Journal of Environmental Biology **October 2007,** 28(4) 851-856 (2007)

Quantification of transition metals in biological samples and its possible impact on ferro-alloy workers

Sandhya Mishra, Dilip S. Ramteke* and Satish R. Wate
***dsramteke@rediffmail.com**

[1]Environmental Impact and Risk Assessment Division, National Environmental Engineering Research Institute, Nehru Marg, Nagpur-440 020, India

(Received: July 11, 2005 ; Revised received: September 15, 2005 ; Accepted: October 10, 2005)

Abstract: *Increased risk of ill-health and diseases has been associated with employment in the ferro-alloy factory. Since measurement of transition metals in human blood and hair, alongwith respective exposure rates, provides a means of assessing individual risk, it has been the most important part of the study. In the study, majority of the elements in the transition series, such as, vanadium (V), chromium (Cr), iron (Fe), manganese (Mn), cobalt, (Co) nickel (Ni), copper (Cu), zinc (Zn), molybdenum (Mo) and cadmium (Cd) were considered which are randomly emitted from the source, that is, manganese ore (used during ferro-alloy manufacturing process). The commonly available transition metals, observed in biological samples of ferro-alloy workers, were found to be Fe, Zn, Co, Ni, Cu, Cr, Cd, V, Mn and Mo in blood, while in hair, Mn, Fe, Zn, Co, Ni, Cu, Cr, Cd, V and Mo were present in decreasing order. Surveillance of bio-concentration of these metals in workers, exposed to close proximity of the coke-ovens and smelting furnaces, revealed that the workers were prone to several physical disorders.*

Key words: *Ferro-alloy factory, Transition element, Exposure rates, Blood, Hair*
PDF file of full length paper is available with author

Introduction

Steels are classified according to the alloying element assay as low-alloy, medium-alloy and high-alloy steels. Great attention is now concentrated on the high-quality steels needed for the development of the chemical, aviation, electrical and other industries. Alloying elements in the form of ferroalloys are also used in the manufacture of high-quality pig iron. Ferro-alloys are essential additive material in steel making and are produced in a variety of processes, including blast furnace (for ferro-manganese), electric arc furnace and thermal fusion processes (Tseng, 2007).

The trace elemental analysis in biological samples has improved significantly over last 40 years and also the improvements are observed in collaboration of instrumentations such as microwave digestion and inductively coupled plasma-mass spectroscopy, which has resulted in improved precision, accuracy and reliability of results obtained from the study. According to many investigators, hair testing has different uses and advantages over blood, since blood tend to show current or recent body status, while hair represents a longer time frame, potentially years.

Since metals emitted from the ferro-alloy factory play an important role from the point of view of occupational health and also minimal attempt has been made to study the acute toxic health effect on workers by the frequent emissions of the transition elements during the ferro-alloy manufacturing process, present study was undertaken to assess and quantify the elements of transition series reflecting its adverse impacts on the ferro-alloy workers, due to increasing range of occupational and environmental exposures. Potential clinical impact was elaborately studied by comprehensive analysis of human body fluids considering blood and hair as biomarkers, the stress was also given to elucidate the future occupational health problems.

Materials and Methods

Reagents: All reagents and chemicals were of “pro-analysis” quality and chemicals were weighed on Mettler Toledo-AG 204 Delta range electronic balance. The water used for solution preparation was de-ionized, distilled and filtered through a Milli -Q-system (Millipore, Bedford, MA). Glasswares were leached with nitric acid (1N) for 48 hr and then thoroughly rinsed with deionized water. Metal standards of definite concentrations were prepared by dilution of a static 1000 ppm multielement (Merck) standards of analytical grade in 1 N HNO_3. The elements were measured by inductively coupled plasma method (model Jobin Yvon) after digestion.

Biological monitoring was performed through socio-economic survey by the selection of industrially affected workers of different age groups working in the factory *viz.,* young, middle aged and older individuals. Grouping of workers was the most important part of the study and was done on the basis of duration of work *i.e.* the length of service and age in years of the workers serving in ferro-alloy factory. Source sampling *i.e.* the manganese ore in the form of raw material, used for ferro-alloys manufacturing, was done to detect the trace elements composition in ore.

