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Short Communication

Chromium toxicity among leather industry workers in Kolkata – a Pilot Study

Maurya PK¹, Chakrabarti A¹, Saha A¹

¹Indian Council of Medical Research (ICMR) - Centre for Ageing & Mental Health, Block DP-1, Sector V, Salt Lake, Kolkata-700091, India

Corresponding author:

Pawan Kumar Maurya ICMR-Centre for Ageing & Mental Health, Block DP-1, Sector V, Salt Lake, Kolkata-700091, India

Telephone: +91-33-23674390

Email: <u>maurya.pk@icmr.gov.in</u>, <u>maurya_pawan@yahoo.com</u> ORCID ID:<u>https://orcid.org/0000-0001-6135-6578</u>

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ABSTRACT

Introduction: Chromium (Cr) exposure is known to cause various health issues such as cancer, dermatitis, respiratory problems, etc. The recent exposure of Cr can be determined by analysis of Cr either in blood/urine/plasma, Cr (III) ions cannot permeate through cell membranes of red blood cells (RBC) because their ionic radii are bigger as compared to Cr (VI), and hence Cr in RBC is an indicator for exposure to Cr (VI) ions. The purpose of this study was to investigate chromium exposure, hygienic habits and the occurrence of dermatological problems with leather industry workers in Kolkata.

Methods: A total of 68 leather industry workers with minimum work exposure of five years and aged between 18-60 years were recruited for this study. The study protocol included a questionnaire and analysis of Cr in blood and urine samples by GF-AAS.

Results: All values were under the Biological Exposure Index (BEI) of 25µg /L at the end of the shift of a five-day work week recommended by the American Conference of Governmental Industrial Hygienists (AcGIH). 15.2% of subjects suffered from dermatological problems at least once in the last year during work in the leather industry.

Conclusion: It was found that workers in the leather industry were not using personal protective equipment (PPE), and the use of PPE must be promoted to them for occupational health and safety.

Keywords: Chromium, Tannery, Atomic Absorption Spectroscopy, Dermatitis, Occupational Health

Introduction

Chromium (Cr) exists in oxidation states ranging from 0 to VI. Cr (III) is an essential micronutrient for humans.¹Cr (VI) (chromate), is genotoxic and a group I carcinogen for humans with sufficient evidence for inhalation and lung cancer. Cr (VI) enters the cells through anion transporters, whereas Cr(III) enters through passive diffusion; as such, extracellular reduction of Cr (VI).²Cr (VI) toxicity effects may involve oxidative stress, inflammation, energy metabolism, protein synthesis endocytosis, ion binding, DNA binding and metabolism, cell morphogenesis, cell cycle regulation, autophagy, apoptosis, cell death, and carcinogenesis in human bronchial epithelial cells.³ Chromium Sulphate is primarily used in the leather industry for tanning and processing. Finished leather is obtained by treating animal hides and skins with basic chromium sulfate, in order to modify the macromolecular structure of collagen and make them suitable for use. It is also used in the synthesis of other chromium-based retanning agents and the production of chromic compounds.⁴

It is estimated that 90% of the leather produced worldwide is tanned with chromium sulfates, the consequence being that chromium exposure may occur from prolonged contact with various leather production processes and products.5 Biological monitoring of any environmental toxicant is important to confirm the exposure either by estimating the toxicant as such or its metabolites in the body, to detect early signs of the onset of the disease, and also to prevent the further progress of the disease among occupationally exposed workers.6 American Conference of Governmental Industrial Hygienists (ACGIH) recommendation for the Threshold Limit Value-Time Weighted Average (TLV-TWA) exposure limit value of 0.5 mg Cr/m³ for chromium metal and Cr (III) compounds, 0.05 mg Cr/m3 for Cr (VI) and 0.01 mg Cr/m3 for insoluble Cr (VI) corresponds to a concentration accumulated over either an 8-h workday or a 40h working week.7-8 In India, the effect on environmental and human health of Cr contamination is reviewed and in a study blood Cr levels of children working in gem-polishing industries were studied.9-11

Maintenance of normal skin barrier function, in occupational settings, is important due to direct contact of various hazards with the skin that might induce skin disease or result in skin absorption of chemicals. Due to Cr (VI) in leather tanning and other processes in leather goods production, skin diseases including irritant and allergic contact dermatitis are common among leather industry workers.¹²⁻¹⁴ The purpose of this study was to investigate chromium exposure, hygienic habits, and the occurrence of dermatological problems among leather industry workers.

