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HAIR AND NAIL HEAVY METAL LEVELS IN RESIDENTS FROM MAIDUGURI, BORNO STATE, NIGERIA: INFLUENCE OF GENDER, AGE, OCCUPATIONALLY EXPOSURE AND SMOKING HABIT

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ABSTRACT

Samples of hair and nail were collected from different subjects with respect to sex, age, occupationally exposed to heavy metals such as subjects working in a lead battery workshop in Maiduguri Metropolis, Borno State, Nigeria. Also hair and nail samples were collected from smoker and non-smoker subjects for heavy metals determination. Sample collection and preparations were carried out using standard procedures. The concentrations of Copper (Cu), Zinc (Zn), Copper (Co), Manganese (Mn), Iron (Fe), Chromium (Cr), Cadmium (Cd) Arsenic (As), Nickel (Ni) and Lead (Pb) were measured using Flame Atomic Absorption Spectrophotometer (AAS, Unicam 969). From the results of this study, high concentrations of all the metals under study were observed to accumulate in the subjects. It was also observed that of all the metals studied, Zn showed the highest concentrations while Cu showed the least levels. Significantly high levels of heavy metals were observed in smokers, compared to a non-smoker ($p<0.05$). The levels of all the metals studied were significantly higher in the toenails compared to fingernail samples ($p<0.05$). The levels of all the metals studied were statistically higher in male subjects compared to female subjects ($p<0.05$). The concentrations of heavy metals in nail samples were significantly higher than hair samples. The present of these metals in the analyst samples is an indication of the presence of these metals in their work environment. Accordingly there is an instantaneous need for public awareness about the hazards of this occupation and smoking habit in order to enable these volunteers take necessary precautionary measures**.**

Keywords: Hair, nail, metals, occupational exposed, smoking habit.

INTRODUCTION

The processes of urban development, coal mining, emission from vehicular activities and agricultural practice which result in the use of fertilizers and pesticides have resulted in the discharged of heavy metal into the environment. Some elements (Zn, Na, Cu, Fe, Mn and K) are essential for various physiological processes; but at higher levels, these elements become dangerous to various body organs, thereby leading to diseases (Florence 1990; Oluwole *et al*., 1994). The blood gives transient concentrations; but nail tissues can provide records of trace element of the human body (Wilhelm and Hafner, 1991). The hair and nail tissues can easily be sampled for analyzed for accumulated toxic and essential metals than other body organ due to its collection, transportation and storage. Occupational workers such as adults working in metals and mining industries are likely to be exposed to toxic metals in their places of work. Humans that are non-occupationally exposed may also suffer from heavy metal contamination by inhaling airborne particulate matter and may also be exposed to heavy metals contamination through food and water. Human may also be exposed to some metals such as copper and lead contained in water pipe as a result of leached from lead and copper piping into water supplies or inhaled occupationally as dust or fumes.

A number of tissues in the human body such as the kidney and liver can be used for metal analysis particularly for heavy metals, but these are not easily accessibltoin living individuals. Specimens readily available for analysis include blood, urine, nails, teeth and hair. Their worth as bioindicator, depends on their capacity to store trace elements. Blood metal levels reflect transient levels whereas hair metal levels show long-term retention, which may be accounted for a long period for exposure (Hopp, 1977; Petering *et al*., 1971; Lake, 1982). Nail also indicate metals body burden (Choudhary *et al*., 1995). Hair and nails are very important for their used as a tool for monitoring environmental pollution or bioaccumulation of heavy metals (Jenkins, 1997). Concentration of metals in hair and nails reflect their mean level in the body during a long period of exposure as compared to body fluids (Foo *et al*., 1993; Mehra, 2002; Suzuki, 1988, Elinder *et al*., 1988). Sukumar and Subramanian, 1992) reported higher levels of heavy metals among industrial workers when compared to control samples that is non-occupationally exposed workers. Human nails have been used in some clinical

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laboratories to determine metabolic disorders, metal environmental exposure and nutritional status (Nowak and Chmielnicka, 2002).

