J. Chemtracks 27 (1&2) 345-350, 2025 Abstracted / Indexed in
A division of the American Chemical Society
Chemical Abstract U.S.A.
ISSN 0973-239X
CODEN:JCOHF7
IMPACT FACTOR : 7.866

Hair and nails as biological indices of exposure to metals

Mahaveer Parihar
Acoustic and Environmental Laboratory
Department of Pure and Applied Chemistry
Maharshi Dayanand Saraswati University Ajmer (Rajasthan, INDIA)
Email : mahaveerparihar336@gmail.com

Manuscript received online 24 September 2025, accepted on 24 December 2025

Abstract : Metal determination in human tissues is a prime application of biological monitoring. The diseased status of exposed human population can be ascertained using biological tissues as diagnostic tools making biomonitoring an important field of research. This paper deals with quantitative determination of Cadmium in hair of male subjects exposed to the metal in workplace alongwith the controls. The concentration of cadmium was assayed by Atomic Absorption Spectrophotometry and results were interpreted in view of the personal and medical details of the subjects chosen for investigation. Significantly high values of Cadmium were present in smokers as compared to non-smokers.

(Keywords : Cadmium, Atomic Absorption Spectrophotometry, Smokers, exposure).

Introduction

Technological advancement and the extensive use of chemicals, especially in metallurgical and chemical industries, have led to a gradual redistribution of various elements from the Earth's crust into the biosphere. Metal particles are often small enough to reach deep into the lungs by being relatively more absorbed. Urban-industrial air may contain metals like Cd, Hg, Pb,Ni, Zn and As[1-4]. Surface and groundwater sources may contain dissolved gases, salts, and trace metals. Toxic metals are present in trace amounts in saline waters of sea. The composition of the soil is influenced by the geological composition of parent rock and altered by human activities. Biological monitoring refers to assessing the presence of harmful agents in humans to know the extent of exposure in immediate environment alongwith facilitating determination of reference levels. Compared to environmental monitoring, biological monitoring offers a broader and more accurate assessment[5].

To measure metal accumulation in humans, biological samples such as fluids and tissues are commonly used. Scalp hair is significant as biological indicator for metal load evaluation, as it possesses a remarkable ability to accumulate and retain toxic elements over time[6]. Hair and nail tissues store trace elements over time, reflecting post exposure and nutritional history. Their non-invasive collection and higher concentrations of trace elements make them ideal for long-term monitoring[7]. Maugh observed that trace elements accumulate in hair at levels significantly higher than in blood or urine[8]. Selecting an appropriate analytical technique for evaluating the concentrations of metals in biological tissues depends on several critical factors: the sensitivity, precision, and accuracy of the method; whether single or multiple elements need to be measured; time efficiency; and cost considerations. Among these, AAS has become particularly favoured due to its ease of operation, specificity, broad dynamic range, speed, and high sensitivity. It quickly surpassed other techniques and became widely used. Furthermore, organizations like IAEA and WHO have played an essential role in standardizing

hair analysis methods. For various trace elements in hair certified values to ensure reliable and accurate data interpretation have been developed.

Cadmium is widely utilized in various industrial applications, including the manufacture of low-melting alloys, soft solders, electroplating and as a deoxidizer in nickel plating and engraving processes. In electrodes cadmium is used for vapor lamps and photoelectric cells, nickel–cadmium (Ni–Cd) storage batteries and in industries such as iron and steel production, phosphate fertilizer manufacturing and zinc smelting[9]. High concentrations of cadmium (Cd) in soil and water can lead to its significant accumulation in food crops. Plants generally exhibit a higher tolerance to cadmium than mammals, which facilitates its bioaccumulation and biomagnification through the food chain[10-12]. Cadmium absorbed through the lungs or intestinal tract is initially deposited in the liver, where it binds to metallothionein, a low-molecular-weight protein with a strong affinity for cadmium, zinc, and copper. Over time, Cd–metallothionein complexes are transported to the kidneys, leading to the accumulation of cadmium primarily in the renal cortex. Cadmium is a non-essential and highly toxic metal with no known physiological function in humans. It has adverse influence on the body systems regardless of the route of exposure - ingestion, inhalation, or injection. Acute Cd toxicity may manifest as nausea, abdominalissues, shortness of breath, headache, fever and choking fits.