Methods

The selected area of the study was Kolkata, the capital of the Indian state of West Bengal. Kolkata

metropolitan area has a population of 1.41 million, according to the 2011 Indian census. West Bengal, particularly Kolkata and its suburbs has developed tremendously into a highly successful Leather & Leather Goods Export Hub from India within a short span of three decades.

A total of 68 leather industry workers with minimum work exposure of five years and aged between 18-60 years were recruited for this study. This Study is approved by the Human Ethics Committee of the Institute. The study protocol included a questionnaire and analysis of blood and urine samples by GF-AAS.

History of occupational exposure, demographic details, and history of skin problems during their different years of occupation was collected through an interview-administered questionnaire. Dermatitis was decided by the self-reported diagnosis of the occurrence of skin lesions by leather industry workers.¹⁵

All chemicals used in the study were of analytical grade or higher. Chromium standard for AAS, NaCl. Triton X-100 was obtained from Sigma Aldrich. Triton X-100 was used as a non-ionic surfactant.0.2% Nitric acid (v/v) was obtained after dilution with ultrapure water obtained by the Merck Synergy water purification system.

Perkin Elmer AA-800 (Waltham, MA, USA) graphite furnace atomic absorption spectroscopy (GF-AAS) was used for Cr analysis. A Zeeman correction was applied for checking the matrix effect. Analysis of Cr was performed at 357.9 nm using a hollow cathode Cr lamp (Perkin Elmer Lumina Lamp). The Lamp was operated at 3 mA and slit-width was kept at 0.05 cm. Graphite tubes (Perkin Elmer THGA Graphite Tubes, Part No.:B3 000641were used for experiments.

Blood samples of subjects were collected by venipuncture and taken in heparinized tubes. The collected samples were brought to the laboratory and kept in a deep fridge at -20 °C. Spot urine samples were collected from the exposed workers before starting the work in the morning (Pre-shift) and also at the end of the shift (Post-shift). The samples were collected in polythene bottles,

brought to the laboratory, and preserved in a deep fridge at -20 °C. To check errors due to sample contamination it was important to clean plastic wares thoroughly. This was achieved by keeping plastic materials in 20% nitric acid for a minimum of 12 h and rinsing three times thoroughly with ultrapure water before use for sample collection. The extract of the fourth was tested with AAS for the absence of Cr and this ensured three times rinsing of plastic wares removed chromium contamination. The blood of subjects was collected by drawing into metal-free Vacutainer tubes (10 mL capacity) supplied by BD Biosciences.

The Standard solution of Cr was 1000 mg/L. 1, 2, 5, 10, 15, and 20 mg/L working standards of Cr for the calibration curve were prepared by appropriate dilution with 2% v/v HNO₃ and 1.0% v/v Triton X-100 solution (Diluent-D).

Analysis of Cr in whole blood and urine samples was performed by the method reported by Devoy et.al with slight modifications to their reported method.⁸ Blood sample (100 μ L) was diluted by a factor of 1:5 by Diluent-D and the urine sample (100 μ L) by a factor of 1:2 by Diluent-D. To analyze Cr in RBC, 1000μ L of blood was left for 60 min at 25°C to allow separation of blood into two fractions viz. A and B: Fraction A, the supernatant (without RBC); and fraction B (with RBC). Fraction B was diluted with 3000 µL of saline solution (1%) and left to stand at room temperature for 20 min, and then centrifuged for 20 min at 3000 rpm. This procedure was repeated three times for sample clean-up with 3000 µL of 1% saline solution. RBC pellet was diluted to 1000 µL and further diluted by a factor of 1:5 by Diluent-D.

Data analysis of the study was performed with SPSS statistical software for windows. Mean \pm S D was calculated in the report.

Results

The sample size, age range, and level of chromium exposure in leather industry workers are presented below (Table 1).