Maiduguri (Lat. 11^{O} 50'N, Log. 13^{O} 13'E) is a capital of Borno State and is located within North east position of Northern Nigeria. The state is underlined by the sediments of the Chad basin. The temperature ranges from 22-28^{O}C, with means of the daily maximum exceeding the onset of the rain during March, April and May. It has a minimum temperature drop as low as 12^{O}C in December-February. Studies have shown that there is a high accumulation of heavy metals in some human system in Borno State, which may be associated with exposure and inhalation of these metals from the environment. This trend poses a major health challenge to the human system. But there are no detailed documented baseline data on the study of Hair and nail metal levels in this area of study, hence the need for this study. This study is the aim of determining heavy metals, which include copper, zinc, iron, lead, chromium, cobalt, manganese, cadmium, arsenic, and nickel in human hair, fingernail and toenail samples of different sex, age groups of lead battery workers and smokers and non-smokers.

MATERIALS AND METHODS

Sampling Area and Collection

Hair and nail samples were from different subjects (occupational exposure and non-occupational exposure) within Maiduguri Metropolis Borno State, Nigeria. Samples were collected from subjects with respect to sex, age and those working in lead battery workshops and smoking and non-smoker. Human hair and nails were samples from six age groups range (10-20, 21-30, 31-40, 41-50, 51-60 and 60-above years). The hair samples were collected from the nape of the scalp of the human head by cutting a distance 2mm from the scalp of the hair by using a sterilized stainless steel scissors washed with ethanol, a neutral solvent to remove external contamination. The hair samples collected were sealed in plastic bags prior to analysis. The nail samples were paired with the hair samples for every individual, Samples were collected for a period of six months.

For a collection of nail samples the hand toes of the male and female volunteers were washed thoroughly with soap and rinse with double deionized water, the hand and toes were dry by using a clean towel in order to remove any metals from external sources. Fingernail and toenail samples of male and female subjects of the six age group cut with sterilized stainless steel scissors. All the nail samples were also sealed in plastic bags prior to analysis.

Collection of Medical History of the Subject

The subject medical histories and other habits were obtained by using a questionnaire. The detail information's include sex, age, smoking and not smoking and occupational and non-occupational exposed workers.

Washing of Hair Samples

The hair samples collected from the six age groups were cut into various pieces so as to ensure feasible and fast digestion of the samples. Hair samples were pre-washed with nonionic detergent and soaked in deionized water for 10 minutes. It was followed by soaking in acetone to remove external contamination and finally the hair samples were washed with deionized water. The samples were dried in an oven at 110^{O}C for 1 hour and finally kept in a desiccator pending analysis.

Washing of Nail Samples

The nail samples were clean of dust particles by using a nonionic detergent (Triton X-100). The hair samples were soaked in acetone to remove any substances as a result of external sources. The samples were the rinse five times with deionized water and dried in the oven at 110^{O}C to obtain a constant weight and latter stored in a dessicator for further analysis.

Digestion of Hair Samples

For each of the hair samples, 3 g was weighed into a clean crucible. It was dried in the oven to partial dryness. The dried hair samples were digested by using 10ml of 6:1 mixture of concentrated nitric acid and perchloric acid, the samples were heated on a hot plate until complete evaporation of the solution to obtain a water clear solution. Each of the digested hair samples were transferred into a 100cm volumetric flask and were made up to the mark with distilled water.

Digestion of Nail Samples

One gram (1g) of the nail samples from the six age groups were placed in a furnace and ashes at 550 ^{O}C for 4 hours. The ashes were digested by using a 10 ml of 6 : 1 mixture of concentrated nitric and perchloric acid. The samples were left overnight at room temperature and subsequently the samples were heated at 180°C until the mixture become water clear and reduce to 1 ml. Each sample solution was then diluted 100ml by using distilled water.

Elemental Analysis of Samples

The levels of Cu, Zn, Co, Mn, Fe, Cr, Cd As, Ni and Pb were determined using Atomic Absorption Spectrophotometer (AAS, Unicam 969). Standard solution of each sample Cu, Zn, Co, Mn, Fe, Cr, Cd As, Ni and Pb were prepared according to Sc 2000 manufacturer procedure for Atomic absorption spectroscopy to be used. A known 1000mg/l concentration of the metal solution was prepared from their salts.

