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Risk assessment of arsenic and other metals via atmospheric particles, and effects of atmospheric exposure and other demographic factors on their accumulations in human scalp hair in urban area of Guangzhou, China

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ABSTRACT

Eighty-eight scalp hair samples were collected from Guangzhou (GZ) urban population (15–65 years) to investigate the accumulation of As and other metals (Cr, Mn, Ni, Cu, Zn, Cd, Sn, Sb, Hg and Pb). Demographic information, including body weight, height, age, gender, habits of smoking and drinking, types of drinking water, duration of stay in GZ, days of stay in GZ per year (days/year), and hours spent in indoor environment per day (h/day), were also recorded during hair sampling to refine the uncertainty of risk assessment derived from exposures to elements via dust and airborne particles. No significant non-carcinogenic risk was found. However, the cancer risks of Cr and As for both ingestion and inhalation exceeded the most tolerable regulated level (1.0×10^{-6}). The environmental exposures to urban dust and airborne particles were observed significantly correlated to accumulations of Cd ($R=0.306$, $p=0.005$) and Ni ($R=0.333$, $p=0.002$) in scalp hair. Furthermore, the hair burden of elements was also significantly ($p<0.05$) dependent on gender (Mn, Ni, Zn, As, Sn and Hg), age (Cr, As, Cd and Hg), duration of stay in GZ (Hg) as well as nutritional and physical status, reflected by BMI and BSA (Cr, Ni, Cd, Sb and Hg). Nutritional and physical status was observed as the exclusive important factor influencing As speciation in human scalp hair. However, habits of smoking and alcohol drinking as well as types of drinking water were not identified as the significant influencing factors on any element ($p>0.05$).

1. Introduction

Pearl River Delta (PRD) region is one of the largest metropolitan regions in China, where the mega cities and a number of recently established urban centers are located with concentrated stationary and mobile pollution sources (such as power plants, factories and traffic emissions) (Shao et al., 2006; Zhang et al., 2008). The city cluster in PRD region possesses the similar circumstance and the populations lead the similar life style. GZ (22°26′–23°56′N, 112°57′–114°03′E) is one of the most densely populated city in PRD region, with a population of over 10 million and an area of 7545 km^2 (Zheng et al., 2011). The contaminations of Cu, Zn, Cd and Pb in the urban deposits of GZ are more severe in the industrial area, compared with the area with limited traffic and industry (Duzgoren-Aydin et al., 2006). One of our previous studies also reported that the contaminations of Cr, Ni, Cu, Sn and Sb contained in road dust were more serious in urban area than those from peri-urban area in GZ, and that Ni, Cr, Hg and Pb were enriched much more in household dust compared with road dust. The same study also employed the bioaccessibilities of elements contained in road dust, household dust and household $PM_{2.5}$ to identify their relative risks. In order to refine the uncertainty caused by the assumption of exposure parameters used in the risk assessment models developed by USEPA (such as exposure frequency, exposure years, averaging time and body weight) (USEPA, 1989, 2009), which might not be authentically applicable in GZ, the present study attempted to collect the general demographic information for the population with the age between 15 and 65 years in GZ urban area using a sample survey of 88 participants. A more detail description about the refinement of daily intakes (DIs) and risk assessments will be given in Section 2.5.

In urban environment, people may be exposed to more toxic elements via ingestion and inhalation of contaminated particulates, compared with rural or non-industrialized areas (Rivai, 2001; Sanna

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et al., 2003). Although there is insufficient epidemiological data to support predictions concerning the health effects based on specific concentration of each element in human scalp hair, it still appears to be suitable in prospective pilot studies identifying subgroups of population at potentially increased risk (Gil et al., 2011). The significantly different levels of elements (such as As, Cd, Cr, Cu, Mn, Ni, Pb, and Zn) in hair between exposed and non-exposed populations have been reported in several previous studies, such as in Karachi, Pakistan (Afridi et al., 2009), areas with high environmental As concentration in Australia (Hinwood et al., 2003), Bandarlampung city, Indonesia (Rivai, 2001), Sardinia, Italy (Sanna et al., 2003) and electronic waste recycling area of Taizhou in Zhejiang province, China (Wang et al., 2009), indicating that environmental exposure can partly affect the hair burden of elements.

