

Manganese and Cobalt Concentrations in Hair and Nail of Some Kano Inhabitants

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ABSTRACT: Manganese and cobalt concentrations in hair and nail were determined by Flame Atomic Absorption Spectrophotometer (AAS). The mean manganese in hair and nail were 0.54 ± 0.35 mg/g and 0.68 ± 0.30 mg/g while the mean cobalt in hair and nail were 0.30 ± 0.24 mg/g and $0.460.37$ mg/g respectively. A progressive increase in cobalt concentrations in hair and nails with age indicated no significant difference in their means suggesting that cobalt in hair and nails originate from a common source. Comparing the mean manganese concentrations in hair with the nails a significant difference is indicated in the two tissues (p<0.05). Human hair and nails are hence recording filaments that can reflect metabolic changes of many elements over long periods of time and hence furnish a post nutritional event of some essential micro-elements.

Key words: Manganese, Cobalt, Hair, Nail, Determination, Pollution

INTRODUCTION

Hair is a site of excretion for essential, nonessential and potentially toxic elements (Ashraf *et al.*, 1995). The amount of an element irreversibly incorporated into growing hair is proportional to the level of the element in other body tissues (Ajayi *et al.*, 2001). Therefore, hair analysis provides an indirect screening test for physiological excess, deficiency or mal-distribution of elements in the body (Adeniyi and Aletor, 1999). Clinical researches indicated that hair levels of specific elements, particularly potentially toxic elements such as cadmium, mercury, lead and arsenic, are highly correlated with pathological disorders (Bache *et al.*, 1991). For such elements, levels in hair may be more indicative of body stores than the levels in blood and urine. Scalp hair is vulnerable to external contamination by water, hair treatments and products (Kasperect *et al.*, 1982; Sturaro *et al.*, 1994; Bertazzo *et al.*, 1996; Rosbong *et al.*, 2003). The data that hair analysis do provide should be considered in conjunction with symptoms, diet analysis, occupation and lifestyle, physical examination and the results of

other laboratory tests. Hair analysis may provide useful insights into the biochemical and hormonal condition of the body (DiPietro *et al.*, 1989; Chattopadhyay *et al.*, 1990; Contiera and Folin, 1994; Nnorom *et al.*, 2005).

Trace metals are important, from nutritional and toxicological points of view. Small amounts of these essential elements are required for the maintenance of growth and normal health. Deficiencies occur when there are inadequate amounts to meet the metabolic needs. Clinical toxicity also occurs if over ingestion of some elements takes place (Baumgatner, 1993). It is present in all healthy tissues, its concentration from one species to the next is fairly constant, the amount of each element is maintained within its required limit, its withdrawal induces reproducibly the same physiological and/or structural abnormalities and their additions to the diet prevents or reverse the abnormalities (Tuormaa, 1995). Non – essential or toxic trace elements include, excess copper, lead, cadmium, mercury and aluminum acquired through environmental contamination (Kasperect *et al.*, 1982; Tuormaa, 1995; Rosbong *et al.*,

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2003). The milk, urine, saliva and sweat measure the component that is absorbed but excreted. The blood measures the component absorbed and temporarily in circulation before excretion and / or storage (EPA, 1980). The hair, nails and teeth are tissues in which trace minerals are sequestered and/or stored and can be used to monitor the highest priority toxic trace metals (Barett, 1985). Manganese is an essential trace mineral in human nutrition (Keen *et al.*, 1999). Manganese is the preferred metal co-factor for *glycosyltransferases* in the synthesis of *glycoproteins* and *glycosaminoglycans* (*mucopolysaccharides*). Manganese and iron scavenge for hydroxyl and superoxide radicals a component of the *metalloenzyme manganese superoxide dismutase* (MnSOD) found in the mitochondria and a constituent of the mitochondrial oxidant defense system. Symptoms associated with Mn deficiency include fatigue, lack of physical endurance, slow growth of fingernails and hair, impaired metabolism of bone and cartilage, dermatitis, weight loss, reduced fertility, increased allergic sensitivities and inflammation. Other deficiency signs include nausea, vomiting, change in hair color and neurologic sequel. Patients with end-stage liver disease accumulate manganese in their basal ganglia. Manganese plays a role in the hepatic encephalopathy in liver failure. It is eliminated primarily through the bile, and hepatic dysfunction leading to depressed manganese excretion (Krieger *et al.*, 1995). Mine workers exposed to high concentrations of manganese dust develop "locuramanganica" or manganese madness with symptoms similar to Parkinson's disease (Nagatomo *et al.*, 1999). Cobalt is an essential nutrient part of vitamin B₁₂. Excess exposure results in medium toxicity. Inhalation of high levels has effects on the lungs including asthma, pneumonia and wheezing (Petering, 1973). Realizing that both toxic metal excesses and trace mineral deficiencies are associated with all forms of reproductive failures, it has been advocated for the need of hair tissue analysis before conception (Barnes and Bradley, 1994; Bradley and Bennett, 1995). The aim of this work was to determine the levels of manganese and cobalt in the population group living in an urbanized and industrialized city of Kano-Nigeria. The