RESULTS AND DISCUSSION

The mean metal concentrations in fingernail and toenail samples of male subject working in a lead battery workshop with respect to age and sex are as presented in Figure 1. The levels of Zn range from 14.60 to 93.40µg/g; 0.78 to 30.44 µg/g Pb; 4.87 to 49.34 µg/g Fe; 1.23 to 23.56 µg/g Ni; 0.03 to 12.43 µg/g As; 0.23 to 3.77 µg/g Cd; 0.34 to 11.87 µg/g Cr; 1.23 to 18.11 µg/g Mn and 0.32 to 6.91 µg/g Cu. From the result of this study the concentrations of all the metals were significantly higher in toenails when compared with finger nails. It was also observed that the levels of these metals were higher in 50 -60 years age group, while 10-20 years age group showed the least concentrations. The concentrations of heavy metals in fingernail and toenail samples of subject working in the lead battery workshop are in the order of Zn> Pb> Fe> Ni> Mn> Cr> As> Cu> Cd.

Figure 2 shows the mean levels of the analyst metals in male and female subject with respect to age, smokers and non-smokers in finger nail samples. The levels of Zn

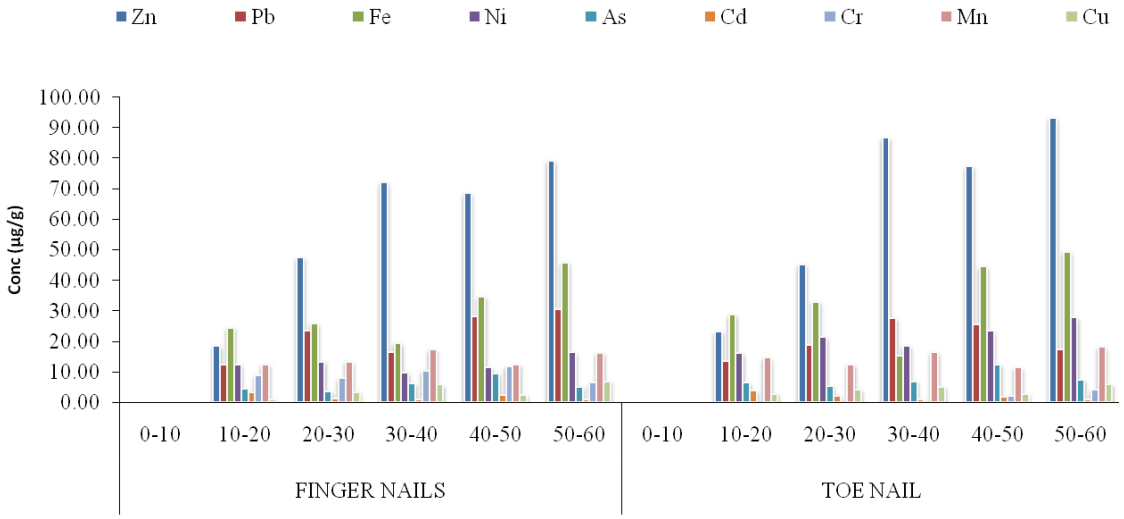

Fig. 1. Mean concentrations of heavy metals in fingernail and toenail samples from male subject working Lead Battery workshop with respect to age group in Maiduguri Metropolis.

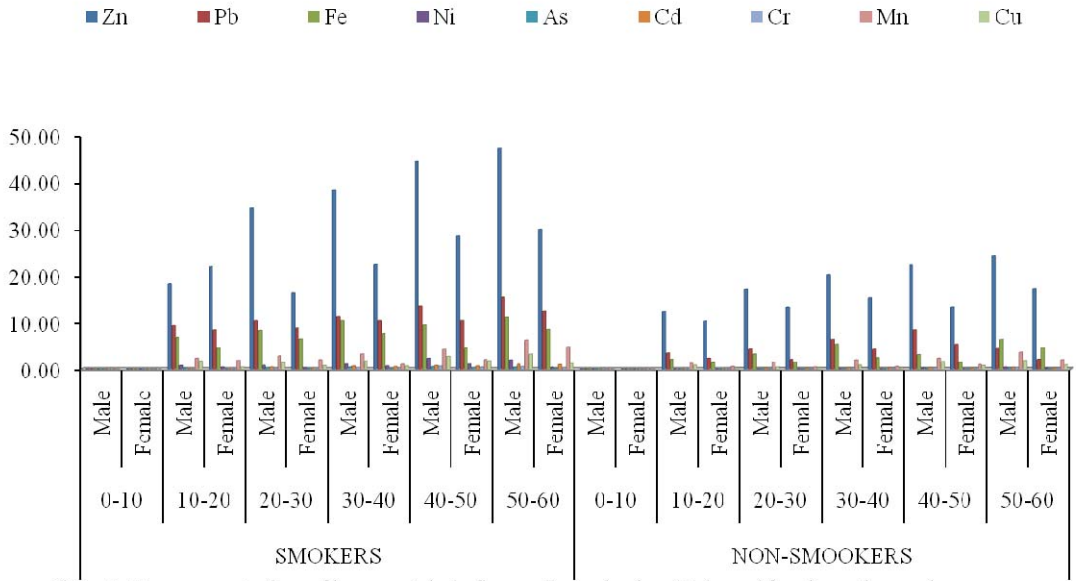

Fig. 2. Mean concentrations of heavy metals in fingernail samples from male and female smokers and non-smokers with respect to age group in Maiduguri Metropolis.

