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Analysis of Heavy Metals in Human Hair Using Atomic Absorption Spectrometry (AAS)

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ABSTRACT

Hair samples of individual were analysed for heavy metals (Cd, Cr, Pb and As) across gender and various occupational distributions by Atomic Absorption Spectrophotometric technique (AAS). The results of replicate analysis shows the following mean concentrations (mg/kg): Cd = 27.8 ± 8.0, Cr = 2.70 ± 0.7, Pb = 73.8 ± 42.3 and As = 222 ± 34.1. The coefficients of variation for the total distribution is; Cd = 28%, Cr = 26%, Pb = 57% and As = 15%. The distribution of the metals follows the series in decreasing order of As > Pb > Cd > Cr, while their coefficients of variation is in the order of Pb > Cd > Cr > As. The result shows the presence of all the metals in relatively large amounts with As having the highest concentration between the two genders. The difference between male and female concentration could be due to individual differences in exposure to heavy metal load as a result of habitual or environmental factors.

Keywords: Heavy Metals; Human Scalp Hair; AAS; Concentration

1. Introduction

Research has shown that there is personal difference in concentrations of trace elements in the human hair according to human life or history such as occupation, sex, age, food, habit, social condition and so on [1]. Lemos *et al.* [2] have also reported that individual's deviation of elemental concentrations reflects the degree of environmental pollutants exposure to the human body, intakes of food and metabolism. Heavy metals, such as chromium, lead, mercury, cadmium, arsenic are extremely toxic even in very small amounts. When any of these elements is present in the environment at high concentrations, living organisms are subjected to strong natural selection for tolerance. Environmental contamination by metals exerts physiological pressures that are clearly too severe for survival of most species by means of phenotypic plasticity or physiological acclimation, rather than genetic adaptation [3]. Heavy metals are poisonous to living organisms including humans due to their biotoxic effects, which could be acute, chronic or sub-chronic, neurotoxic, carcinogenic, mutagenic or teratogenic [4]. Cadmium is toxic at extremely low level, it is also associated with bone defects like osteomalacia, increased blood pressure and myocardic dysfunctions. McCluggage [5] reported that severe exposure to cadmium may result in pulmonary oedema and death. Smoking has also been reported to be a contributing factor to higher bioaccumulation of cadmium [6]. Chromium is an essential nutrient in our diet that helps insulin to maintain normal glucose level. Chromium toxicity can cause stomach upsets, ulcer, kidney-, liver-damage and even death. Femer [7] reported that lead is the most significant of the toxic heavy metals and the inorganic forms are absorbed through ingestion of food and water as well as inhalation. Apart from the teratogenic effects of lead, its poisoning also causes inhibition of the synthesis of haemoglobin, dysfunctions in the kidneys, joints and reproductive systems, acute and chronic damage to the central nervous system, etc. [8]. Workers with chronic headache and dizziness have higher levels of Cr and Pb in the scalp hair samples, such as in those working in a fireworks factory [9]. Arsenic toxicity symptoms depends on the chemical form ingested [10]. Arsenic acts to coagulate protein, forms complexes with coenzymes and inhibits the production of adenosine triphosphate during respiration [11].

Hair analysis is inexpensive and fast; it also detects and measures the content of heavy metals and minerals of the hair. The Global Environmental Monitoring System (GEMS) of the United Nations Environment Program selected human hair as one of the important monitoring materials for worldwide biological monitoring of pollution [12]. Therefore analyses of heavy metals (Cr, Pb, Cd and As) in human scalp hair serves as an assessment for environmental contamination and can be used to sensitise individuals towards maintaining a healthier life style in their environments.

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2. Materials and Methods

All reagents (absolute ethanol, HNO_3, 20% H_2O_2) used were analytical grade reagents obtained from Sigma Chemical Company, St Louis, USA. Atomic absorption spectrometer (Younglin AAS 8010) used was obtained from Younglin Instrument Ltd, South Korea.

2.1. Sample Collection

Freshly cut human hair samples were collected from the head of 51 individuals between the ages of 7 - 55 years (35 males and 16 females) across several occupational distributions within Makurdi metropolis in Central Nigeria (latitude 7˚44' and longitude 8˚31'). The samples were quickly transferred in to coded polythene bags, sealed tightly and kept for pre-treatment. Prior to sample collection, questionnaires were distributed to respondents which contained highlights of information such as the gender, age, occupation, population density of residential area, type of food consumed, water source, presence of refuse dump in the area of residence, behavioural pattern etc. Height and body mass of the consenting individuals were also taken.

