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Arsenic exposure levels in relation to different working departments in a copper mining and smelting plant

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HIGHLIGHTS

- The highest urinary levels of iAs, MMA and DMA all were found in copper smelters.
- Workers engaged in electrolytic procession had higher urinary iAs% and lower PMI.
- Different working departments increased the risk of TAs exceeded BEI after adjusting confounders.
- Seafood and years of employment may influence SMI.

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ABSTRACT

The investigation was carried out to evaluate arsenic exposure and the urine metabolite profiles of workers with different working departments, including administration (Group1), copper ore mining (Group2), copper ore grinding (Group3), electrolytic procession (Group4) and copper smelting (Group5) in a Copper mining and processing plant in China. Information about characteristics of each subject was obtained by questionnaire and inorganic arsenic (iAs), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) in urine were determined. The highest urinary levels of iAs, MMA and DMA all were found in the Group 5. Group 4 workers had a higher iAs% and a lower PMI compared to Group 3. The urinary total As (TAs) levels of 54.7% subjects exceeded 50 μg/g Cr, and the highest percentage (93.3%) was found in Group 5, smelters. The results of the present study indicate that workers in copper production plant indeed exposed to As, especially for smelters and workers of electrolytic process.

1. Introduction

Inorganic arsenic (iAs) exposure is a significant problem and potential occupational hazard in copper mining and smelting. Several epidemiologic studies showed that exposure to arsenic (As) increased lung cancer risk among the copper smelter workers (Jarup et al., 1989; Enterline et al., 1995; Lubin et al., 2000). Arsenic has been classified by the International Agency for Research on Cancer (IARC) as a human carcinogen of group 1 (IARC, 2004). The copper industry activities involve in the processes of copper ore mining, grinding and milling, extractive mining and electrolysis, smelting et al., and the possible exposure to As could be through the inhalation/dermal contact with the arsenic-bound particles and ingestion through hand–mouth activity within these processes. The World Health Organization (WHO, 2001) have reported that miners and smelter workers inhaled high levels of inorganic arsenic in airborne dust, and the workers in copper industry have been considered as a highly arsenic-exposed population.

After absorption, As is distributed in all body systems through blood and undergoes successive reductions and methylations metabolism, and leading to the excretion of inorganic species and organic methylated metabolites of monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). Approximately 40%–60% of the ingested form and 55%–80% of the inhaled form is excreted in the urine, mainly within 3–4 days (Buchet et al., 1981; Vahter, 1983). Urinary As concentration was shown to be a reliable indicator of recent exposure to As, and it has been used in some studies with people environmental and occupational exposed to this element

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(Lin et al., 1998; Wilhelm et al., 2005). The proportion of As methylated metabolites in urine has been used to evaluate iAs methylation efficiency in humans (Hopenhayn-Rich et al., 1996; Loffredo et al., 2003). It has been extensively reported (Mitra et al., 2004; Steinmaus et al., 2005; Heck et al., 2007) that As excretion profile and relative proportion of the inorganic and methylated urinary species were related with environmental arsenic levels, individual arsenicosis risk, sex, age, nutritional status and body weight.

Although many previous studies performed their investigation on the As exposure of workers in the process of copper ore refining, research on the As exposure of workers with different type of work are scarce to report. It is noteworthy to analysis and compare to the urinary As levels and profile of workers engaged in different jobs in the copper industry in order to provide the protective suggestion. To this end, the current investigation was carried out to evaluate As exposure and the urine metabolite profiles of five groups workers with different jobs in a copper mining and processing plant in China.

2. Materials and methods

2.1. Subjects

A total of 170 male workers in 5 different departments (groups) of a copper mining and processing plant, located in the northeastern part of China were randomly recruited in this study. In the plant, copper ore is mined and copper is produced from its ore by a smelting and electrolytic process. Of these individuals, 19 were administrative employees (Group 1), 83 copper ore miners (Group 2) worked underground, 26 subjects worked for copper ore grinding and milling (Group 3), 27 worked in electrolytic procession (Group 4) and 15 were copper smelters (Group 5). All subjects gave informed consent to take part in the research. The study was approved by the China Medical University Ethics Committee. Several trained interviewers used a questionnaire to collect subject age, job history, alcohol habit, smoking habit, sources of drinking water, dietary habits (including consumption of seafood, meat, vegetable and fruit in the 3 days preceding urine sampling), drug history, health status and other lifestyle factors. Blood pressure, height and weight were measured and body mass index (BMI) was calculated as weight in kilograms divided by height in meters squared. BMI of participants were classified into healthy weight (<23), overweight (23–25) and obesity (>25) as the standard of Asian (Li and Fu, 2001). All subjects with urinary creatinine values outside the range of 0.3–3.0 g/L, recommended by WHO for the acceptability of urine samples for biological monitoring (WHO, 1996), were excluded. All the subjects included in the present study performed the same tasks for all the years that they had been employed in the plant. Spot urine samples were collected in PVC bottles from all participants at the end of the shift or at the beginning of the next shift, kept on ice, immediately transferred to the laboratory in China Medical University and stored at −20 °C, and analyzed within 1 week of collection.