ranges from 10.23 to 47.34 µg/g; 2.11 to 15.45 µg/g Pb; 1.34 to 11.22 µg/g; Fe; 0.01 to 2.34 µg/g Ni; 0.01 to 0.53 µg/g As; 0.01 to 1.07 µg/g Cd; 0.01 to 0.63 µg/g Cr; 0.45 to 6.22 µg/g Mn; 0.21 to 3.22 µg/g Cu. That of toenail samples is as presented in Table 1. Zn ranges from 9.34 to 48.21 µg/g; 1.02 to 16.45 µg/g Pb; 1.34 to 12.43 µg/g; Fe; 0.01 to 2.88 µg/g Ni; 0.01 to 0.76 µg/g As; 0.01 to 1.65 µg/g Cd; 0.01 to 0.73 µg/g Cr; 0.67 to 8.67 µg/g Mn; 0.31 to 4.23 µg/g Cu. Male subject showed the highest concentrations, while female subject showed the least concentrations. The levels of these metals increase with respect to age. Metal concentrations (Fig. 2 and Table 1) were higher in smoker subject when compared to the non-smoker subject. In addition, Statistical analysis using Anova ($p<0.05$) shows that there were significant variations between the concentrations of heavy metals in fingernail samples when compared to toenail samples.

The mean metal concentration in human hair samples with respect to age from male subject working in three lead battery workshops are as presented in figure 3. The levels of Zn range from 12.34 to 44.00 µg/g; 6.70 to 12.45 µg/g Pb; 24.45 to 38.00 µg/g Fe; 4.56 to 11.45 µg/g Ni; 1.08 to 3.87 µg/g As; 0.67 to 2.06 µg/g Cd; 2.67 to 4.06 µg/g Cr; 2.56 to 6.76 µg/g Mn and 0.06 to 1.67 µg/g Cu. The levels of the metals were in the following order Zn> Fe> Pb> Ni> Mn> Cr> As> Cd> Cu.

Table 2 shows the mean metal levels in male hair samples with respect to age, smokers and non-smokers. The levels of Zn ranges from 0.89 to 21.99 µg/g; 0.56 to 10.68 µg/g Pb; 0.53 to 8.99 µg/g; Fe; 0.01 to 0.87 µg/g Ni; 0.01 to 0.38 µg/g As; 0.01 to 0.85 µg/g Cd; 0.01 to 0.55 µg/g Cr; 0.34 to 3.76 µg/g Mn; 0.12 to 2.86 µg/g Cu. The levels of these metals increased with respect to age. The concentrations of all the metals in the hair samples were statistically higher in smoker subjects when compared to non-smoker subjects.

Figure 4 shows the mean concentrations of heavy metals in fingernail when compared to hair samples from same male subjects working in the lead battery workshop. The levels of Zn ranged from 10.44 to 65.33 µg/g; 19.45 to 51.87 µg/g Pb; 27.43 to 41.20 µg/g; Fe; 0.67 to 16.34 µg/g Ni; 0.34 to 4.11 µg/g As; 0.04 to 5.77 µg/g Cd; 1.33 to 17.34 µg/g Cr; 2.56 to 15.44 µg/g Mn; 0.0.56 to 4.33 µg/g Cu.

Figure 5 shows a comparison of heavy metals in fingernails and hair samples from smokers of the same

Table 1. Mean concentrations of heavy metals in toenail samples from Male and female smokers and non-smokers with respect to age group in Maiduguri Metropolis.

