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ORIGINAL ARTICLE

Relationship between lead, cadmium, zinc, manganese and iron in hair of environmentally exposed subjects

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Abstract Trace level analysis of two toxic metals lead and cadmium and three essential metals zinc, manganese and iron was examined in hair of 25 workers of metals finishing units and metal recycling units of State of Rajasthan, India, as Exposed Group (EG). Twenty-five subjects as controls were selected from the office staff of the same units Control Group A (CGA) and 25 subjects selected from the population of State of Rajasthan, India, who were not exposed to metal pollution at their work place were selected as another control group Control Group B (CGB). Head hair samples were collected, decontaminated and digested followed by analysis for trace levels of Pb, Cd, Zn, Mn and Fe by Atomic Absorption Spectrophotometer (AAS), ECIL Model-AAS4141 using air acetylene flame. The significant levels of metals in between EG, CGA and CGB have been computed by Student's '*t*' test. The Pearson rank correlation of the data of five metals revealed significant positive correlation between Mn/Cd, Mn/Pb, Mn/Fe, Cd/Pb, Cd/Fe and Pb/Fe in hair of Exposed Group (EG), Mn/Zn, Mn/Cd, Mn/Pb, Zn/Cd, Zn/Pb, Cd/Pb and Cd/Fe in hair of Control Group A (CGA) and Mn/Cd in hair of Control Group B (CGB). Significant negative correlation was observed between Pb/Fe in hair of CGB.

1. Introduction

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 elements (Barrett, 1985). Hair has several ideal attributes for such use, it is easy to collect and store, and many minor and trace elements can be determined in such specimens with good precision and sensitivity by a variety of analytical techniques (Mehra et al., 2010a; Sela et al., 2007; Steely et al., 2007; Goulle et al., 2005). In the present study totally 75 subjects were included for metal

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concentration in hair, which were divided into three groups of 'Exposed Group' (EG), 'Control Group A' (CGA) and 'Control Group B' (CGB). Concentration of two toxic metals lead (Pb) and cadmium (Cd) and three trace metals manganese (Mn), Zinc (Zn) and Iron (Fe) in hair samples of all subjects was determined. It was also the main aim of this study to determine the correlation, if any, between the concentrations of Mn, Zn, Pb, Cd and Fe in hair as all the metals under this study are heavy metals. The main aim of this study was to identify the population at risk to metals at work environment. Study of such type will help in generating state specific, country specific data of metal concentration in biological tissue.

2. Materials and methods

The present study was conducted in metal finishing units and metal recycling units of State of Rajasthan, India. These units recycle the waste metals like batteries, electric appliances, cable wires, etc. and finishing of recycled metals for further use. Thus 25 male workers of these units were included as 'Exposed Group' (EG). Twenty-five male subjects as controls were selected from the office staff of the same units and included in study as 'Control Group A' (CGA) and 25 male subjects selected from the population of State of Rajasthan, India, who were not exposed to metal pollution at their work place and included as 'Control Group B' (CGB). All 75 subjects included in the study were of 25–45 years of age. About 1 g of head hair samples were collected from the nape region of all subjects with 1 cm. distance from the scalp using sterilized stainless steel scissor washed with ethanol. All hair samples were sealed in a precoated airtight plastic bag and brought to the laboratory for quantitative analysis. A questionnaire as recommended by the World Health Organization was used to obtain the personal and medical details of all 75 subjects included in the study. The hair samples were cut into pieces of 1 cm so as to insure feasible and fast digestion. All samples are pretreated for the removal of external contamination. Samples were washed using nonionic detergent Triton X-100 and soaked in deionized water for 10 min this was followed by washing with acetone and deionized water. Subsequently hair samples were dried in oven at 110 °C for 1 h and kept in desiccators. All decontaminated samples were then digested using nitric acid and perchloric acid in 6:1 ratio to get white residue which was dissolved in 0.1 N nitric acid to get a clear colorless solution (Babu et al., 2009; Mehra and Juneja, 2004; Mehra, 2002).