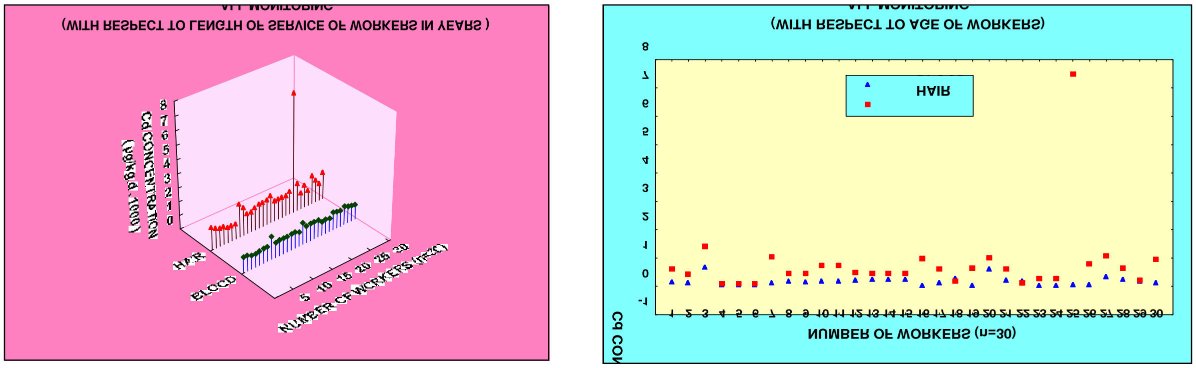

Fig. 1: Levels of transition metals in blood and hair of ferro-alloy workers cadmium

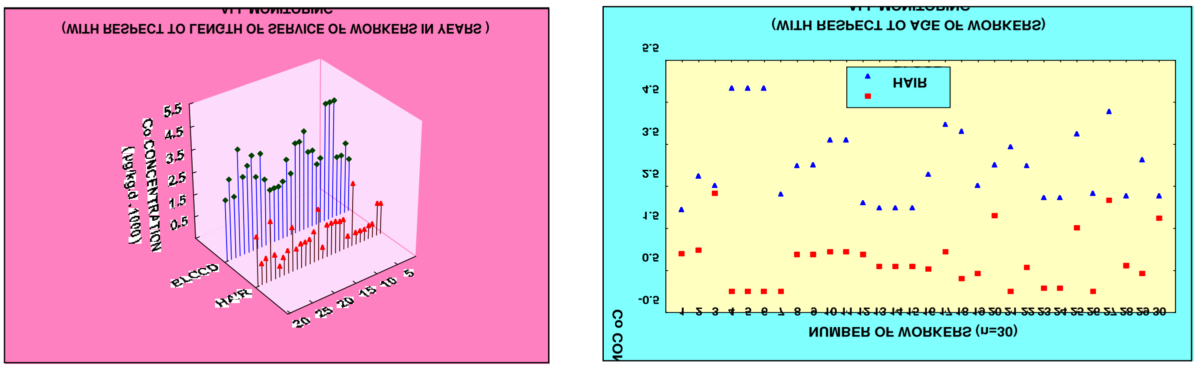

Fig. 2: Levels of transition metals in blood and hair of ferro-alloy workers cobalt

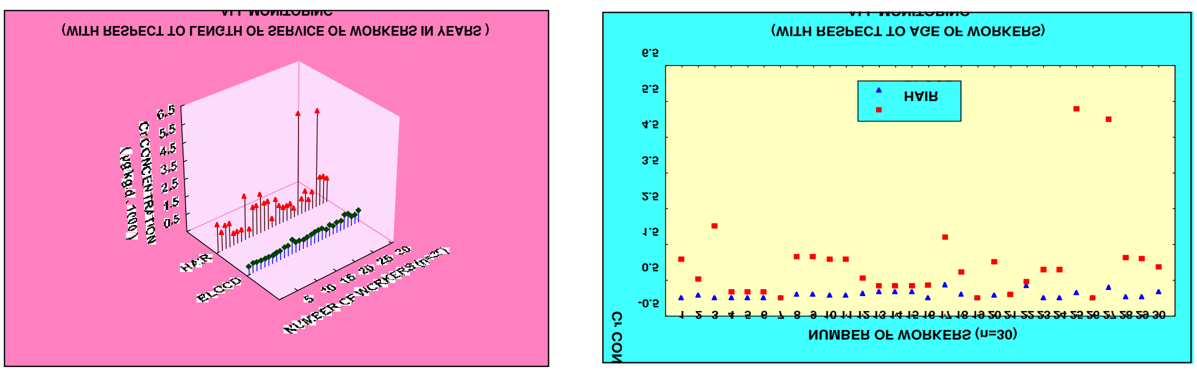

Fig. 3: Levels of transition metals in blood and hair of ferro-alloy workers chromium