	Age group	Sex	Zn	Pb	Fe	Ni	As	Cd	Cr	Mn	Cu
SMOKERS	0-10	Male	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Female	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10-20	Male	19.20	10.34	8.56	0.65	0.33	0.01	0.01	3.22	2.11
		Female	21.20	8.45	4.98	0.55	0.01	0.01	0.01	2.65	1.08
	20-30	Male	36.40	9.34	9.34	0.86	0.42	0.51	0.43	4.22	2.65
		Female	19.20	8.00	7.45	0.39	0.12	0.25	0.21	2.54	1.11
	30-40	Male	35.60	10.34	11.22	1.54	0.47	0.71	0.53	5.67	3.23
		Female	21.20	8.45	8.34	0.87	0.21	0.45	0.21	2.33	0.54
	40-50	Male	42.30	13.89	9.21	2.88	0.65	0.79	0.68	6.45	1.99
		Female	27.30	11.34	5.33	1.87	0.41	0.65	0.42	3.24	1.32
	50-60	Male	48.21	16.45	12.43	2.77	0.76	1.65	0.73	8.67	4.23
		Female	27.34	13.24	9.11	1.23	0.32	1.02	0.43	6.55	2.34
NON-SMOKERS	0-10	Male	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		Female	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10-20	Male	10.34	1.45	1.34	0.03	0.02	0.01	0.03	1.45	0.77
		Female	9.34	1.02	2.34	0.01	0.01	0.01	0.02	1.05	0.31
	20-30	Male	20.34	4.34	3.75	0.06	0.04	0.26	0.04	2.12	0.48
		Female	15.34	2.11	2.15	0.04	0.03	0.13	0.01	0.67	0.31
	30-40	Male	22.30	5.46	6.34	0.15	0.07	0.32	0.18	2.34	1.34
		Female	17.23	4.00	3.00	0.07	0.02	0.22	0.11	1.33	1.00
	40-50	Male	20.33	8.11	4.65	0.32	0.25	0.35	0.34	2.89	2.34
		Female	14.34	6.01	2.34	0.07	0.01	0.18	0.01	1.34	1.40
	50-60	Male	22.40	4.87	7.00	0.52	0.24	0.51	0.41	3.99	2.30
		Female	18.30	3.45	5.10	0.22	0.12	0.22	0.25	2.56	2.65

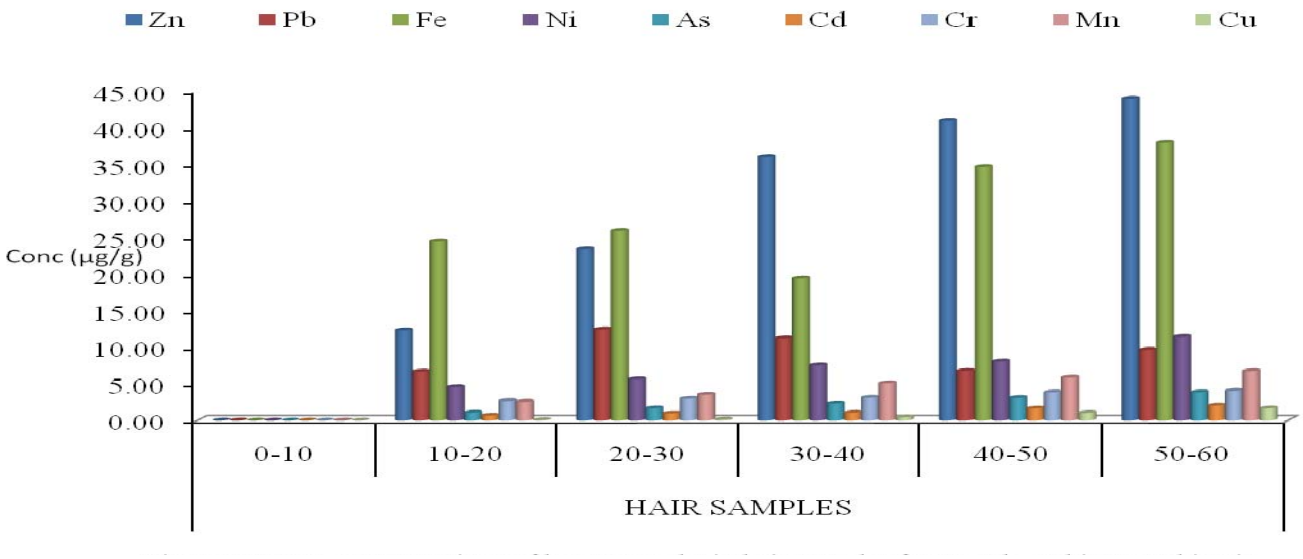

Fig. 3. Mean concentrations of heavy metals in hair samples from male subject working in lead battery workshop with respect to age group in Maiduguri Metropolis.

