ARTICLE IN PRESS

Journal of Trace Elements in Medicine and Biology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Trace Elements in Medicine and Biology

journal homepage: www.elsevier.com/locate/jtemb

Toxicology

# Assessment of hair metal levels in aluminium plant workers using scalp hair ICP-DRC-MS analysis

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ARTICLE INFO

*Keywords:*
Primary aluminium production
Exposure
Cadmium
Lead
Arsenic
Risk

ABSTRACT

The objective of the present study was to assess the level of aluminium and toxic metals in hair of workers occupationally exposed to aluminium. 124 employees of the aluminium plant working in the hydrometallurgical (n = 43) and sintering units (n = 41), as well as 40 occupationally nonexposed controls were examined. Hair aluminium (Al), arsenic (As), beryllium (Be), cadmium (Cd), mercury (Hg), nickel (Ni), lead (Pb), and tin (Sn) content was assessed using inductively-coupled plasma mass spectrometry. The obtained data demonstrate that aluminium plant workers had significantly higher levels of hair Al (28.8 (15.4–58.6) vs 7.8 (4.3–14.2) μg/g, $p < 0.001$), Cd (0.053 (0.032 – 0.095) vs 0.025 (0.014 – 0.043) μg/g, $p < 0.001$) and Pb (0.672 (0.299–1.310) vs 0.322 (0.170 – 0.609) μg/g, $p = 0.012$) than the controls, respectively. Further analysis demonstrated that persons involved in different technological processes were characterized by distinct hair metal profiles. Hair Al, Be, Cd, Ni, Pb, and Sn levels in men working in the sintering unit of the aluminium plant exceeded the respective control values. In turn, workers of the hydrometallurgical unit were characterized by more than 2-fold higher levels of Al and Cd in hair as compared to the controls. The results of the present study demonstrate that workers of the aluminium plant are characterized by increased risk of Al as well as As, Cd, Pb, and Sn exposure.

## 1. Introduction

Aluminium is the widespread metal comprising 8.23% of the Earth's crust by weight [1]. Due to its physical and chemical properties it is widely used in various fields of modern industry including construction, food production, electronics, pharmacy, etc. [2]. Production of aluminium (both primary and secondary) is increasing worldwide [3]. In particular, global consumption of aluminium has increased from 29 Mt in 1994 to 45 Mt in 2004. The top-5 consumers of Al are USA, China, Japan, Germany, and Russia. In turn, the main producers of bauxite and alumina are Australia, Brazil, and China. Kazakhstan is also rich in bauxite reserves and its production [4].

In 2007, bauxite reserves in Kazakhstan were estimated to be 200 Mt, accounting for 1% of total value worldwide. At the same time, the total value of bauxite produced in Kazakstan accounted for 3% of global production (4.7 Mt) [4,5].

At the same time, aluminium exposure also has a significant adverse effect on human health [2] due to its prooxidant, proinflammatory, excitotoxic and immune-modulatory properties [6]. The growing body of data demonstrate that aluminium may have neurotoxic effects [7]. However, association between Al exposure and Alzheimer's disease or autism is still questionable [8]. Moreover, the existing studies demonstrate a link between aluminium and breast cancer [9]. Evidence on the association between occupational aluminium exposure and pulmonary fibrosis [10], lung cancer [11], and neurological dysfunction [12] exist. Therefore, monitoring of human exposure to aluminium is of great importance.

Hair is widely used for biomonitoring of metal exposure due to a number of advantages like high mineralization and irreversible incorporation of metals into hair matrix [13]. In contrast to blood and urine, where metal levels are strictly regulated by homeostatic mechanisms [14], hair may be used for assessment of exposure history for several months due to accumulation of metals [15]. In addition, due to ability to absorb metals from environment hair may be used in biomonitoring studies [16]. Previous data demonstrate that hair may be used as a valuable marker of occupational exposure to metals and

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https://doi.org/10.1016/j.jtemb.2018.06.014
Received 7 September 2017; Received in revised form 14 June 2018; Accepted 15 June 2018
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Please cite this article as: Skalny, A.V., Journal of Trace Elements in Medicine and Biology (2018), https://doi.org/10.1016/j.jtemb.2018.06.014

metalloids [17,18]. Moreover, the hair metal level was also shown to be associated with adverse health effects in occupationally exposed persons [19].

Taking into account the toxic effects of metal co-exposure [20], other toxic metals should be also monitored in persons exposed to aluminium. Therefore, the objective of the present study was to assess the level of aluminium and other toxic elements in hair of persons occupationally exposed to aluminium.

## 2. Materials and methods

The protocol of the present investigation was approved by the Local Ethics Committee. The sampling and experimental procedures were performed in agreement with the principles of the Declaration of Helsinki and later amendments. All participants have provided informed consent prior to the examination.