2.2. Sample Cleaning/Digestion

The hair samples collected were cut to about 200 - 250 mg using stainless steel scissors rinsed in ethanol, then coded and stored. The stored samples were further cut into approximately 0.125 in (0.3 cm) pieces and mixed to allow a representative subsampling of the hair specimens and were washed according to the recommendation of International Atomic Energy Agency (IAEA) [13]. Exactly 0.1065 g of hair sample was weighed accurately into a 50 mL crucible. The sample was covered with 8 mL conc. HNO_3, after which the crucible was covered with the crucible lid and placed on a hot plate. Hair was digested at 70˚C - 85˚C for about 25 minutes or until the hair is completely digested and the solution becomes clear. The crucible was not allowed to go dry until the digestion was complete. After cooling to room temperature inside the fume hood, 1 mL of 30% H_2O_2 was added to each sample, and heated again on hot plate at the lowest setting (first setting *i.e.* 42˚C) just until bubbling stops. After this, heat was increased to about 80˚C or as needed until the volume is reduced to about 2.5 mL [14]. The contents of each crucible were quantitatively transferred to a cleaned and dried 100 mL volumetric flask. The digestion vessel was rinsed three times with 1.5 mL each with deionised water and added to the volumetric flask and made up to volume with deionised water. (It could be filtered using Whatman paper no. 1 and no. 40 if the solution looks cloudy to prevent clogging the nebulizer). It was then transferred to a cleaned sample bottle, corked, labelled well and stored in the refrigerator until ready to be analysed. Standard solutions of all the metals investigated were prepared from concentration levels of 1 - 20 ppb.

3. Results and Discussion

The results of AAS analysis shows, the ranges in concentrations of heavy metals (mg/kg) as follows: Cr varies from 0.33 - 16.16; Pb varies from 5.80 - 347.19; Cd ranges from 2.46 - 130.17 while As ranges from 21.29 - 447.04. **Table 1** shows the distribution of heavy metals among male samples by age with As having the highest concentration (243 ± 125 mg/kg) within 21 - 31 years of age interval.

The distribution of the metals among female samples by age are shown in **Table 2,** where all the metals analysed were more distributed around age bracket of 21 - 31 years except Cd where the highest was between 7 - 20 years. The distribution and the average concentration of heavy metals by age in the entire samples is shown in **Table 3** in which Cr has the least concentration but has a high value between the ages 21 - 31 and ≥ 43 and As has the highest concentration followed by Pb and Cd.

The total mean concentrations of the metals (mg/kg) were Cr = 2.70 ± 0.7, Cd = 27.8 ± 8.0, Pb = 73.8 ± 42.3 and As = 222 ± 34.1 as also shown in **Figure 1**. This shows that As has the highest and Cr the least concentration. The total coefficient of variation were; Cr = 26%, Cd = 29%, Pb = 57%, and As = 15%. This indicates that

Table 1. Distribution and mean concentration (mg/kg) of heavy metal in male samples by age.

Range (years)	Number of male	Heavy metals			
		Cr	Cd	Pb	As
7 - 20	4	4.31 ± 4.10	40.5 ± 5.90	104 ± 73.7	241 ± 210
21 - 31	19	3.57 ± 4.00	28.7 ± 22.2	42.4 ± 30.3	243 ± 125
32 - 42	7	1.64 ± 0.90	20.1 ± 12.0	24.6 ± 30.0	181 ± 114
≥43	5	3.66 ± 2.60	28.5 ± 21.9	60.8 ± 4.10	211 ± 133

Table 2. Distribution and mean concentration (mg/kg) of heavy metal in female samples by age.

Range (years)	Number of female	Heavy metals			
		Cr	Cd	Pb	As
7 - 20	5	1.08 ± 0.800	31.9 ± 0	127 ± 78.3	298 ± 0
21 - 31	10	2.60 ± 2.10	27.0 ±17	194 ± 158	223 ± 200
32 - 42	-	-	-	-	-
≥43	1	0.72 ± 0.00	2.46 ± 0.00	40.51 ± 0.00	Nil

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Table 3. Summary of distribution and average concentration (mg/kg) of heavy metal in the 51 samples by age.

Range (years)	Heavy metals			
	Cr	Cd	Pb	As
7 - 20	2.70 ± 3.23	38.8 ± 6.37	118 ± 67.7	260 ± 153
21 - 31	3.28 ± 3.56	28.2 ± 20.3	98.4 ± 121	233 ± 144
32 - 42	1.64 ± 0.94	20.1 ± 12.0	24.6 ± 30.0	181 ± 114
≥43	3.17 ± 2.58	24.2 ± 22.3	54.0 ± 12.0	211 ± 133

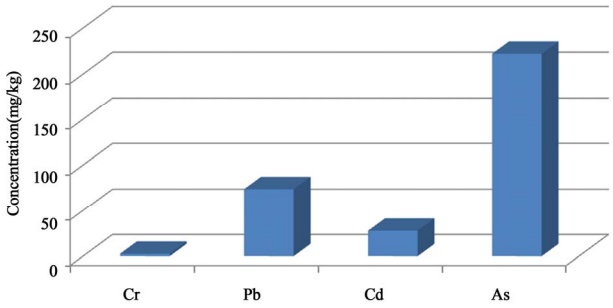

Figure 1. Total mean distribution of individual heavy metals using AAS technique.

lead has the highest coefficient of variation while arsenic has the least. Since coefficient of variation is a measure of dispersion, the implication is that while lead is widely dispersed among the sampled population, arsenic is more closely dispersed within same sample population. Based on AAS analysis, the average concentration of Cr, and Cd are higher in males while that of Pb and As are higher in females as shown in **Figures 2** and **3**. According to Lee *et al* [15] this could be attributed to use of cosmetic products by females among other sources.