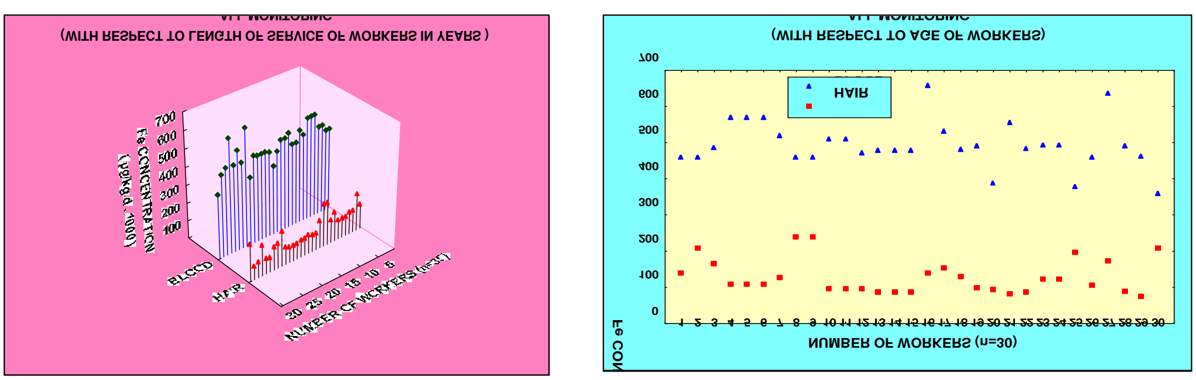

Fig. 4: Levels of transition metals in blood and hair of ferro-alloy workers copper

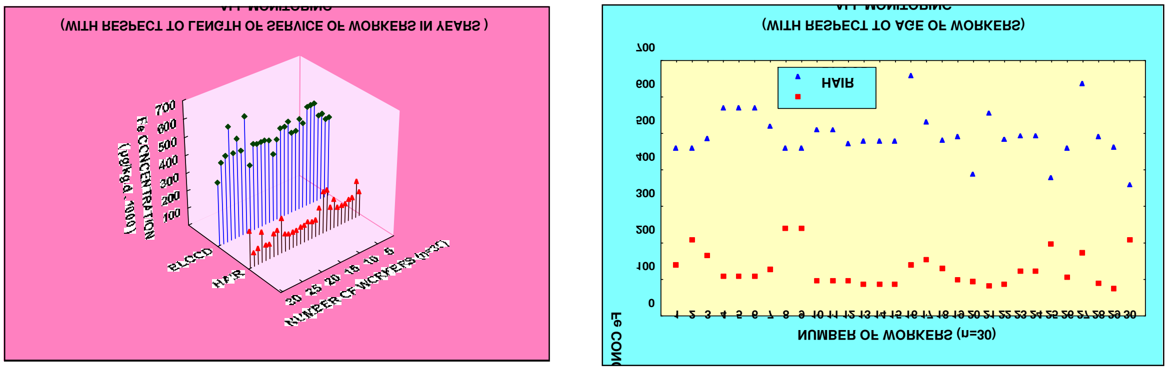

Fig. 5: Levels of transition metals in blood and hair of ferro-alloy workers iron