dependence of the hair and fingernail contents on age and gender were examined.

MATERIALS & METHODS

Both hair and fingernails were sampled in the year 2004-2007 from (350) for hair and (300) for fingernails subjects living in urban population group in Kano-Nigeria. Samples were collected from subjects in the age range of 1-55 years. Nail samples were collected in polyethylene containers. Hair samples were cut at the root of the occipital area of each subject. Surface contamination and grease were removed by washing the samples in detergent and distilled water after which they were kept in an alcohol-ether mixture for 45 mins and dried at 60°C for 72hr (Nowak, 1998).

About 0.50g of each sample was digested in 10cm³ concentrated HNO₃ and the resulting solution was evaporated to dryness and redissolved in 0.1M nitric acid (Mehra and Juneja, 2005; Erzen and Kragelj, 2003; Seidel *et al.*, 2001; Hinwood *et al.*, 2003). Trace metal concentrations were determined by Flame Atomic Absorption on a Buck Model 210 VGP Spectrophotometer attached to IBM personal computer. The result of the absorbance of each sample was the average of ten sequential readings. Background light absorption and scattering were compensated for either by deuterium hollow cathode lamp or by tungsten/halogen lamp. Distilled water was digested as blank using the same procedure previously described (Ayodele and Abubakar, 1998; Ayodele and Abubakar, 2001). All statistical computations either were on the PC 486 66MHZ microcomputer using the integrated statistical package for windows from Umstat Ltd. (London) or dedicated micro instructions for the Excel spread sheets from Microsoft. The approach enabled the advantages of the various computational and graphical facilities of both types of software's to be used with the ability to read different file formats. The analyses of variance (ANOVA) were carried out according to described procedures (O'Mahony, 1986).

RESULTS & DISCUSSION

The concentration of Mn and Co in hair and nails varied among individuals, thus large number of samples from a population was analyzed and the results treated statistically for meaningful that

correlation. The trace metal concentrations in hair and nails were determined using atomic absorption spectroscopic method. The age of the donors, sex and occupation were noted where necessary. The frequency distribution patterns for the elements in hair nails vary widely among individuals, thus large number of samples from a population were treated statistically for meaningful correction. The Mn and Co metals in these samples, their mean and coefficient of variation are employed in assessing their levels. The frequency distribution pattern for the age of donors (years) is as shown in Fig.1. The distribution is multimodal and is skewed towards high frequency of low age with a mean age of 27.51 ± 16.50 years. The frequency distribution pattern for manganese in hair is shown in Fig.2. The distribution is multimodal and is skewed towards high frequency of low concentration with a mean and standard deviation of 0.54 ± 0.35 mg/g while the frequency distribution pattern for manganese in nails (Fig.3) is multimodal and is skewed towards high frequency of low concentration with a mean and standard deviation of 0.68 ± 0.30 μ g/g. Though the patterns are similar in both hair and nails, Pearson comparison has shown no correlation between the manganese content in hair and nails ($p < 0.05$) (Table 1). Similarly, the analysis of variance (ANOVA) revealed that the mean concentration of manganese in hair is not significantly different from

in the nails at $p > 0.05$ (Table 2). The levels obtained in this study are in agreement with mean intake of manganese worldwide which ranges from 0.52 to 10.8 mg (Ferguson *et al.*, 1983; Foo *et al.*, 1993). Manganese concentration in hair and nails with respect to age is as shown in Fig.4. Manganese levels in both hair and nails decreased with age, but the decrease was pronounced in hair, indicating that manganese may be playing some physiological functions. The frequency distribution pattern for cobalt in hair is as shown in Fig. 5. The distribution is bimodal and is skewed towards high frequency of low concentration with a mean and standard deviation of 0.30 ± 0.24 mg/g. The frequency distribution pattern for cobalt in nails is as shown in Fig. 6. The distribution is multimodal and is skewed towards high frequency of low concentration with a mean and standard deviation of 0.46 ± 0.37 mg/g. A strong correlation exist between the cobalt content in hair and in nails ($p < 0.01$) but the ANOVA (Table 4) indicated no significance difference between the mean cobalt concentration in hair and in nails at $p > 0.05$. Fig.7. represents cobalt concentration in hair and nails with respect to age. The pattern illustrates similar trends indicating the common source of the metal in them. Cobalt may not be age dependent because the concentration of 0.40 mg/g was observed in all age groups. Though cobalt in hair increased with age, the