Table 2. Mean concentrations of heavy metals in hair samples from Male smokers and non-smokers, with respect to age groups in Maiduguri Metropolis.

	Age Group	**Zn**	**Pb**	**Fe**	**Ni**	**As**	**Cd**	**Cr**	**Mn**	**Cu**	**Cu**
SMOKERS	0-10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10-20	6.67	4.56	2.44	0.11	0.02	0.01	0.01	1.00	1.09	0.77
	20-30	9.07	5.66	4.87	0.26	0.06	0.06	0.11	1.55	1.07	0.89
	30-40	14.56	7.45	6.78	0.33	0.09	0.12	0.26	1.98	1.45	1.00
	40-50	18.03	9.55	8.45	0.74	0.33	0.55	0.55	2.54	2.08	1.66
	50-60	21.99	10.68	8.99	0.87	0.38	0.85	0.48	3.76	2.79	2.86
NON-SMOKERS	0-10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10-20	0.89	0.56	0.53	0.01	0.01	0.01	0.01	0.34	0.02	0.12
	20-30	1.58	0.96	0.70	0.02	0.01	0.08	0.01	0.75	0.21	0.55
	30-40	2.65	1.87	1.08	0.01	0.03	0.11	0.07	1.07	0.65	0.61
	40-50	4.88	2.98	1.83	0.03	0.08	0.27	0.10	1.37	0.95	1.03
	50-60	7.71	3.00	2.18	0.19	0.11	0.30	0.15	2.00	1.00	1.33

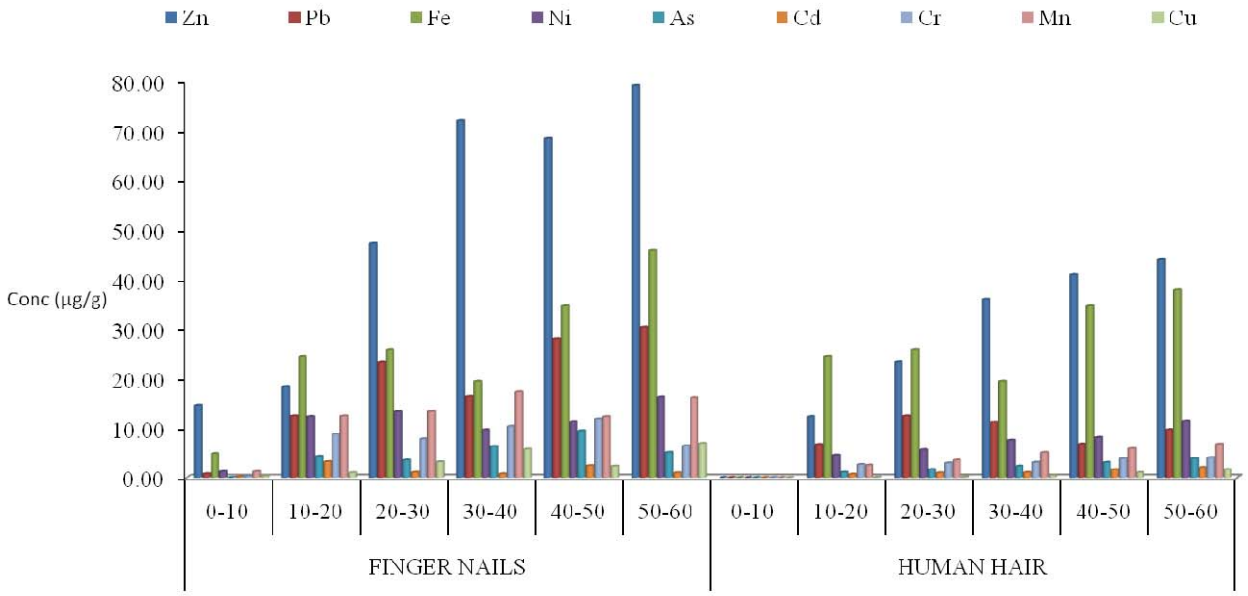

Fig. 4. Comparison in the concentrations of heavy metals fingernail and hair samples from same male subject working in lead battery workshop with respect to age group in Maiduguri Metropolis.