Experimental

Hair and fingernails were sampled from male workers employed in Automobile Workshops, Locomotive Workshops, Jewellery Manufacturing Units and Metal Finishing Workshops to evaluate occupational exposure to cadmium. Age- and sex-matched controls with no metal exposure were also included. Each participant completed a detailed questionnaire covering personal, environmental and medical history to aid in sample classification during data analysis.Washing of samples was done with Triton X-100, deionised water and acetone,then dried and subsequently digested using a wet acid digestion method to obtain a clear aqueous solution.Cadmium levels were obtained using AAS ECIL-4129 (Atomic Absorption Spectrophotometer). The Cd lampwas operated at a wavelength of 228.8 nm, lamp current of 4 mA and spectral bandwidth of 0.5 nm, with an integration time of 3 seconds per measurement. AAS was calibrated by diluting a 1000 ppm Cd stock solution to various concentrations and determining their concentrations. Each standard was subjected to similar conditions as the samples, and a calibration curve was constructed by plotting absorbance against concentration. The system sensitivity under standard conditions was approximately 0.02 µg/mL Cd for 1% absorption.

Results and Discussion

Cadmium levels in fingernails and hair of male subjects from different occupational environments were evaluated across varying age groups and exposure parameters.Table 1 presents the mean Cd levels and standard deviations in both tissues as a function of age. Cd levels showed a gradual decrease followed by increase from 11-20 to 50-60 years age group. However, Ashraf et al[13] observed no consistent age-related pattern in Cd concentrations, whereas Petering et al[14] reported that Cd in male hair increased up to 20 years of age and remained stable or slightly declined thereafter.The mean Cd concentrations and standard deviations in the biopsy materials of workers from various occupations such as Automobile Workshops, Locomotive Workshops, Jewellery Manufacturing Units and Metal Finishing Workshops are summarized in Table 2. Comparative analysis between the tissues revealed that Cd levels were relatively more in nail samples than in hair, consistent with previous observations[15]. This difference can be partly attributed to the effect of hair treatments

and washing practices that may remove trace quantities of metals like Ni, Pb, and Cd, resulting in relatively lower levels in hair. Overall, workers occupationally exposed to metal-rich environments exhibited higher Cd concentrations in both tissues. However, not all occupational categories showed statistically significant differences. Bustueva et al[16] have reported high Cd levels in workers from lead battery manufacturing units.

Table-1
Range and mean cadmium levels (μg/g) in hair and finger nails of subjects of varying age groups

Age in years	No. of samples	Hair		Fingernails	
		Range(μg/g)	Mean± SD(μg/g)	Range (μg/g)	Mean± SD (μg/g)
11-20	47	0.02-4.49	1.34 (1.32)	0.28-7.23	4.60 (2.47)
21-30	77	0.02-4.17	0.62 (0.79)	0.60-7.82	4.17 (2.08)
31-40	71	0.03-4.63	0.89 (1.10)	0.22-6.56	3.50 (2.33)
41-50	79	0.02-3.73	0.55 (0.93)	0.35-6.71	4.36 (1.14)
51-60	66	0.02-15.64	1.17 (2.12)	0.28-7.34	4.59 (2.11)

Table 2
Range and mean cadmium levels (μg/g) in hair and finger nails of subjects with different occupational exposure.

Subjects	Age in years	No. of samples	Hair		Fingernails	
			Range(μg/g)	Mean± SD (μg/g)	Range (μg/g)	Mean± SD (μg/g)
Control	11-30	22	0.02-4.39	0.56 (1.39)	0.28-8.22	1.39 (2.46)
Automobile Workshop	11-30	24	0.06-2.78	1.67 (0.88)*	0.62-6.09	2.90 (2.44) *
Locomotive Workshop	11-30	23	0.02-3.18	1.77 (0.90)*	0.62-6.81	3.86 (2.00) *
Jwellery Manufacturing Units	11-30	26	0.02-2.94	1.52 (0.73)*	0.59-6.81	2.66 (2.03)
Metal Finishing Workshops	11-30	29	0.05-4.49	1.25 (1.25)	0.59-7.82	3.02 (2.32) *
Control	31-60	41	0.02-2.33	0.52 (0.62)	0.29-6.93	1.93 (2.22)
Automobile Workshop	31-60	43	0.03-3.94	1.64 (1.06) *	0.30-6.81	3.49 (2.41) *
Locomotive Workshop	31-60	42	0.02-2.49	1.46 (0.65) *	0.63-6.81	3.69 (1.71) *
Jwellery Manufacturing Units	31-60	46	0.02-15.64	1.29 (2.50)	0.22-7.34	3.55 (2.21) *
Metal Finishing Workshops	31-60	44	0.09-3.92	1.85 (0.93) *	0.62-6.95	3.63 (1.95) *