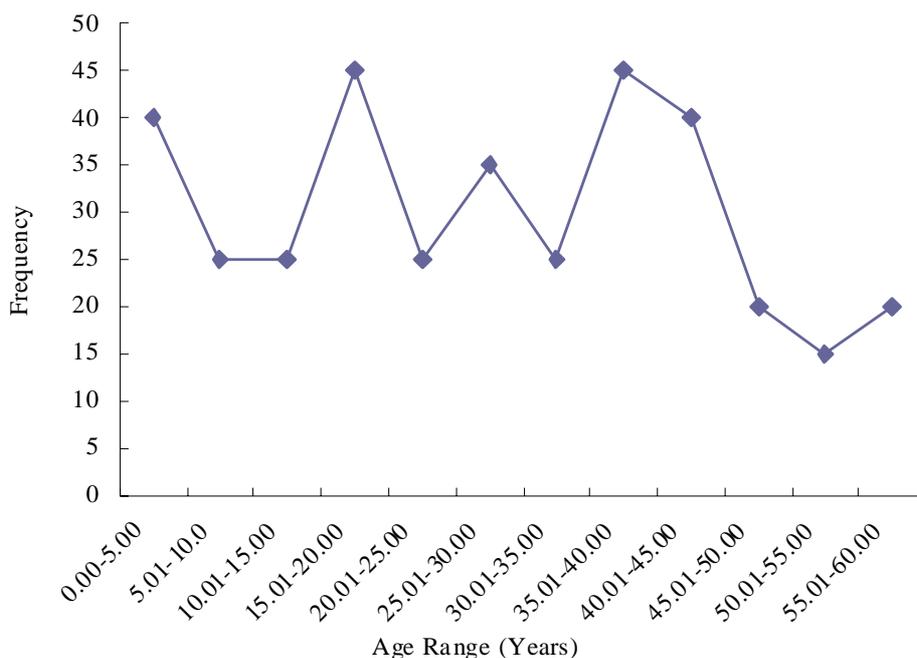


Fig. 1. Frequency Distribution Pattern for Age (years) of Donors

Mn & Co Concentration in Hair and Nail

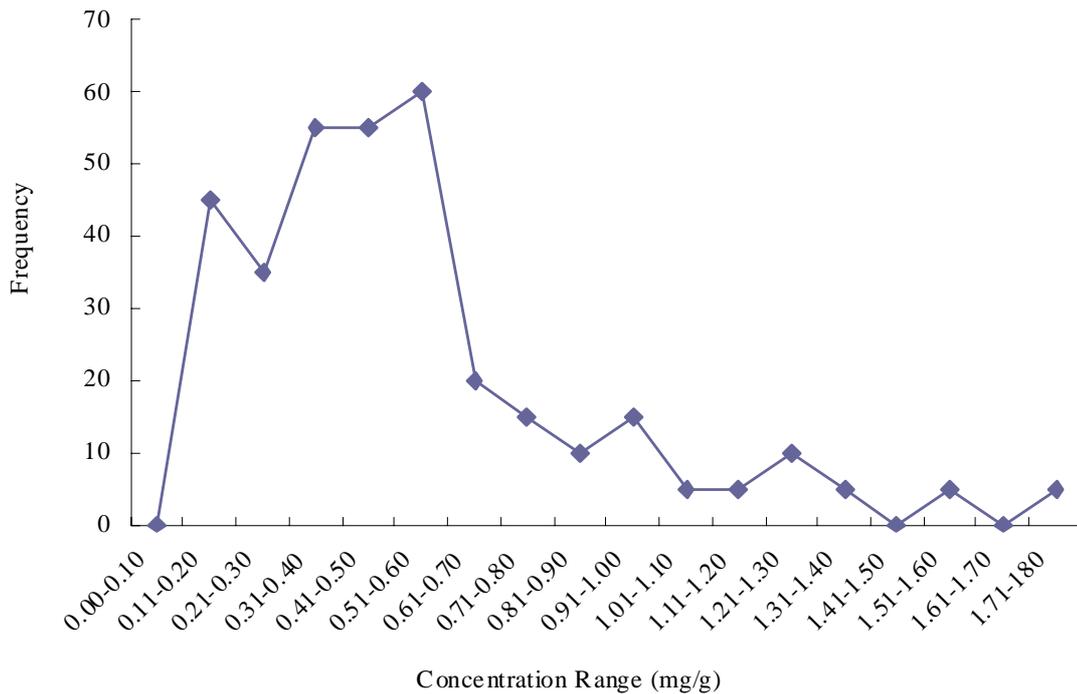


Fig. 2. Frequency Distribution Pattern for Manganese in Hair

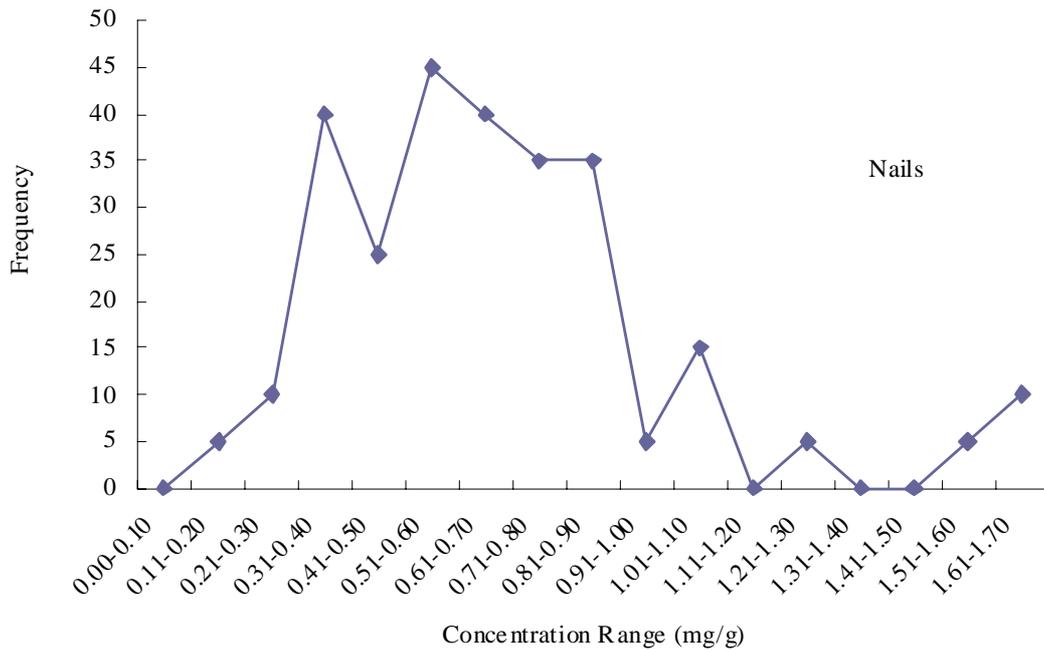


Fig. 3. Frequency Distribution Pattern for Manganese in Nails

pattern appeared linear when compared with that of nails. These data are in agreement with values earlier reported (Weber *et al.*, 1990; Hashem and Otham, 2001). From the levels of cobalt obtained, it is reasonable to believe that manganese and cobalt are playing some physiological roles in the respiratory organs where it plays special functions in man.

Table 1. Parametric Correlation Coefficients for Manganese in Hair and Nails

	Hair	Nails
Hair Pearson correlation	1	0.91
Sig. (2-tailed)	.	501
N	350	300
Nails Pearson Correlation	0.91	1
Sig. (2-tailed)	507	.
N	300	300