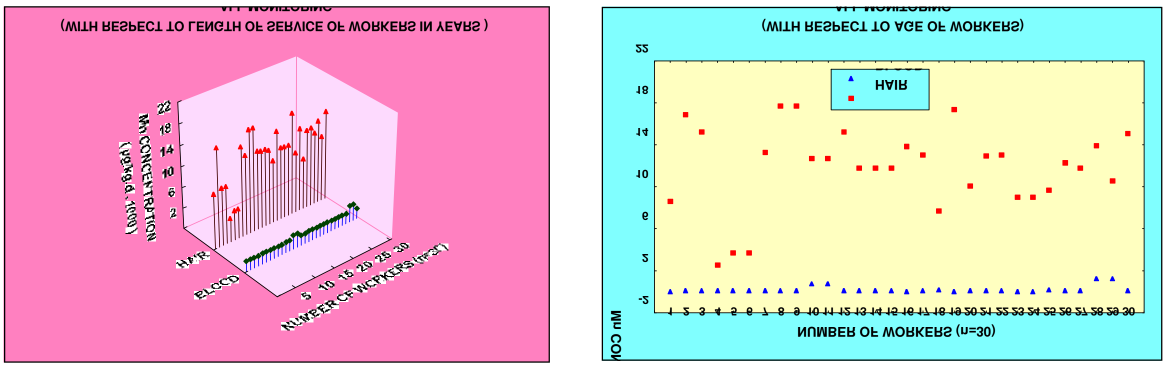

Fig. 6: Levels of transition metals in blood and hair of ferro-alloy workers manganese

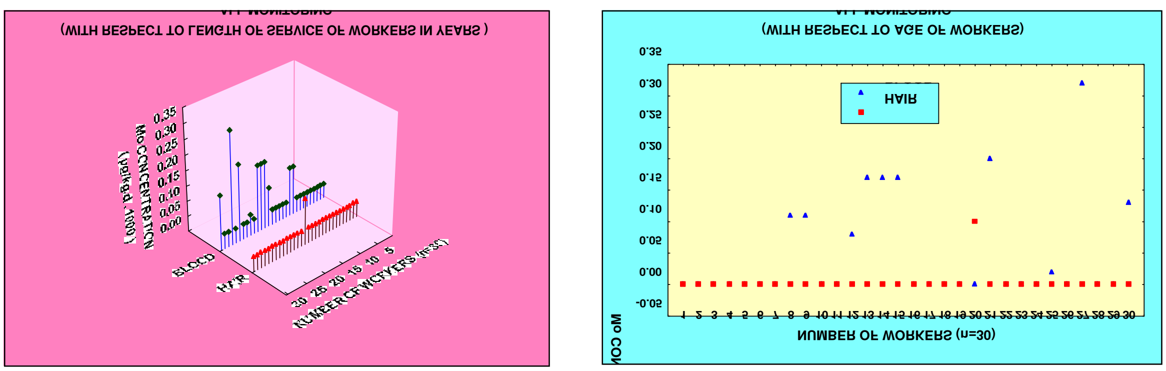

Fig. 7: Levels of transition metals in blood and hair of ferro-alloy workers molybdenum

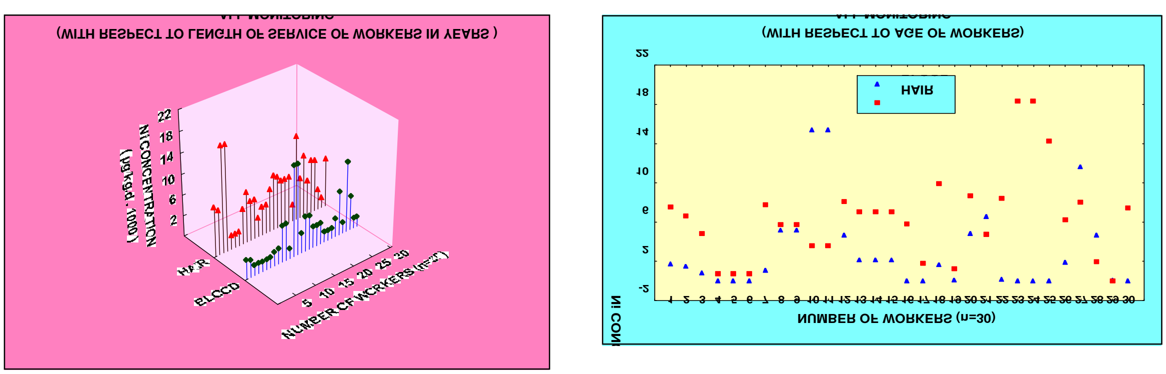

Fig. 8: Levels of transition metals in blood and hair of ferro-alloy workers nickel

Biological monitoring of the occupational (critical) population via blood and hair, reflecting the higher degree of exposure was carried out by identifying the workers in the critical population of the ferro-alloy factory based on the period of work and age. Total 30 workers were identified and three sets of sample were collected to check the reproducibility of the results in terms of metal concentrations.