The concentration of manganese, zinc, lead, cadmium and iron in hair was determined by using Atomic Absorption Spectrophotometer (AAS), ECIL Model-AAS4141 using air acetylene flame. The main instrumental parameters (like wave length, band width, lamp current) were set up separately for the estimation of specific metals by Atomic Absorption Spectrophotometer. All reagents used in the present study were of Anal R grade and measures were taken to avoid contamination of hair samples, glasswares, instruments and chemicals. The value of metal concentrations in hair was expressed as the mean value in μg/g with standard deviation. The statistical significance of mean values between the three groups was determined by applying Student's '*t*' test with level of significance set at $P < 0.005$. Pearson rank correlation was carried out to obtain the correlation of metals.

3. Results and discussion

The mean concentration of Mn in hair of EG was significantly higher ($P < 0.05$) than both the Control Groups CGA and CGB and Mn concentration in hair of CGA was also significantly higher than CGB. No significant difference ($P < 0.05$) of Zn concentration in hair of CGA and CGB was found but Zn concentration in hair of subjects of both CGA and CGB was significantly higher ($P < 0.05$) than the Exposed Groups. Cadmium concentration in hair of Exposed Groups and CGA was significantly higher ($P < 0.05$) than CGB, but the difference in cadmium concentration in hair of EG was not significantly different from CGA. The mean concentration of Pb in hair of Exposed Group was significantly higher ($P < 0.05$) than both the Control Groups A and B and Pb concentration in hair of CGA was also significantly higher ($P < 0.05$) than CGB. Iron concentration in hair of EG and CGA was significantly higher ($P < 0.05$) than CGB, iron concentration in hair of EG was higher than CGA this difference was not significant ($P < 0.05$).

Perusal of data in Table 1 shows the higher level of manganese, lead, cadmium and iron in hair of subjects of Exposed Group than CGA and CGB. The significant difference in the values shows that this difference is not by chance but the subjects of Exposed Group are actually exposed to these metals in their work environment. Significantly higher values of manganese, lead, cadmium and iron in hair of CGA as compared to CGB suggest that office staff of metal finishing unit and metal recycling unit is also exposed to these metals at their workplace. Significantly low concentration of zinc in hair of subjects of EG was obtained as compared to CGA and CGB. This lower value of Zn in hair of EG might be due to replacement of Zn from its biological binding sites by other metals. These results indicate that metal concentration in hair is a function of metal in the work environment which is also supported by Buchancova et al. (1993) and our earlier works (Mehra and Juneja, 2005; Mehra et al., 2010b).

Pearson rank correlation was calculated to study the interaction and correlation between metals under study in hair. Table 2 summarizes the details of correlation between Mn, Zn, Cd, Pb and Fe in hair of subjects of Exposed Group. Strong positive significant correlation ($P < 0.05$) was observed between Mn/Cd, Mn/Pb, Mn/Fe, Cd/Pb, Cd/Fe and Pb/Fe. Positive correlation was also observed between Mn/Zn and Zn/Cd but this correlation was not significant ($P < 0.05$). Negative correlation was observed between Zn/Pb and Zn/Fe but this correlation was also not significant ($P < 0.05$). Correlation between all five metals under study in hair of Control Group A is given in Table 3. Strong positive significant correlation ($P < 0.05$) was observed between Mn/Zn, Mn/Cd, Mn/Pb, Zn/Cd, Zn/Pb, Cd/Pb and Cd/Fe. Positive correlation was also observed between Mn/Fe but this correlation was not significant ($P < 0.05$). Negative correlation was observed between Zn/Fe and Pb/Fe but this correlation was also not significant ($P < 0.05$).

Results of correlation between Mn, Zn, Cd, Pb and Fe in hair of Control Group B are summarized in Table 4. Significant positive correlation ($P < 0.05$) was observed between Mn/Cd and significant negative correlation ($P < 0.05$) was observed between Pb/Fe. Correlation between Mn/Zn, Mn/Pb, Mn/Fe, Zn/Cd, Zn/Pb, Zn/Fe, Cd/Pb and Cd was not significant ($P < 0.05$) in hair of Control Group B. The signif-

Table 1 Manganese, zinc, cadmium, lead and iron levels (in µg/g) in hair samples of Exposed Group, Control Group A and Control Group B.