Human scalp hair is predominantly composed of keratin, a protein rich in cysteine sulfhydryl (thiol) groups with binding affinity for various elements. Elements can be accumulated in hair shaft through the blood stream in hair root (McLean et al., 2009; Noguchi et al., 2012). Numerous studies had confirmed that many elements (Al, Cd, Co, Cr, Cu, Pb and Hg) link their concentrations in hair with those distributed in nails (Gault et al., 2008; Ohno et al., 2007; Rodushkin and Axelsson, 2000), urine (Ohno et al., 2007), blood (Rodrigues et al., 2008) and other internal organs (such as liver, kidney and lung) (McLean et al., 2009). Compared with other human samples (blood, urine, milk, saliva etc…), hair is more convenient to collect, transport and store. Furthermore, it can reflect the long-term exposure (weeks to years depending on the length). These advantages led to the widespread use of trace elements analyses in hair to assess environmental exposures for wildlife and human (Gault et al., 2008; McLean et al., 2009; Samanta et al., 2004; Wang et al., 2009). However, the interference caused by exogenous contamination on human scalp hair (such as deposits of sebum, sweat, polluted air residues and the residues of cosmetic or pharmaceutical products) should be carefully considered and dealt with.

In addition to the environmental exposure, it has been widely observed that age, gender, tobacco and alcohol consumption (Chojnacka et al., 2010; Rodushkin and Axelsson, 2000; Vance et al., 1988; Concha et al., 1998; Lindberg et al., 2008), diet (Shao et al., 2012), drinking water (Gault et al., 2008), and nutritional factors (Gamble et al., 2005; Hall et al., 2009) could also affect the body burdens of elements.

Different from other metals, As is a metalloid and one of the most toxic elements. Inorganic As and its compounds have been classified as Group 1 human carcinogens by the International Agency for Research on Cancer (IARC, 1987) and as dangerous substances for the environment by the European Union (EU, 1967). Furthermore, DMA^V was also identified as animal carcinogen (IARC, 2004). In general, it has been recognized that the inorganic As species are more toxic than most of the organic ones (except for the trivalent organoarsenicals), and that inorganic trivalent arsenicals (iAs^{III}) is more toxic than inorganic pentavalent arsenicals (iAs^V) (B′hymer and Caruso, 2004; Dopp et al., 2004; Duker et al., 2005). Thus, speciation deserved more attention in hair accumulation of As, which is usually used as an indicator of long-term exposure to As.

With the background mentioned above, the present study aims to (1) refine the uncertainty of risk assessments of As and other metals (Cr, Mn, Ni, Cu, Zn, Cd, Sn, Sb, Hg and Pb) via urban dust and airborne particles in GZ; (2) identify the correlations between DIs of elements and their accumulation in human scalp hair; (3) compare the extent of these elements in the hair samples of GZ urban population with the non-exposed reference populations, other urban populations, as well as the environmental and occupational exposed populations around the world; lastly (4) reveal the effects of other demographic factors (such as age, gender, duration of stay in GZ, habits of smoking and drinking, types of drinking water and nutritional status) on the extent of elemental accumulation in human scalp hair.

2. Materials and methodology

2.1. Collection of demographic information and scalp hair sample

Eighty-eight hair samples from the occipital portion of the head were cut close to the scalp, and then placed in identified plastic seal bags (McDowell et al., 2004). All of the participants had lived in GZ urban area for at least 5 years. At the same time, each participant was given a questionnaire to collect the general information, including height, body weight, gender, age, habits of tobacco smoking and alcohol drinking, types of drinking water, duration of stay in GZ, days/year of stay in GZ, and h/day spent in indoor environment.