*Values significant at $P<0.05$ level

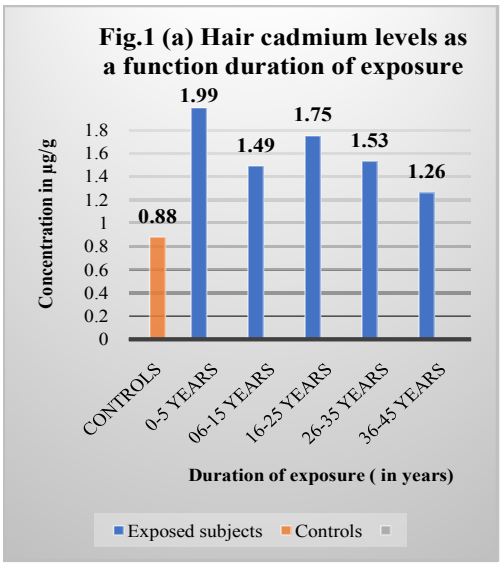


Fig.1 (a) Hair cadmium levels as a function duration of exposure
Concentration in µg/g
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0.88
1.99
1.49
1.75
1.53
1.26
CONTROLS
0-5 YEARS
06-15 YEARS
16-25 YEARS
26-35 YEARS
36-45 YEARS
Duration of exposure (in years)
Exposed subjects
Controls

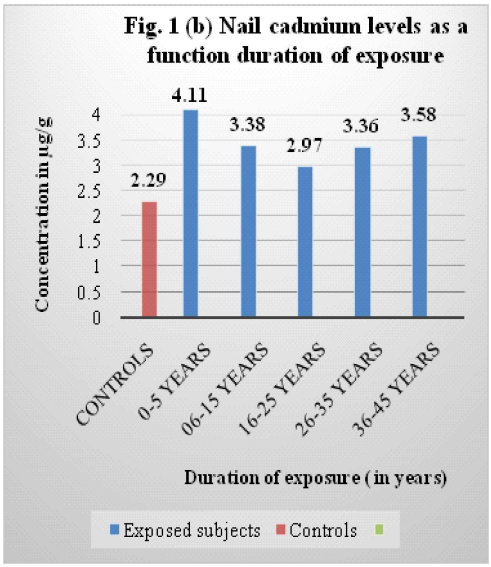


Fig. 1 (b) Nail cadmium levels as a function duration of exposure
Concentration in µg/g
4
3.5
3
2.5
2
1.5
1
0.5
0
2.29
4.11
3.38
2.97
3.36
3.58
CONTROLS
0-5 YEARS
06-15 YEARS
16-25 YEARS
26-35 YEARS
36-45 YEARS
Duration of exposure (in years)
Exposed subjects
Controls