A total of 124 men took part in the present study. 84 employees of the aluminium plant in North-Eastern Kazakhstan working in the hydrometallurgical (n = 43) and sintering units (n = 41) of the plant presented the occupationally exposed groups. Briefly, the main technological process in the hydrometallurgical unit is the production of alumina from bauxite using the Bayer process. In turn, sintering unit performs recovery of alumina from Bayer red mud [21]. In 2012, the total amount of bauxite, aluminium oxide, and aluminium produced by the studied plant was 5.17, 1.51, and 0.249 Mt [5]. 40 healthy men living in more than 1.0 km from the plant in the north-western part of the city and not involved in industrial processes were used as the occupationally non-exposed controls (Fig. 1). The examinees in all groups were age- and body mass index (BMI)-matched to prevent the influence of ageing [22] and obesity [23] on hair metal levels. Age and BMI in the controls, hydrometallurgical and sintering unit workers were 36.6 ± 10.2 years and 24.7 ± 3.5 $kg/m^2$, 36.3 ± 11.1 years and 24.5 ± 4.4 $kg/m^2$, and 36.0 ± 11.3 years and 24.3 ± 5.2 $kg/m^2$, respectively. No significant difference in working experience between the hydrometallurgical (11 ± 6 years) and sintering unit (9 ± 5 years) workers was detected. In addition, to avoid the influence of side factors on hair metal levels, the following exclusion criteria were used: i) current and former smoking; ii) excessive alcohol consumption; iii) acute and chronic infectious diseases (including gastritis that requires the use of alumunium-containing antacids); iv) surgical and traumatic diseases; v) metallic implants (including dental amalgams); vi) endocrine disorders; vii) vegetarianism and other specific dietary patterns (including the use of herbs that may be the source of alumunium); viii) dyed hair. Therefore, only healthy workers of aluminium plant and control persons were enrolled in the current study. Data on health condition are collected yearly during mandatory physical examination.

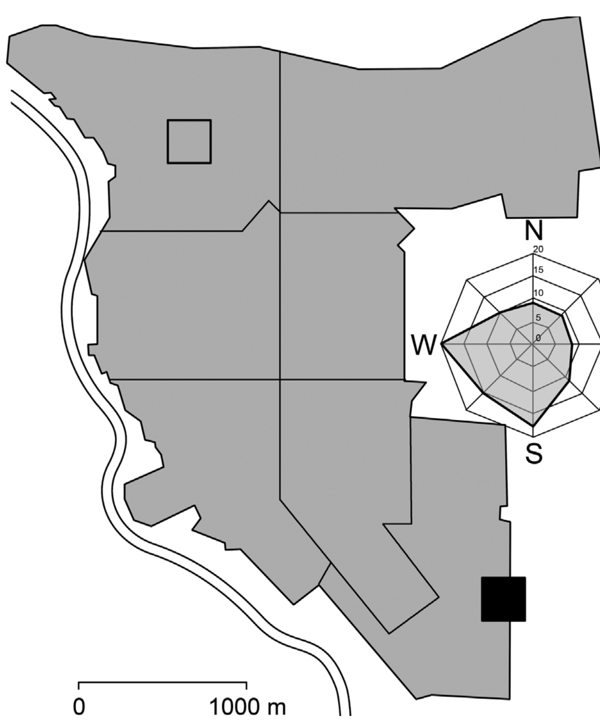


**Fig. 1.** Location of the aluminium plant (filled box) and the areas of control species sampling (empty box).

The aluminium plant is the one of the ten largest producers of alumina in the world. The plant produces up to 1.7 million tons of metallurgic alumina that is exported to China and Russia. At the moment of investigation, the total number of employees of aluminium plant was 6,117, whereas 1262 of them were working in hazardous conditions. The system of health protection and safety is implemented in the plant. All employees are equipped with personal protective equipment: coveralls, safety shoes, gloves, helmet, balaclava, protective goggles, respirator, safety belt, dielectric bots, antinoise headphones (all protective equipment is certified No. KZ 41400285, No KZ 41400348). The overalls are cleaned by the plant's laundry. All units are equipped with the sanitary facilities (wardrobe, shower room, dining room). The collective protective equipment includes aspiration and exhaust ventilation systems, noise protection system, as well as system of prevention of electrical damage. All persons working in hazardous conditions receive milk that is widely used for health protection in hazardous occupational conditions, as well as detergents (soap, powders). All protective activities are controlled by internal and external commissions.

Indoor atmospheric pollution is regularly monitored by the environmental laboratory and the data obtained are compared with the existing maximum permissible concentrations (MPC). The results of monitoring demonstrate that the rate of indoor environmental pollution is within the limits provided by national regulations (Table 1).

All employees are provided with similar meals in the dining room. The dining room is equipped with ceramic dish and stainless steel kitchen utensils, whereas the use of aluminium utensils is avoided. Tap water is used for drinking and preparation of meals. Systematic analysis of tap water demonstrates that the level of the studied metals is lower than MPC [24].

Hair sampling was performed after regular mandatory physical examination of the workers that excluded occupational and non-occupational pathology. All examinees have washed their hair at the day of sampling using their usual commercially available shampoos. Despite different chemical composition of shampoos, their use did not significantly affect hair metal content [25]. Occipital scalp hair samples were collected using ethanol-precleaned stainless scissors. Only proximal parts of strands were used for analysis. Prior to digestion, the hair samples were subjected to washing with acetone with subsequent rinsing with distilled deionized water for three times and drying in the air (60 °C). The existing data demonstrate that such type of washing procedure removes mechanical contamination (dust) but does not remove metals bound to hair matrix [26].

A total of 50 mg of washed hair samples were introduced into Teflon tubes containing concentrated nitric acid ($HNO_3$). Digestion procedure was performed in Berghof Speedwave 4 (Berghof Products & Instruments, Germany) system at 170–180 °C for 20 min. The obtained

**Table 1**
Data on atmospheric pollution monitoring of the working environment.

| Parameter | MPC | Hydrometallurgical unit | Sintering unit |
|---|---|---|---|
| Alkaline aerosol ($mg/m^3$) | 0.5 | 0.14 ± 0.04 | 0.14 ± 0.06 |
| Abrasive dust ($mg/m^3$) | 6 | 2.8 ± 0.9 | 3.3 ± 1.2 |
| Metal dust ($mg/m^3$) | 10 | 2.3 ± 0.8 | 4.1 ± 1.5 |
| Alumina dust ($mg/m^3$) | 6 | 3.8 ± 2.0 | 5.4 ± 2.1 |

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