Metals	Exposed Group		Control Group A		Control Group B	
	Range	Mean (±S.D.)	Range	Mean (±S.D.)	Range	Mean (±S.D.)
Mn	32.039–64.243	74.424 (±49.895)[a,b]	31.5608–65.662	46.473 (±7.779)[a]	1.373–54.508	31.807 (±11.250)
Zn	0.081–41.389	55.970 (±67.464)[a,b]	87.279–222.607	153.038 (±32.867)	67.434–170.947	144.930 (±23.227)
Cd	1.242–3.188	3.309 (±2.465)[a]	1.563–3.948	2.421 (±0.495)[a]	0.356–1.971	1.219 (±0.478)
Pb	26.563–54.519	57.754 (±29.016)[a,b]	21.953–65.662	38.119 (±9.771)[a]	12.297–44.014	24.225 (±8.690)
Fe	150.591–239.917	515.894 (±474.392)[a]	32.921–1123.215	203.527 (±227.244)[a]	29.559–166.409	60.774 (±36.606)

S.D. = standard deviation.
[a] Significantly different from Control Group B by $P < 0.05$.
[b] Significantly different from Control Group A by $P < 0.05$.

Table 2 Pearson rank correlation coefficient of manganese, zinc, cadmium, lead and iron in hair of subjects of Exposed Group.

Metals	Mn	Zn	Cd	Pb	Fe
Mn	0	–	–	–	–
Zn	0.044615	0	–	–	–
Cd	0.909231*	0.115385	0	–	–
Pb	0.933077*	−0.10077	0.922308*	0	–
Fe	0.824615*	−0.01154	0.646154*	0.734615*	0

* Significant correlation by $P < 0.05$.

Table 3 Pearson rank correlation coefficient of manganese, zinc, cadmium, lead and iron in hair of subjects of Control Group A.

Metals	Mn	Zn	Cd	Pb	Fe
Mn	0	–	–	–	–
Zn	0.744615*	0	–	–	–
Cd	0.753077*	0.567692*	0	–	–
Pb	0.770000*	0.821538*	0.685385*	0	–
Fe	0.329231	−0.02692	0.408462*	−0.08385	0

* Significant correlation by $P < 0.05$.

Table 4 Pearson rank correlation coefficient of manganese, zinc, cadmium, lead and iron in hair of subjects of Control Group B.

Metals	Mn	Zn	Cd	Pb	Fe
Mn	0	–	–	–	–
Zn	0.002308	0	–	–	–
Cd	0.640769*	0.340769	0	–	–
Pb	0.179231	0.007692	0.004615	0	–
Fe	−0.14462	0.184615	0.099231	−0.51385*	0

* Significant correlation by $P < 0.05$.

icant negative correlation between Pb/Fe in hair of Control Group B is in support to the study carried by Nowak and Chmielnicka (2000) that lead significantly influences the concentration of iron.

Metal concentration in plasma relating other biopsy tissues and fluids is studied by various workers (Araki et al., 1986; Kim et al., 2010) but very few studies of human subjects have attempted to investigate the interaction of metals including adverse health effects. The significant difference of metal concentration in hair of workers with different work environment is also supported by our earlier works (Mehra and Thakur, 2010; Mehra et al., 2011). The results presented in Tables 2–4 suggest that various toxic and trace metals can interact by influencing each other's absorption retention distribution and bioavailability in the body this is in support to the reported work (Al-Nasser and Hashem, 1998; Pizent et al., 2003). The positive correlation between Pb and Cd in hair supports the study done by Telisman et al. (2000) on trace metal level in blood and seminal fluid.

4. Conclusion

Evaluation of the toxic effects of lead and cadmium in subjects in polluted work environment is mainly based on the concentrations of those toxic metals in hair. Hair can accumulate not only toxic metals such as lead and cadmium but also essential metals like zinc, manganese and iron can be taken into consideration when evaluating metal pollution in environment. The study results indicate the necessity of controlling and adjusting the pollution of metals in workplace.

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