Blood samples were collected in marked tubes containing EDTA (Ethylene di amine tetra acetic acid) as anticoagulant, properly sealed and were preserved in the icebox containing dry ice in the field and then brought to the laboratory for further analysis. Once the samples were allowed to equilibrate to room temperature microwave was adopted for sample digestion to ensure the completion of digestion and concentration. Digestion was carried out with 2 g of anticoagulated blood samples with addition of 6 ml nitric acid and 1ml of H_2O_2 in a Teflon-lined, high-pressure decomposition vessel in microwave furnace.

Hair samples of workers were collected from the proximal end of the scalp (specially from the occipitonuchal region), since recently grown and the first 1-5 mm of the proximal end of the hair from the scalp were considered as best while sampling. Hairs, free from external source of contamination were kept in properly numbered sealed plastics bags. Subsequently, finely cut 0.25 g hair samples were digested after washing with distilled water (Ryabuthin, 1980).

Results and Discussion

Several studies were carried out by different researchers to enumerate the levels of metals in blood and hair in workers working under different exposed and unexposed conditions related to different industries.

Snyder *et al.* (1975) estimated 36 μg Cd in the whole blood of 70 kg reference man and over 70% of the cadmium in the blood was bound to erythrocytes. Levels in whole blood of non-occupationally exposed persons were generally <10.5 μg/kg (median 1.6 μg/kg). Baddeley *et al.* (1983) found cadmium levels in blood > 11.07 μg/ kg in 6 of 57 exposed workers (10.5%) and 2 of 54 unexposed persons (3.7%). In general, levels of cadmium in blood were comparatively less than the liver. In the present study, cadmium concentration in blood was observed to be higher in the workers, since the source *i.e.* manganese ore for ferro-alloy workers constituted 16.8-93.6 mg/kg of cadmium with which the workers were directly in contact. The persons, working near the furnace, showed 9.7 mg/kg of cadmium in hair (with work period 5 years and age only 25 years), as depicted in Fig. 1. While small quantities of cadmium were recorded in hair (USEPA, 1980; Stokinger, 1981).

Cole and Carson (1980), reported mean values of cobalt in whole blood samples and blood fractions of unexposed individuals. It was observed to be 0.53-251 μg/kg in whole blood sample. In the present study, high levels of cobalt ranging from 1.37-5.35 mg/kg were reported in blood samples of ferro-alloy workers, whereas in hair, levels ranged from 1.97-10.2 mg/kg (Fig. 2).

Many of the researchers (Stokinger, 1981; Lauwerys, 1983) stated that although Cr levels in blood are of little or no relevance in monitoring exposure but with relatively high exposure levels (usually occupational), chromium levels in the blood cells provide indications of exposure to compounds of Cr(VI) and not Cr(III) (ASTDR, 1989). In hair, values reported in the range from 0.2 to 2.0 mg Cr/kg (Langard and Norseth, 1977). In ferro-alloy workers, the blood chromium were ranged from 0.02–0.57 mg/kg, whereas in hair chromium levels ranged from 2.3-10.9 mg/kg, as shown in Fig. 3. Higher values were observed in workers working near the furnace, involved in the process of smelting of ores.

It is reported that in normal blood samples copper concentrations in 243 adults from U.S. cities were observed to be in the range of 0.178 to 3.873 mg/kg. Levels were abnormally high in two cities (Billings, Montana and El Paso, Texas), where workers were working in copper smelters. During the study, the levels of copper in ferro-alloy workers were found to be about 0.4 – 2.1 mg/ kg, this might be due to the high inhalation uptake, since elevated concentrations were also observed in the ambient air of ferro alloy factory. In hair, copper concentration was observed in the range of 7.1–7.2 mg/kg in ferro-alloy workers, as graphically illustrated in Fig. 4.

Toxic signs are caused by free iron that appears after the carrier is saturated. Workers with iron pneumoconiosis had an average 1.6 mg Fe/kg in serum compared to 1.27 mg Fe/kg in non-exposed workers (Stokinger, 1981). The evidence in growing body also suggests that free iron in body fluids promotes bacterial growth. Therefore occupation that entail exposure to iron fumes of dust carry an increased risk of infection, which was also evident in the study, since the ferro alloy workers exposed to prolonged coal dust and iron exposure constituted high iron levels in blood (358–568 mg/kg and 210-805 mg/kg respectively) and were frequently encountered with diseases due to bacterial infections. In hair, levels of observed iron in the range of 103–1616 mg/kg in ferro alloy workers, as shown in Fig. 5.