** Correlation is significant at the 0.01 level

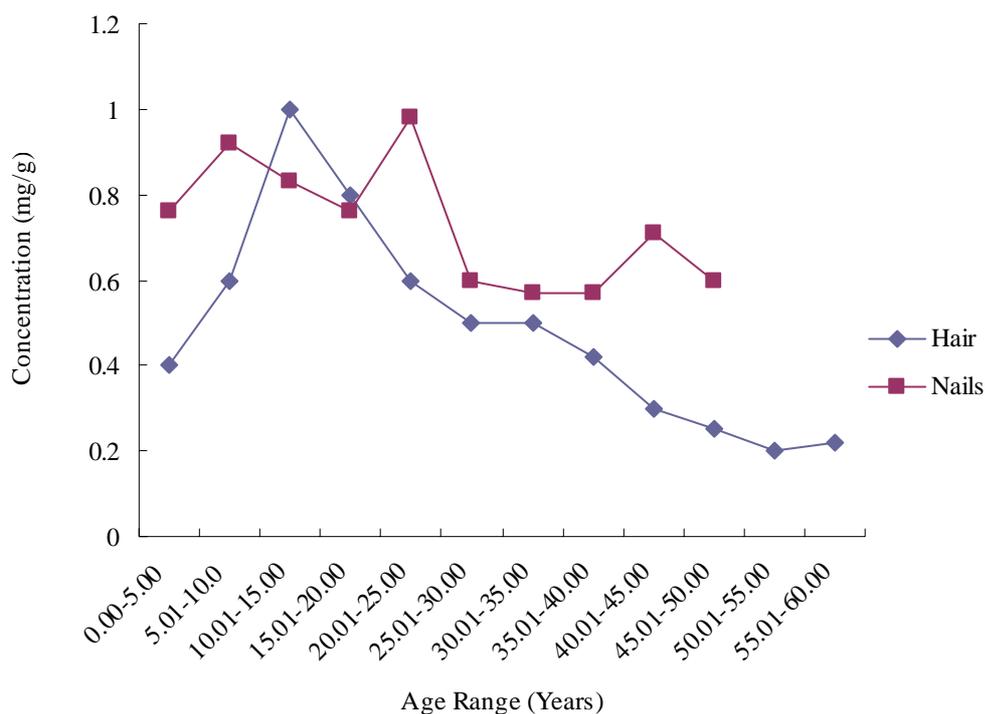


Fig. 4. Manganese Concentration (mg/g) in hair and Nails with respect to age

Table 2. Analysis of variance for Manganese in Hair and Nails

Source of variation	SS	Df	MS	F	P-value	F crit
Between Groups	0.574568	1	0.57456818	6.38530834	0.0136633	3.9290115
Within Group	9.872764	108	0.09141448			
Total	10.44733					

Table 3. Parametric Correlation Coefficients for Cobalt in Hair and Nails

	Hair	Nails
Hair Pearson correlation	1	0.703
Sig. (2-tailed)	.	0.000
N	350	300
Nails Pearson Correlation	0.703	1
Sig. (2-tailed)	0.000	.
N	300	300

** Correlation is significant at the 0.01 level

Table 4. Analysis of variance for Cobalt in Hair and Nails

Source of variation	SS	Df	MS	F	P-value	F crit
Between Groups	0.787965	1	0.78796455	8.17959992	0.0050864	3.9290115
Within Group	10.40395	108	0.0963329			
Total	11.1992	109				