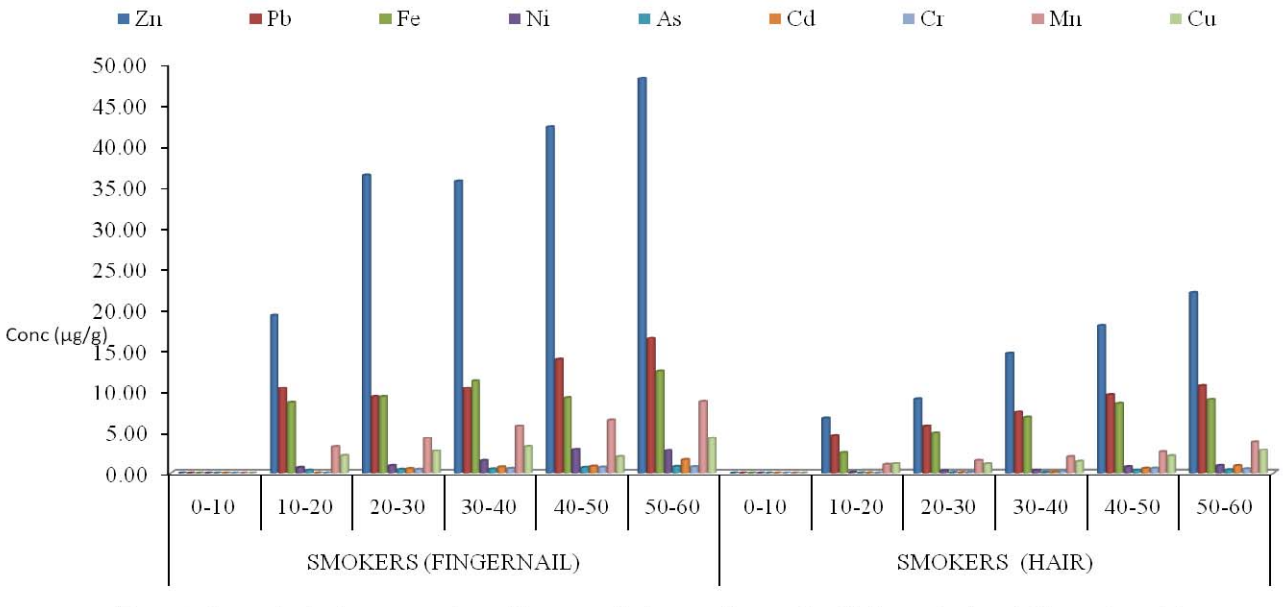

Fig. 5. Comparison in the concentrations of heavy metals between fingernail and hair samples from same male smokers with respect to age group in Maiduguri Metropolis.

subject. The levels of Zn ranged 6.67 to 48.21 µg/g; 4.56 to 16.45 µg/g Pb; 2.44 to 12.43 µg/g; Fe; 0.11 to 2.77 µg/g Ni; 0.02 to 0.76 µg/g As; 0.01 to 0.79 µg/g Cd; 0.01 to 0.73 µg/g Cr; 1.00 to 8.67 µg/g Mn; 1.09 to 4.23 µg/g Cu.

The results of this study show that heavy metals in nails and hair samples from different subject accumulate differently based on exposure. It was observed that the highest concentration of Zn (93.40µg/g) was obtained in the toenail of subject working in the lead battery workshop. The levels of Pb 49.34 were highest in the toenail of subject of lead battery workers when compared to smoker subject, such differences recorded might be attributed to exposure of subject working lead battery workers (Rauf and Jevis, 1992; Takagi *et al*., 1986; Ward *et al*., 1987). This indicates that the concentrations of metals in the body are a function of metal in the work environment, this was in line with the work of Buchancova *et al*. (1993). A similar trend was observed for Fe, Ni, As, Cd, Cr, Mn and Cu with elevated level in toenail than fingernail samples, the highest levels of all the metals in toenail samples when compared to fingernail samples might be attributed to the fact that a fingernail grows continuously at a faster rate of 0.05-1.2 mm per week while toenails grows at a slower rate and thus provide a longer integrated period for the metal accumulation compared to fingernail (Barbosa *et al*., 2005).