2.2. Urinary arsenic analysis

Determination of arsenic species, iAs, MMA, DMA, and trimethylated arsenic (TMA) in urine was performed by atomic absorption spectrophotometer (AA-6800, Shimadzu Co. Kyoto, Japan) with an arsenic speciation pretreatment system (ASA-2sp, Shimadzu Co. Kyoto, Japan). The detection limit of each of the four chemical species of arsenic (iAs, MMA, DMA, TMA) was 1 ng, and the coefficient of variation was <5%. Quantitation of As species were performed as described previously (Xu et al., 2009). Because TMA was not inorganic arsenic metabolite in urine, we reported the total arsenic (TAs) concentrations by summing up the concentrations of iAs, MMA, and DMA. Under our analytical conditions, differentiation of the trivalent forms from the pentavalent forms of As cannot be performed. Quality control for arsenic determinations included the analysis of Standard Reference Material of freeze-dried urine (SRM 2670). The certified concentration value for arsenic was (480 ± 100) μg/L. The value measured in present laboratory was (476 ± 22) μg/L. The reliability of arsenic species separation was checked by the analytical recoveries of added arsenic species. Spiking control urine sample with known amounts of iAs, MMA, DMA and TMA (10 μg/L, respectively) was assessed, and the recoveries of iAs, MMA, DMA and TMA were 82–93%, 86–98%, 88–97% and 83–99%, respectively. The final reported urinary As species concentration was routinely adjusted by individual urinary creatinine level measured by Jaffe reaction by the method reported previously to remove the influence of the effect of urine dilution on exposure biomarkers measured in spot sample (Sun et al., 2007). Results of urine samples were reported as micrograms As per gram creatinine. Based on the determination of As species in urine, percentages of urinary As metabolites (iAs%, MMA% and DMA%) and two methylation indices, the primary methylation index (PMI) and the secondary methylation index (SMI), were calculated as (MMA + DMA)/TAs and DMA/(MMA + DMA) (Sun et al., 2007), to assess the As methylation capacity.

2.3. Statistical analysis

Statistical analysis was performed with the SPSS statistical package (SPSS version 17 for windows). Normal distribution of variables was tested by the Kolmogorov–Smirnov test. Non-normally distributed variables were transformed logarithmically. Normally distributed and logarithmic transformation normalized variables were analyzed with parametric tests and with non-parametric tests in other cases. Chi-square test (maximum likelihood method) was used for the analysis of independent qualitative variables. Multiple linear regression models were used to evaluate the effects of variables on TAs levels and SMI value. The odds ratio (OR) was calculated by a logistic regression analysis to evaluate the risk of As concentration in urine exceeded 50 μg/g Cr. We adjusted age, different working type, years of employment, smoking habit, seafood consumption in recent 3 days, BMI, drinking water source type and alcohol consumption in 3 recent days as covariates that may affect As concentration in urine. The data are expressed as mean and standard deviation (SD). A probability of 0.05 or less was considered as significant.

3. Results

3.1. General characteristics of the study subjects

None of subjects in this study showed cutaneous signs of arsenicism like hyperpigmentation, hypopigmentation, palmoplantar hyperkeratosis or raindrop pigmentation. A description of some characteristics of the five groups studied is presented in Table 1. The average ages of Group 1, Group 2, Group 3, Group 4 and Group 5 workers were 44.4 ± 10.4, 44.7 ± 7.4, 43.4 ± 8.5, 44.7 ± 7.0, and 42.3 ± 5.1 years, respectively. The average years of employment of five groups were from 16.0 to 17.6, and there were no significant differences for age and years of employment among five groups. Concerning smoking habits, 73.5% of the subjects were smokers. Some differences in the percentage of smokers among the five groups were observed, and Group2 and 3 had more smokers than the Group 1 and 5. There also were differences in alcohol consumption: Group2 consumed more alcohol in recent 3 days than