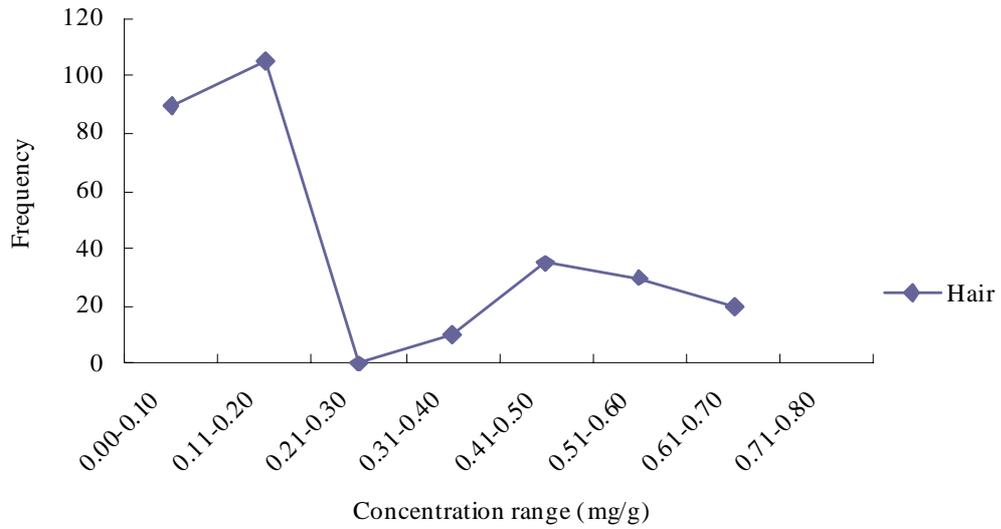


Fig. 5. Frequency Distribution Pattern for Cobalt in Hair

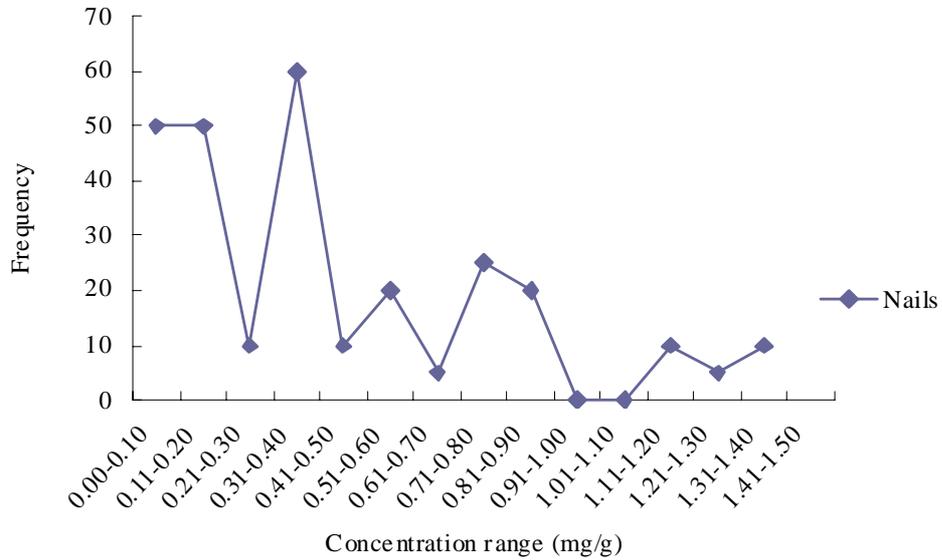


Fig. 6. Frequency Distribution Pattern for Cobalt in Nails

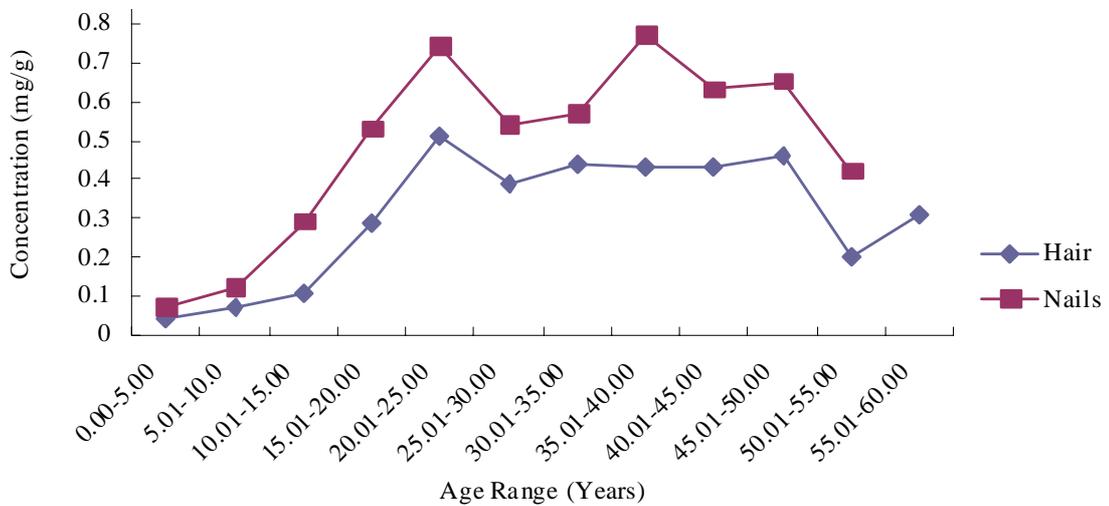


Fig. 7. Cobalt concentration (mg/g) in Hair and Nails with respect to age

CONCLUSION

Human exposure to toxic trace elements has been the focus of increasing attention among researchers, formulators and managers of health and nutrition policies due to its damages to health. The levels Mn and Co in hair and nails vary and may be affected by various factors (Siedel *et al.*, 2001). Age was observed to be a factor influencing their levels. The values of two elements recorded revealed sex dependence. Hair colour, nutritional status, geographic, racial/ethnic and ecological can have a significant impact on the levels of these elements in hair and nails (Sandra and Silva, 2002; Chojnacka and Gorecki, 2006a&b); but no correlation with any of these factors was observed, since our samples were collected from the same geographical location. The high trace element levels in hair and nails makes analysis easy; slow metabolic turnover rate of hair; and its being a reliable status of body without daily variation. The collection of samples were simple and non traumatic. Hair and nails may be regarded as complementary to body fluids in biological monitoring. Comparing hair and nails as points of excretion the latter appear superior to the former. The former enables monitoring of elements accumulated over a time span up to several months. They are easily sampled, handled and transported, and less prone to post – sampling contamination because of higher elemental concentration. Therefore human hair and nails are recording filaments that reflect metabolic changes of many elements over long periods of time and hence furnish post nutritional event as dietary levels of some essential micro – elements have been reported corresponding to hair concentrations of the elements (Maugh, 1978).

REFERENCES

- Adeniyi, F. A. and Anetor, J. I. (1999). Lead poisoning in two distant states of Nigeria: an indication of the real size of the problem. *Afri. J. Med. Sci.*, **28**, 107-112.
- Ashraf, W., Jaffer, M., Anwer, K. and Ehsan, U. (1995). Age and sex based comparative distribution of selected metals in the scalp hair of an urban population from two cities in Pakistan. *Environ. Pollut.*, **87**, 61-64.
- Ajayi, S. O., Odukoye, O. O. and Onianwa, P. C. (2001). Lead content of human scalp hair in Southwestern Nigeria. *Nig. J. Sci.*, **35**, 183-187.