Prior to chemical analysis, a standardized washing protocol, established by International Atomic Emergency Agency (IAEA), was used to wash the hair samples to avoid the exogenous contamination. In brief, hair samples were cut into small pieces (2–3 mm) and washed with acetone (extra pure, Merck) and Milli *Q* water alternately, following the sequence: acetone – three times of Milli *Q* water – acetone. The samples were immersed completely in acetone and Milli *Q* water with constant stirring for each time (Afridi et al., 2011; Mandal et al., 2003).

2.2. Determination of total elements contents

An aliquot of 0.2 g of washed hair sample was introduced to 2 ml 65 percent nitric acid (Sigma-Aldrich Chemical Co) and subjected to microwave digestion (Chen et al., 2008). The extracts were fixed up to 25 ml with Milli-*Q* water then filtered with 5C Whatman filter paper and 0.45 μm syringe filter successively. The total contents of elements were determined using ICP-MS (Perkin Elmer Elan 9000) except for Hg, which was detected with direct mercury detector (DMA-80, Milestone). Standard addition method was used for each sample to eliminate the interference of $^{40}Ar^{35}Cl$ and $^{40}Ar^{12}C$ on ^{75}As and ^{52}Cr respectively in the determination using ICP-MS. Two standard reference materials (SRMs) of human scalp hair (IEAE-086 and NIES-13) and method blanks were digested and determined in parallel with the hair samples. The SRM of IEAE-086 was used only for Zn, Cu, Mn and low level of Hg (ppb level), while NIES-13 was used for other elements and high level of Hg (ppm level). The average recovery rates varied from 87.8 percent for Cr to 113.4 percent for Zn.

2.3. Determination of As species (inorganic trivalent arsenical iAs^{III}, inorganic pentavalent arsenical iAs^V, monomethylarsenic acid MMA and dimethylarsenic acid DMA)

Aliquots of 0.1–0.2 g of hair sample were soaked in 5 ml Milli-*Q* water and incubated at 90 °C for 8 h (Mandal et al., 2003). The extracted arsenicals were analyzed by Agilent 1100 series HPLC system (Agilent Technologies, Santa Clara, CA, USA), after being filtered by 5C Whatman filter paper and 0.45 μm syringe filter.

The condition of HPLC system was as reported in Wu et al. (2011). Injection volume was set as 50 μl of extracts and the HPLC mobile phase flow rate was maintained at 1.0 ml/min. The mobile phase for anion-exchange chromatography included ultra pure (>18 MΩ cm) deionized water and 20 mM $NH_4H_2PO_4$ (Sigma-Aldrich Chemical Co.) (pH = 4.66) (Chen et al., 2008). The recoveries using the heating method to extract As species ranged from 56 percent to 89 percent, with the mean of 72.3 percent.

Retention time for the As species was determined using mixed standards of 50 μg/l arsenic (III) oxide (iAs^{III}), arsenic (V) oxide (iAs^V), cacodylic acid (DMA) (all from Sigma-Aldrich Chemical Co), and methylarsonic acid (MMA) (Wako Pure Chemical Industries, Ltd). Peaks of different As species were identified by the comparison with the retention times of individual standard compounds. The detection limit for each As species was 1 μg/l.

2.4. Calculations of body mass index (BMI) and body surface area (BSA)

Body mass index (BMI) and body surface area (BSA) were used to reflect the human nutritional and physical status of the GZ population in the present study. They were calculated using Eqs.(1) and (2) (Lindberg et al., 2008).

$$\mathrm{BMI(kg/m^2)} = \frac{\text{Body weight(kg)}}{\text{Height(m)}^2} \quad (1)$$

$$\mathrm{BSA} = \text{Body weight (kg)}^{0.425} \times \text{Height(cm)}^{0.725} \times 0.007184 \quad (2)$$

2.5. Refinement of uncertainty in risk assessment of exposures to As and other metals via urban dust and airborne particles in GZ based on the recorded demographic information

The oral DIs of elements via indoor dust (household dust) and outdoor dust (road dust) in the present study were calculated using Eqs. (3)–(4) (USEPA, 1989). The inhalation concentration via household $PM_{2.5}$ was obtained from Eq. (5) (USEPA, 2009). In Eqs. (3)–(5), 95 percent UCL is 95 percent upper confidence