The standard deviation is higher in females for Pb and Cd while it is higher for Cr in males. This indicates that the deviation in the individual content of heavy metals is more pronounced in females compared to males. The coefficient of variation (CV) for Cr, Cd and As are higher in females except Pb which is higher in males.

The mean concentration of heavy metals in both males and females were compared statistically at 0.05 probability which showed significant difference in all the elemental content. Similar samples analysed by x-ray fluorescence analysis showed that the average concentrations of Cr in XRF method for both genders were relatively higher than that in AAS method [16]. This is likely due to the non-destructive nature of sample matrix used in XRF analysis as the samples were not digested before analysis [17], where as, the samples for AAS were completely digested before analysis. This could lead to loss of volatile proportion of analytes. Also, a difference was observed between the concentration of Cr in XRF technique and AAS method when compared statistically [16].

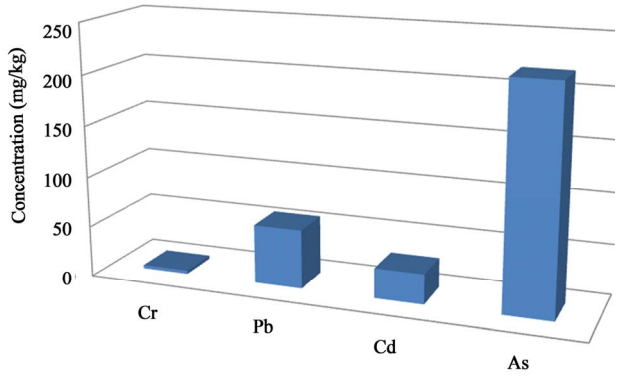

Figure 2. Average concentration of heavy metals in males using AAS technique.

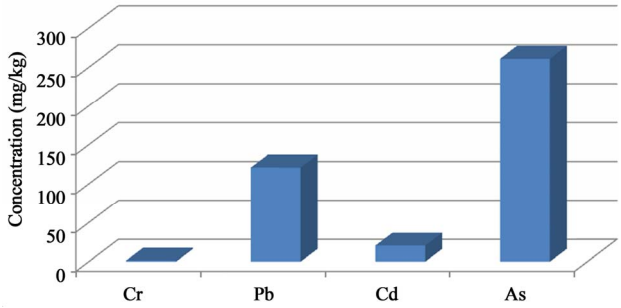

Figure 3. Average concentration of heavy metals in females using AAS technique.

The difference between the concentration of the same element (Cr) in same gender under two methods where as, it showed no difference under same method could have resulted from method variability such as sensitivity, detection limit, analytical conditions of instrument, pretreatment methods, possibility of the sample matrix being contaminated by exogenous material and the efficiency of the analyst [12,18]. The difference between male and female concentration could be due to individual differences in heavy metal load as a result of habitual or environmental factors.

The distribution of the metals follows the series: As > Pb > Cd > Cr, while their general coefficients of variation is of the order: Pb > Cd > Cr > As. This showed that Pb recorded the highest variation in the distribution among individual respondents as compared to As which has the least. Lead has diffuse possible sources which could be from drinking water, which for most respondents were tap water (boilers ring in the pipes) and bore holes. Others are packaging materials, contaminated food grown in lead-deposited soils either from point or non-point sources, use of agrochemicals during cropping season, use of leaded fuels, lead plate accumulators, use of alloys like solder, bearing metals, type metals etc. The high accumulation of As could have resulted from the use of insecticides, doping agents in semi-conductors, use of some lead-based alloys to promote hardening etc. [19].

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4. Conclusion

Analysis carried out by AAS technique for As, Cd, Cr and Pb indicates the presence of all the metals in relatively large amounts with As having the highest concentration across age distribution and between the two genders. The presence of all the heavy metals under investigation is a clear indication of the environmental content as well as the behavioural pattern of the respondents who are randomly selected from the general society. As and Pb were much higher in females than males probably due to use of cosmetics formulations and hair treatment among them. For all the four different heavy metals determined, the coefficients of variation were higher for three elements (Cr, Cd and Pb) among the females while only As has higher coefficient of variation among the males. This reflects 75% of the total population which indicates that these metals have greater degree of dispersion among the female population than the males.

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