Nail samples were observed to accumulate higher concentrations of heavy metals when compared to hair samples, such differences might be attributed to the incorporation of elements into the keratin structure of hair takes place by binding to the sulfhydryl groups that are present in the follicular protein. In this regard, the detergents such assoap, and shampoos, hair pomades, lotions, hair bleaches and dyes actually compete with the complexing ability of these reactive sites, thus leading to a significant leaching of elements from the shaft bulk (Sonofonte *et al*., 2000). The presence of all the metal studied in smoker when compared with non-smokers might be attributed to absorption tobacco leaves in the soil which these plants are being grown. The tobacco plant absorbs heavy metals most probably from the soil as a result of the use of fertilizer and pesticides (Wagner, 1993). Other environmental factors that may influence the uptake of heavy metals by tobacco plants include the pH of soil, contaminated irrigated water and sewage sludge used as fertilizers (Kazi *et al*., 2009). The concentrations of all the metal studied in hair and nail samples from lead battery workers and smokers and non-smokers subject increases significantly from 10-20years to 50-60 years. The younger group showed least levels when compared with the older groups. Nail samples from same subject also showed significantly higher levels of heavy metals when compared to hair samples and are similar to the works carried out by Foo *et al*. (1993).

Chromium is a relatively scarce metal that occurs in several states. The most toxic of these states is the chromium VI or hexavalent state. Compare the Cr content of the samples with the levels in hair and nails for healthy individuals from various countries (Cr in Italy is 0.03 to 19.7 Mg/kg, England 0.03 to 1.88 Mg/kg, USA 0.20 to 0.23 Mg/kg). Based on these values it is clear that the concentrations of Cr in the hair and nail samples were higher than the lower limits for other researcher (Ward, 1988; ML, 1989; Sonofonte *et al*., 2000). Hence, considering the bioaccumulation nature of Cr and the pattern of exposure as showed in the results one cannot rule out the long term health complications of Cr in the various subjects.

The toxicity of lead is dependent on the life stage of the organism, and the presence of organic material. Decreases in water pH can increase the bioavailability of lead in the system (Hellawell, 1986). Lead can cause damage to the nervous system and the kidneys and it is suspected to be carcinogenic (Radojevic and Bashkin, 1999). Children exposed to high lead levels are particularly at risk. The levels of lead in the analyzed hair and nail samples studied exceeded the upper limits for the various countries Italy (Sonofonte *et al*., 2000) is 0.03 Mg/kg; Japan (Kamakura, 1983) 1.4 Mg/kg; USA (ML, 1989) 0.44 Mg/kg), indicating the presence of this metal in the environment and the workplace and smoking habit of the subjects, as well as their proneness to illness and hazards of this metal in cases of long term exposure.

Iron and Copper concentrations were generally lower in the entire sample analyzed when compared to other researcher (Sonofonte *et al*., 2000; Ward, 1988; ML, 1989 and Ryan *et al*., 1978). Toxicity of iron in humans has been found to bring about vomiting, cardiovascular collapse and diarrhoea. While iron deficiency may lead to failure of blood clotting (Turnland, 1988). Copper is a common environmental metal and is essential in cellular metabolism but at high concentrations it can be highly toxic to fish (Grosell *et al*., 1997). Copper is an essential substance to human life, however, in high concentrations, it can cause anaemia, liver and kidney damage, stomach and intestinal irritation (Turnland, 1988). Copper is generally remobilised with acid-base ion exchange or oxidation mechanism (Gomez *et al*., 2000). Long term exposure of copper may lead to liver and kidney damage (EPA, 1999). Hence, these Cu and Fe concentrations in the samples are essential for hair growth.

Cadmium has a range of negative physiological effects on organism, such as decreased growth rates and negative effects on embryonic development (Newman and

Mcintosh, 1991). Arsenic is a highly toxic metalloid element (Pizzaro *et al*., 2003). It is widely distributed as a trace element in rocks and soils and is mainly mobilised by microbial activities (Garcia-sanchez and Alvarez-ayuso, 2003). The levels of cadmium and As in the hair and nail samples were above the reference values of various studies (Ward, 1988; ML, 1989 and Sonofonte *et al*., 2000). The bioaccumulation nature of Cd and As and the pattern of exposure as showed in the results, one cannot rule out the long term health complications of Cd in the various subjects.

CONCLUSION

The present study reveals high concentrations of some heavy metals in hair and nail samples of lead battery workshop and smoker and non-smoker subject. The concentrations of all the metals in the hair and nail samples were higher in smoker subject when compared to the non-smoker subject. The present of these metals in the analyst samples is an indication of the presence of these metals in their work environment.

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