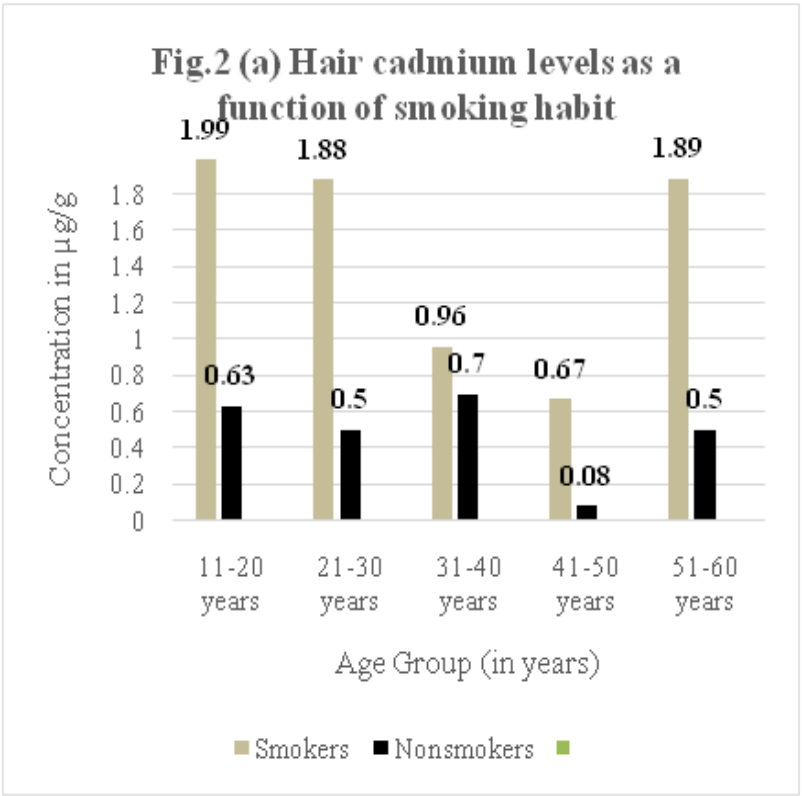
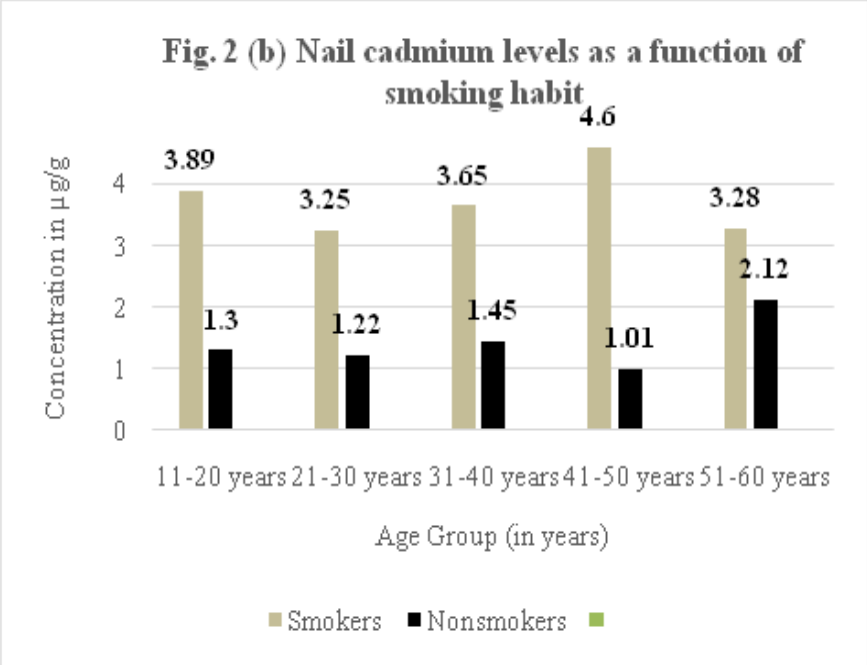


Fig.2 (a) Hair cadmium levels as a function of smoking habit
Concentration in µg/g
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1.99
0.63
1.88
0.5
0.96
0.7
0.67
0.08
1.89
0.5
11-20 years
21-30 years
31-40 years
41-50 years
51-60 years
Age Group (in years)
Smokers
Nonsmokers



In Fig. 1 (a) & 1 (b)] categorizes exposed and unexposed individuals into five exposure duration groups 0-5, 6-15, 16-25, 26-35 and 36-45 years, excluding outliers. Results demonstrated a clear increase in Cd concentrations in nail samples with prolonged exposure duration except 6-15 & 16-25 years. No consistent trend was observed in hair sample

Differences in Cd levels among exposed subjects were found to be significant when subjected to appropriate statistical methods. The results infer that body burden of Cd, as reflected by the analysis, correlates with environmental or occupational metal exposure. Cd is taken up primarily via inhalation of workplace fumes and ingestion through contaminated food and water. The overall low concentrations observed suggest that Cd is not abundantly present in the surrounding environment.

Fig. 2 (a) and 2 (b) summarizes Cd concentrations in relation to smoking habits across age groups. No definitive age-related pattern was evident; however, mean Cd levels were higher in smokers compared to non-smokers. Sukumar and Subramanian[17] have reported similar results. Statistical analysis (Student's *t*-test) confirmed that Cd concentrations in hair and nails were significantly influenced by smoking habits.

Similar results are found by several researchers[18-23]. Lekouch et al[24] found elevated Cd levels in the hair of smokers (3.5 ± 1.1 µg/g) relative to non-smokers, though differences were statistically nonsignificant. Hartwell et al[25] observed significant increases in Cd levels in both hair and blood of smokers. Rauhamaa et al[26]estimated that smoking one pack of cigarettes per day results in the inhalation of approximately 0.9 µg Cd daily. Conversely, Moon et al[24] and Ahmed &Elmubarakfound no significant impact of smoking on hair Cd concentrations.

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