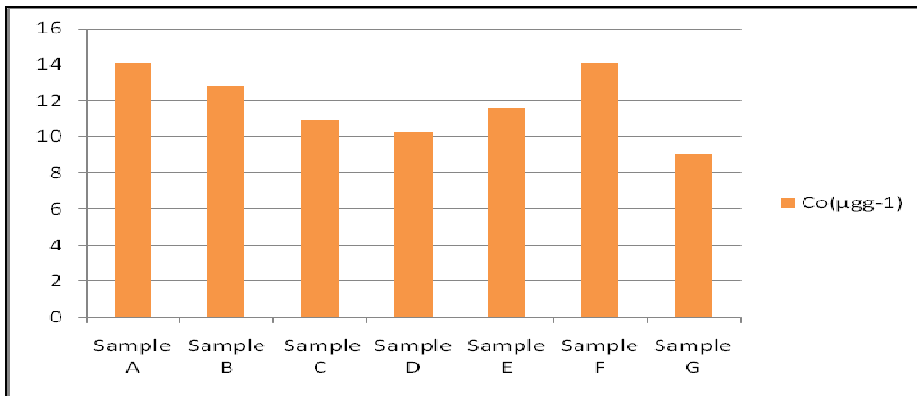


Figure 6: Variation of means Co concentration from the various sampling sites

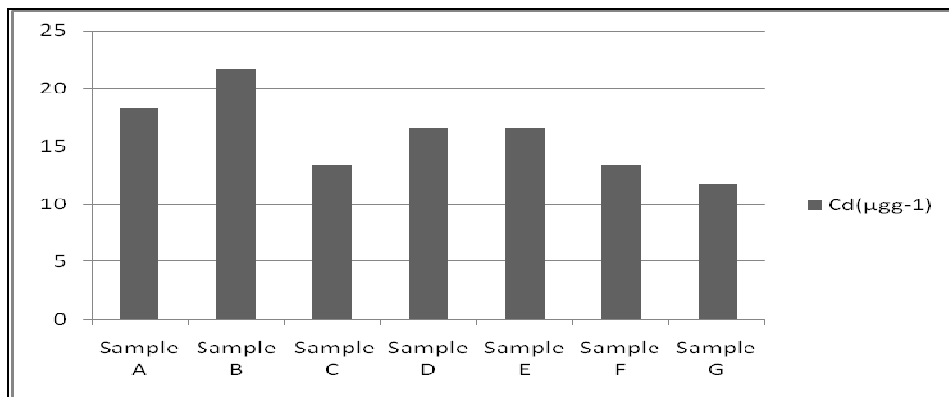


Figure 7: Variation of means Cd concentration from the various sampling sites

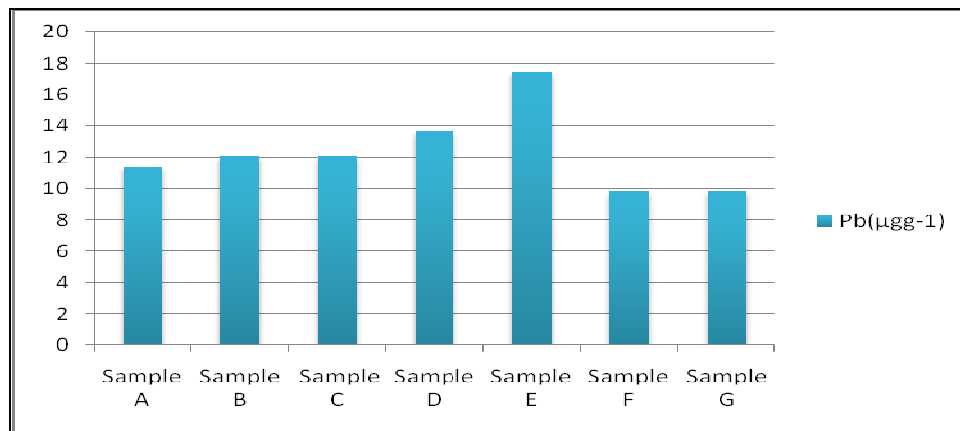


Figure 8: Variation of means Pb concentration from the various sampling sites

The means concentrations of Ni in the soils determined are shown in figure 2.0; and were within the range of 14.10-29.45 $\mu\text{g g}^{-1}$ , means Ni concentrations determined in the present study is slightly higher the one reported by (Inuwa et al 2007), but lower than the one reported by (M. Coskun et al, 2006). Generally nickel content of 100 $\mu\text{g g}^{-1}$  is recognized as an acceptable level in farmland soils (Kabata-pendias and Pandias, 1999). Therefore; the means Ni concentrations determined in the present study remained within the natural limits of 10-50  $\mu\text{g g}^{-1}$  (Fabis, 1987). According to geo accumulation index, samples from Yan-sama and confluence were uncontaminated with Ni, while those from GLT, Mario, Mahaza, Fata and Kumbotso old dump-site were moderately contaminated. The means concentration of the Ni in the soil from Yan-sama town (14.10 $\mu\text{g g}^{-1}$ ) was not surprising because, it's relatively lower than its values obtained from all tanneries, confluence, and old dump site respectively, which could be attributed to the industrial activities and discharged the soil were constantly receiving. Moreover, the means concentrations of Ni in all the samples analyzed are within the permissible limits set by FEPA (1991).

The means concentrations of Zn in the soils determined are shown in figure 3.0; soil sample from GLT, Fata and Mario tanneries shows the highest means concentration while Kumbotso old dump site and confluence has the least means contents, likewise; control site recorded the means content of 9.7 $\mu\text{g g}^{-1}$ . These result indicate high amount of Zn in the samples studied as compare with the result reported by (Tsafe, 2.67 $\mu\text{g g}^{-1}$ ; 2012), but lower than (29.38-21.29 $\mu\text{g g}^{-1}$  and 23.32-16.23 $\mu\text{g g}^{-1}$ ) reported by (Babatunde et al 2014; and Koki and Jimoh 2013;) respectively. The high value of Zn observed in the samples from the vicinities of the tanneries and confluence could be attributed to the emission of exhaust by the constant movement of heavy vehicles in the areas. However the means concentration of Zn in all the samples had exceeded the natural range of (1.00 to 9.00  $\mu\text{g g}^{-1}$ ; Bowen, 1979).