15.2% of subjects suffered from dermatological problems at least once in the last one year during work in the leather industry. The distribution of Cr levels in total blood, RBC and urine of dermatitis patients and healthy subjects are shown below (Figure 1).

Sample	Age	Level of chromium in	Level of chromium	Level of chromium in urine
size	range	whole blood (µg/L)	in RBC (µg/L)	(µg/L)/Specific Gravity
		Mean±SD	Mean±SD	Mean±SD
		Range	Range	Range
		8.37±6.39	3.91±2.81	7.15±5.72
68	18-60			
		1.04-24.83	1.01-17.26	1.07-25.00

Table1: Sample size, age range, and Level of chromium in leather industry workers.

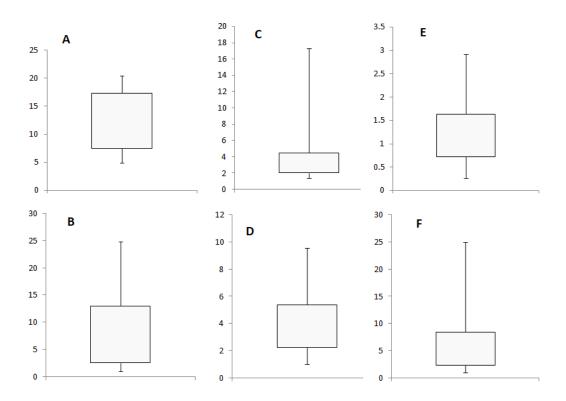


Figure 1: Distribution of Cr level in total blood of dermatitis patients (A) and healthy subjects (B); distribution of Cr level in RBC of dermatitis patients (C) and healthy subjects (D); distribution of Cr level in urine of dermatitis patients (E) and healthy subjects (F).

Discussion

Cr in urine is considered a trustworthy and sensitive indicator of Cr exposure. Analyzing Cr by AAS cannot give information on exposure by Cr (III) or Cr (VI), speciation is possible only by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). However, by analyzing Cr in RBC it is possible to indirectly measure the Cr (VI). Cr (III) ions cannot permeate through cell membranes of red blood cells (RBC) because their ionic radii are bigger as compared to Cr (VI), and hence Cr in RBC is an indicator for exposure to Cr (VI) ions.8 In this study Cr (VI) exposure was assessed by GF-AAS. Differences in urinary dilution were corrected by measuring the specific gravity of urine, which is the ratio of the relative density of urine to water.16

This study gives information about Cr exposure in leather industry workers in Kolkata. All results showed BEI under the AcGIH limit of $25\mu g$ /L at the end of the shift of a five-day workweek. AcGIH does not recommend BEI values for Cr exposure in whole blood or RBC. In this study, Cr exposure was detected in whole blood, RBC and

urine. RBC Cr is indicative of permeation of Cr (VI) ions through RBC and it will be available for detection till the cell lives (3 months or more).

Direct exposure to Cr and its complexes to the skin triggers dry skin, irritation and allergic reaction to the skin due to the cytotoxic properties of Cr; this may be diagnosed as irritant dermatitis. The immune system of the body may also respond in the form of inflammation due to Cr and this may be diagnosed as contact dermatitis. Contact dermatitis is triggered in two phases, in the first phase skin-Cr interaction happens and this step is known as the induction step whereas in the second phase immune system of the body responds in form of inflammation and this step is known as sensitization. For sensitization, a certain level of Cr exposure is required and this level is known as the threshold level.¹⁷

It was also found that leather industry workers were not using personal protective equipment during their work, which was against occupational safety and exposing their skin directly in contact with Cr and triggered dermatitis.

Conclusion

All results showed BEI under the AcGIH limit (25µg /L at the end of shift of a five-day work week), but AcGIH does not recommend BEI values for Cr exposure in whole blood or RBC.BEI for blood level Cr may be included by AcGIH, this will give information on exposure to Cr(VI). Workers were not using personal protective equipment during their work, which expose them to Cr and may lead to the dermatological problem. However, this was a pilot study and further study with a statistically appropriate sample size should be conducted for complete information. Meanwhile, workers should use personal protective equipment for occupational health and safety.

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