Manganese concentrations were reported to be 25 times higher in the red blood cells than in the serum. Since a significant relation between manganese exposure and blood concentrations in workers was not found by earlier research groups, it is said that no correlation may be possible with the severity of chronic toxicity symptoms because of the differences in individual susceptibility (Lauwery's, 1983; Hamilton and Hardy, 1974). The most hazardous exposure occurs in mining and smelting of ores. In the present study, the levels of manganese in blood of ferro-alloy workers was found to be in the range from 0.04-0.95 mg/kg. Elevated levels of manganese in hair were observed in ferro-alloy workers with a high concentration range of 368-3379 mg/kg (Fig. 6).

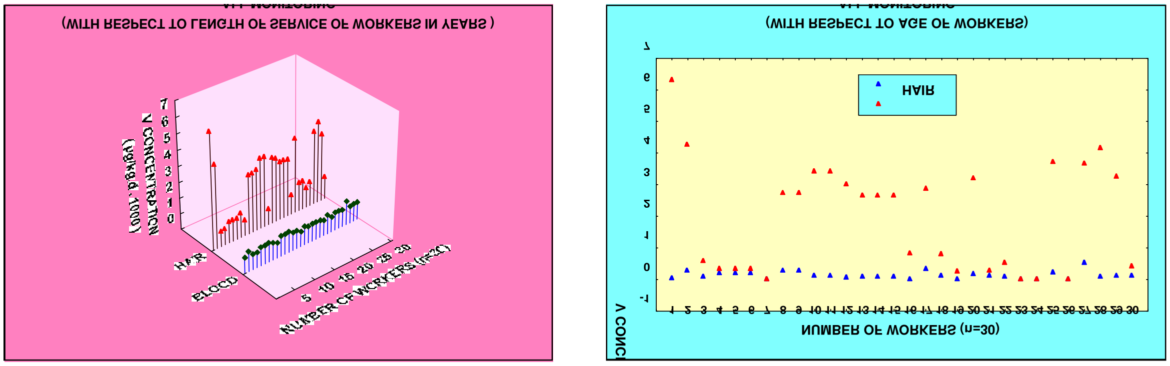

Fig. 9: Levels of transition metals in blood and hair of ferro-alloy workers vanadium

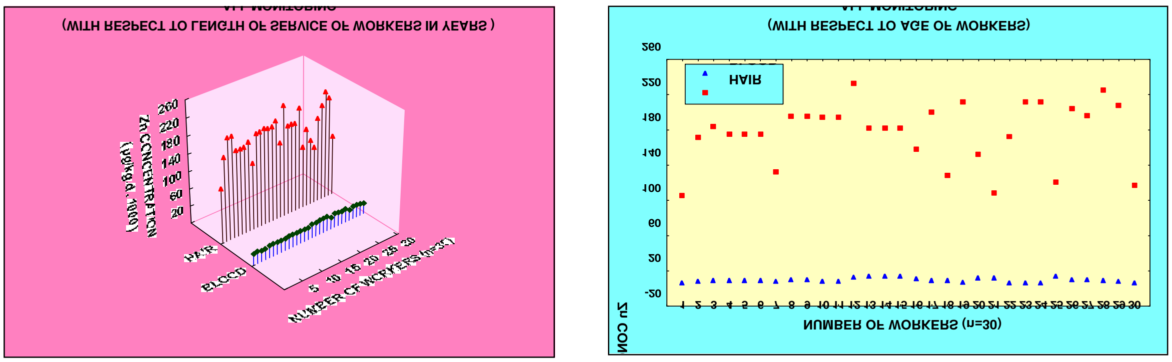

Fig. 10: Levels of transition metals in blood and hair of ferro-alloy workers zinc

In blood and hair, molybdenum levels were not detectable in ferro alloy workers as depicted in Fig. 7. However, normal mean blood values (detected in 48 of 229 samples) were reported as 5.2-166 mg/kg.

Levels of nickel in blood in ferro-alloy workers ranged from not detectable to 6.4 mg/kg. High levels of nickel *i.e.* 9.5 to 20.93 mg/kg with 10-12 years of exposure and age above 40 years were reported in workers working in direct contact with the smelting fumes. Level of nickel, in atmosphere around the ferro-alloy factory, was found to be as high as 960 mg/m^3 giving an inhalational uptake of 0.0065 µg/kg. This might be the reason for high concentration level of nickel in workers working in ferro-alloy factory. Nickel concentration in hair was found in the range of 5-48 mg/kg (Fig. 8).