The means concentration of Cu range from 25.74 to 37.85 $\mu\text{g g}^{-1}$  were shown in figure 4.0; the highest means concentration been observed in soil sample from Mario 37.85 $\mu\text{g g}^{-1}$ ; and least content in the sample from Mahaza 25.74 $\mu\text{g g}^{-1}$ , sample from the control site has similar Cu means concentration with the soils sample from Kumbotso old dump-site (25.75 $\mu\text{g g}^{-1}$ ) but slightly higher compared to the soils sample from Mahaza (25.74 $\mu\text{g g}^{-1}$ ) the means concentration of Cu from this research were higher than the values of (1.59 $\mu\text{g g}^{-1}$  in Kabata 1986), and (22.14  $\mu\text{g g}^{-1}$  in Babatunde et al, 2014). This trend was obtainable for Cu (1.28 $\pm$ 0.065, 0.14 $\pm$ 0.01 and 0.067 $\mu\text{g g}^{-1}$ ) reported by (Tsafe, 2012); although smaller than the values of (58.30-207  $\mu\text{g g}^{-1}$ , 50  $\mu\text{g g}^{-1}$ , 47  $\mu\text{g g}^{-1}$ ; 61  $\mu\text{g g}^{-1}$  obtained by (Awode et al, 2008); (Fisseha et al., 2008); (Ndiokwere, 1984) respectively. The actual source of the metals in the solid minerals could be attributed to the background level of metals in soil originating from the parent rock; however, 73.3  $\mu\text{g g}^{-1}$  Cu concentrations were recommended as the maximum limits for vegetables (Weigert, 1991). Cu is toxic to man at concentration of 250mg/day and causes anemia, liver, kidney damage, stomach and intestinal irritation etc. Cu environmental pollution could be by atmospheric deposition from metal industries and power plants that are burning fossil fuels, and as such all the soils used for this research are moderately contaminated, especially the soil samples from Mario, GLT, confluence and Fata respectively.

Figure 5.0 shows that means concentration of Cr in the soils ranged from 30.57  $\mu\text{g g}^{-1}$  to 56.95  $\mu\text{g g}^{-1}$  and are within the range reported by (Birnin Yauri and Argungu, 2002; Sani 2003; Aydinalp and Marinova 2003). The result were seem to be higher than the values of (0.453  $\mu\text{g g}^{-1}$  in Ayolagha 2000; 29.75  $\mu\text{g g}^{-1}$  in Adelokan and Abegunde 2011; 1.13  $\mu\text{g g}^{-1}$  in Abubakar and Ayodele 2002) but much lower than the values of (104.20-230.0  $\mu\text{g g}^{-1}$  and 85.3  $\mu\text{g g}^{-1}$  reported by Awode et al., 2008; and Inuwa et al 2007) respectively. The high levels of Cr could be due to the availability of chromium salt as the major tanning agent used constantly by the industries and the emission of exhaust by the heavy vehicles. The means concentration of Cr in the soil sample taken from Kumbotso old dump-site of 56.95  $\mu\text{g g}^{-1}$  is relatively high, which might be attributed to the facts that all the tanneries around the area dumped their waste directly in the area, as such received high amount of Cr, the above suggestion is also valid to the soil sample taken from the confluence with Cr content of 54.15  $\mu\text{g g}^{-1}$ . Similarly the levels of Cr in the all soils samples were higher than the established critical limits of 0.5 to 10  $\mu\text{g g}^{-1}$  causing toxicity in plants and 200 mgday<sup>-1</sup> causing toxicity in humans recommended by (WHO/FAO 2001).