- Ayodele, J. T. and Abubakar, M. B. (1998). Trace element contamination of rain water in the semi arid region of Kano. *Environ. Manag. Heath*, **9**, 176-81.
- Ayodele, J. T. and Abubakar, M. B. (2001). Cleopatra bulimoides and mutellarubens as bioindicators of trace metals in Tiga Dam, Kano, and Nigeria. *Research J. Sci.*, **7**, 45-9.
- Bache, C. A., Lisk, D. J., Scarlett, J. M. and Carbone, L. G. (1991). Epidemiologic study of cadmium and lead in the hair of ceramists and dental personnel. *J. Toxicol. Environ. Health*, **34**, 423-431.
- Barnes, B. and Bradley, S. G. (1994). Planning for healthy Baby Essential for all future parents. Vermillion, London, UK. 23-59.
- Barrett, S. (1985). Commercial hair analysis: Science or scam? *JAMA*, **254**, 1041-5.
- Baumgartner, T. G. (1993). Trace Elements in clinical nutrition. *Nutrition in Clinical Practice*, **8**, 251-63.
- Bertazzo, A., Costa, C., Biasiolo, M., Allegri, G., Cirrincone, G. and Presti, G. (1996). Determination of copper and zinc levels in human hair: influence of age, sex and hair pigmentation. *Bio. Trace. Elem. Res.*, **52**, 37-53.
- Bradley, S. G. and Bennett, N. (1995). Preparation for pregnancy: An essential Guide. Argyll publishing, UK.
- Chattopadhyay, P. K., Joshi, H. C. and Samaddar, K. R. (1990). Hair cadmium level of smoker and non-smoker human volunteers in and around Calcutta City. *Bull. Environ. Contam. Toxicol.*, **45**, 177-180.
- Chojnacka, A. and Gorecki, H. G. (2006a). The effect of age, sex, smoking habit and hair colour on the composition of hair. *Environ. Toxicol. Pharmacol.*, **22**, 52-57.
- Chojnacka, A. and Gorecki, H. G. (2006b). The influence of living habits and family relationships on element concentrations in human hair. *Sci. Total Environ.*, **366**, 612-620.
- Contiera, E. and Folin, M. (1994). Trace elements nutritional status. Use of hair as a diagnostic tool. *Biol. Trace. Elem. Res.*, **40**, 151-160.
- DiPietro, E. S., Phillips, D. L., Paschal, D. C. and Neese, J. W. (1989). Determination of trace elements in human hair. Reference intervals for 28 elements in nonoccupationally exposed adults in the US and effects of hair treatments. *Biol. Trace. Elem. Res.*, **22**, 83-100.
- EPA (1980). Environmental protection Agency, Biological monitoring trace metals. EPA600/3 – 80 – 89, USA.
- Erzen, I. and Kragelj, L. Z. (2003). Cadmium Measurements in Blood and Hair of Occupationally Non-exposed Military Recruits in the Foods of plant Origin produced in Slovenia. *Croatian Medical Journal*, **44** (5), 538-544.