In the present study, the levels of vanadium in blood of the ferro-alloy workers were observed from not detectable levels to 0.45 mg/kg due to high atmospheric vanadium, ranging from 100-300 mg/m^3 with inhalation uptake of 0.0027-0.0096 mg/kg at a duration of exposure more than 5 years. In hair, vanadium levels ranged from 1.7 to 10.0 mg/kg in ferro-alloy workers (Fig. 9) whereas, the levels of vanadium in unexposed persons were reported as 0.99 to 2.98 mg/kg.

The National Research Council report (1978) compiled extensive data on zinc concentrations in blood. The report concluded that 1.055 mg Zn/kg is the mean concentration in serum of both men and women while whole blood contained about five times higher concentrations of zinc, red cells contained about 10 times higher concentrations than that in the serum. Higher levels of zinc in hair is due to several factors, such as black colour of hair, use of cosmetics, shampoos, drug use, race and nationality like ethnic origin influences zinc levels in hair and the most important is the environmental factor (Briggs *et al.*, 1972). It was observed in the present study that zinc levels in blood of ferro-alloy workers ranged from 4-23 mg/kg due to elevated zinc levels in the atmosphere of plant area (5-50 µg Zn/m^3). The frequent deposition of zinc in hair might also be the reason for their elevated levels in hair varying from 72-326 mg/kg in ferro alloy workers with long duration of exposure (Fig. 10).

The study revealed the identification and quantification of the transition metals in blood and hair, which were present in ferro-alloys and prelude the toxicity levels imposed in the workers working in the factory due to long–term exposure as per the age group and working period

Acknowledgments

This study was supported by a Fellowship grant from Council of Scientific and Industrial Research, New Delhi. The authors sincerely thank to Dr. S. Devotta, Director, National Environmental Engineering Research Institute, Nagpur. Also the authors cordially thank to Instrumentation Division, NEERI for their enthusiastic help in sample measurement.

References

ATSDR.: Public Health Statement: Chromium (1989).

Baddeley, H., B.J. Thomas, B.W. Thomas and V. Summers: Liver cadmium concentrations in metal industry workers. *Br. J. Radiol.*, **56**, 449-451 (1983).

Cole, C.J., B.L. Carson: Cobalt in the food chain. *In:*Trace metals in the environment. Vol. 6-Cobalt (*Eds.*: I.C. Smith and B.L. Carson). Ann. Arbor, Michigan: Ann Arbor Science publishers, Inc. The Butterworth Group. Chapter 7. pp. 774-924 (1980).

Hamilton, A. and H. L. Hardy: Manganese, Industrial Toxicology, 3rd Edn., Publishing Sciences Group, Acton, 127 (1974).

Langard, S. and T. Norseth: Chromium. *In:* Toxicology of metals. Vol. II (*Ed.*: V.A. Springfield). National Technical Information Service. pp. 164-187, PB-268 324 (1977).

Lauwerys, R.R.: Chapter II. Biological monitoring of exposure to inorganic and organometallic substances. *In:* Industrial chemical exposure: Guidelines for biological monitoring (*Ed.*: C.A. Davis). Biomedical Publications. pp. 9-50 (1983).

Ryabukhin, T.S.: *In*: International coordinated program on activation analysis of trace elements pollutants in human hair. Hair trace elements and human illness (*Eds.*: A.C. Brown and R.G. Brown). Praeger Publication (1980).

Snyder, W.S., M.J. Cook, E.S. Nasset, L.R. Karhausen, G.P. Howells and I.H. Tipton: International commission on radiological protection. Report of the task group on reference man. New York. ICRP Publication 23 (1975).

Stokinger, H.E.: The metals. *In*: Patty's industrial hygiene and toxicology. 3rd Edn. Volume IIA (*Eds.:* G.D. Clayton and F.E. Clayton). New York - A Wiley-Interscience Publication. John Wiley and Sons. Chapter 29. pp. 1493-206 (1981).

Tseng, Chin-Hsiao: Metabolism of inorganic arsenic and non-cancerous health hazards associated with chronic exposure in humans. *J. Environ. Biol.,* **28**, 349-357 (2007).

USEPA.: Environmental Protection Agency. Ambient water quality criteria for cadmium. Springfield, VA: National Technical Information Service. PB81-117368 (1980).