The means concentration of Co in the soils samples studied were shown in figure 6.0, the highest means concentration were observed in the soil sample from Mahaza tannery 14.10  $\mu\text{g g}^{-1}$ , while the control site recorded the lowest means concentration of 9.00  $\mu\text{g g}^{-1}$  respectively, the means concentration for this study are in the range of 14.1  $\mu\text{g g}^{-1}$ >12.8  $\mu\text{g g}^{-1}$ >11.55  $\mu\text{g g}^{-1}$ >10.90  $\mu\text{g g}^{-1}$ >10.25  $\mu\text{g g}^{-1}$ ,

which is higher than the values 0.02-2.00  $\mu\text{g g}^{-1}$  obtained by (Akan et al, 2009). However, the means concentrations of Co were lower than the values of (14.56  $\mu\text{g g}^{-1}$ -21.45 $\mu\text{g g}^{-1}$ ) reported by (Akan et al., 2008).

The means concentration of Cd in the soils studied were shown in figure 7.0. The present study, confirmed the means concentration of Cd in the soil within the range of 11.65 to 21.65  $\mu\text{g g}^{-1}$ , higher than the tolerable limit of (0.1 to 0.7  $\mu\text{g g}^{-1}$ ) as reported by (Fabis, 1987). In the same vein, the means Cd concentration in the soil samples of Fata tannery, has the highest means content of 21.65  $\mu\text{g g}^{-1}$  while the control site recorded the means concentration of 11.65  $\mu\text{g g}^{-1}$ , the result for this analysis were also higher than the values of (0.56  $\pm$  0.05 $\mu\text{g g}^{-1}$ ; 0.30 $\pm$ 0.01 reported by (Uwah, 2011; and Inuwa et al., 2007) respectively. The high means concentration Cd in the present study could be due to the discharge of effluents into the source environment by the industries, wear and tear of cars and trucks tyres around the area; therefore the means concentration of the studied heavy metals seem to depend with time taken to discharge them into the environment.

Figure 8.0, indicated the means content of Pb in the soils studied; Pb means concentration in the soil shows a range of 17.45  $\mu\text{g g}^{-1}$  to 9.85  $\mu\text{g g}^{-1}$ . Highest (17.45  $\mu\text{g g}^{-1}$ ) was found at confluence and the lowest (9.85  $\mu\text{g g}^{-1}$ ) at Kumbotso old dump site and control site respectively; the lowest means concentration at the control site (Yan-sama town) and Kumbotso old dump site might due to the less traffic density and atmospheric condition (i.e. wind speed and direction). The highest Pb means concentration is at least four times lower than the maximum concentration of (100  $\mu\text{g g}^{-1}$  dry soil) found in soil (Sezgin et al., 2003). The higher Pb means concentrations in the study area may be as a result of atmospheric deposition from mixed anthropogenic sources including, motor vehicle emissions, and sewage sludge additions or through other industrial emissions (Kachenko and Singh, 2005). It could also be due to the use of lead compound (tetra ethyl Lead) as an additive, which is an important source of lead (Pb) in automobile exhaust emission (Aliyu and Bello, 2004 and Tangahu et al, 2011). Lead is widely known to be toxic even at low concentration especially in young children and causes hyperactivity, deficits in fine motor function, hand-eye coordination etc.

#### 4. Conclusion

The concentration of heavy in the soils samples around Challawa industrial estate was successfully determined using atomic absorption spectrophotometry which revealed the mean concentration of those metals in the sequence Cr>Cu>Ni>Cd>Zn>Pb. Generally, the levels of the studied heavy metals in the soil samples from the study areas were observed to be higher than those obtained from the control site; however the concentration of most of these metals have exceeded the permissible level. Hence urgent steps should be taken by government and other environmental protection agencies to curtail this issue.

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