- Fergusson, J. E., Holzbecher, J. and Ryan, D. E. (1983). The sorption of copper [II], manganese [II], zinc [II], and arsenic [III] into human hair and their desorption. *Sci. Total Environ.*, **26**, 121-135.
- Foo, S. C., Khoo, N. Y., Heng, A., Chua, L. H., Chia, S. E., Ong, C. N., Ngim, C.H. and Jeyaratnam, J. (1993). Metals in hair as biological indices for exposure. *Int. Arch. Occup. Environ. Health*, **65**, S83-S86.
- Hashem, A. R. and Othman, M. R. (2001). Hair and Nails labels of Iron of some Healthy volunteer Women from Saudi Arabia. *The Sciences*, **1** (1), 28-29.
- Hinwood, A. Sim, R. M., Jolley, D., Klerk, N., Bastone, E. B., Gerostamoulos, J. and Drummer, O. H. (2003). Hair and Toenail Arsenic Concentrations of Residents Living in Areas with High Environmental Arsenic Concentrations. *Environ. Health Persps.*, **111**, 187-193.
- Kaspeck, K; Iyengar, G. V. Feinendengen, L. E; Hashish, S and Mahfouz, M (1982). Multi-element analysis of finger nail, scalp hair and water samples from Egypt. *Sci. Total Environ.*, **22**, 149-168.
- Keen, C. L., Ensunsa, J. L. and Watson, M. H. (1999). Nutritional aspects of manganese from Experimental studies. *Neurotoxicol.*, **20**, 213-23.
- Krieger, D., Krieger, S., and Jansen, O. (1995). Manganese and chromic hepatic excephalopathy. *Lancet*, **346**, 270-74.
- Maugh, T. H. (1978). Hair: A Diagnostic tool to complement blood, serum and urine. *Science*, **202**, 1271-73.
- Mehra, R. and Juneja, M. (2005). Fingernails as biological indices of metal exposure. *J. Biosci.*, **30**, 101-105.
- Nagatomo, S., Umehara, F. and Hanada, K. (1999). Manganese intoxication during total parental nutrition. *J. Neurol. Sci.*, **162**, 102-105.
- Nnorom, I. C., Igwe, J. C. and Ejimone, J. C. (2005). Multielement analyses of human scalp hair samples from three distant towns in Southeastern Nigeria. *Afri. J. Biotech.*, **4**, 1124-1127.
- Nowak, B. (1998). Contents and relationship of elements in human hair for a non-industrialized population in Poland. *Sci. Total Environ.*, **209**, 59-68.
- O'Mahony, M. (1986). *Sensory Evaluation of food. Statistical methods and procedures.* Marcel Dekker Inc. New York, USA.
- Petering, H. G., Yeager, D. W. and Witherup, S. O. (1973). Trace metal content of hair. *Arch. Environ. Health*, **27**, 327-330.
- Rosbong, I., Nihigard, B. and Gerhardsson, L. (2003). Hair element concentration in female in oneacid and onealkaline area in southern Sweden. *Ambio*, **32**, 440-446.
- Sandra, C., and Silva, S. (2002). Parameters of evaluation of Zinc nutritional status. Comparison between zinc hair rates and serum alkaline phosphates in Pre-Scholars of the Municipality of Joao Pessoa, Paraiba. *Rev. Bras. Saude. Mater. infant*, **2**(3), 1519-3829.
- Siedel, S. Kreutzer, R. Smith, D. McNeel, S. and Gilliss, D. (2001). Assessment of Commercial Laboratories Performing Hair Mineral Analysis. *J. Amer. Medical Association*, **285**, 67-72.
- Sturaro, A, Pavoli, G, Doretti, L. and Costa, C. (1994). The influence of colour, age, sex on the content of zinc, copper, nickel, manganese and lead in human hair. *Biol. Trace. Elem. Res.*, **40**, 1-8.
- Tuomaa, T. E. (1995). Adverse effects of zinc deficiency: A review from the literature. *J. Orthomol. Med.*, **10**, 150-64.
- Weber, C. W., Nelson, G. W., Vasquez de vaquera, M. and Pearson, P. B. (1990). Trace elements in the hair, of healthy and malnourished children. *J. Trop. pediatr.*, **36**, 230-4.