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Biomarkers of arsenic exposure in arsenic-affected areas of the Hetao Basin, Inner Mongolia

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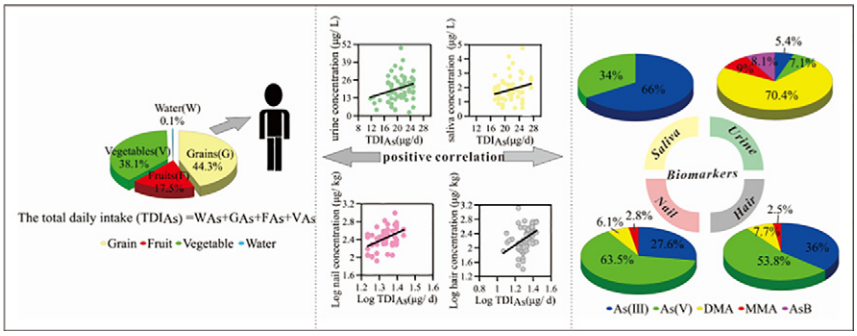
HIGHLIGHTS

- Only inorganic As was found in saliva samples.
- Both organic and inorganic As were observed in urine, hair and nail samples.
- Saliva was a potential biomarker for chronic As exposure.
- The major pathway of As intake was from grains, fruits and vegetables.
- Arsenic intake from crops had potential risk to residents' health.

GRAPHICAL ABSTRACT



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ABSTRACT

Seventy saliva samples, seventy urine samples, seventy nail samples, seventy hair samples, eight drinking water samples and ninety-three crop samples were collected from four villages of the Hetao Basin in Inner Mongolia to determine arsenic (As) exposure biomarkers and evaluate relationship between As uptake and human health risk. Trivalent As (As(III)), pentavalent As (As(V)), dimethylarsinic acid (DMA), arsenobetaine (AsB) and monomethylarsonic acid (MMA) were found in all urine samples. Only As(III) and As(V) were detected in saliva samples. In nail and hair samples, DMA, MMA, As(III) and As(V) were observed. Based on total As contents in crops and drinking water, the local residents' daily intake of total arsenic (TDI_{As}), the hazard quotient (HQ), and the cancer risk (R) were assessed. Male, older and cases of skin lesion participants generally had higher As contents in saliva, urine, nail and hair samples in relative to others. Salivary, urinary, nail and hair As were not significantly affected by body mass index (BMI) and smoking. Good correlations were observed between TDI_{As} and salivary, urinary, nail and hair As, showing that saliva, urine, nail and hair samples can be used as biomarkers of As exposure. Individually, levels of arsenicosis were positively correlated with TDI_{As}. The relationship between TDI_{As} and prevalence of arsenicosis concluded that, although As levels in crops and drinking water did not exceed national standards, they still pose a potential threat to human health. It was suggested that the maximum permissible levels of crop As and drinking water As should be re-evaluated for protecting human health.

Abbreviations: As, arsenic; TDI_{As}, the total daily intake of As; AsB, arsenobetaine; DMA, dimethylarsinic acid; MMA, monomethylarsonic acid.

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1. Introduction

Arsenic (As), as a highly toxic element, is listed as the level one carcinogen by International Agency for Research on Cancer (IARC, 2004). Long-term exposure to As may lead to skin cancer, lung cancer, liver cancer and bladder cancer and significantly increase cancer risk (IARC, 2004; Bates et al., 1992; Chen et al., 2007). Since there is no effective treatment of endemic arsenicosis, early detection of As exposure is the key to prevent As poisoning. Using highly sensitive biomarkers can directly measure the levels of As exposure and the toxic effects for early diagnosis and prevention. Currently, urine, blood, hair and nail are mainly used for screening of As exposure (Hughes, 2006). In recent years, saliva samples, as a rapid, noninvasive detection means, attracted researcher's attention and aroused great interest. Scientists have examined the exposure conditions of lead (Almeida et al., 2009), cadmium (Talio et al., 2010) and mercury (Fakour et al., 2010) by using the saliva samples, and found that contents of harmful elements in saliva reflect the body's exposure. The ability to quantify the individual As species and the noninvasive collection of saliva samples make As speciation in saliva a potentially useful biomonitoring approach for assessing human exposure to As (Yuan et al., 2008). Comparison of total As concentration between urine and saliva after consumption of seafood in human and between blood and saliva after oral administration of sodium arsenite to SD rats further verify that salivary As should be taken as a biomarker for assessing As exposure in human (Wang et al., 2011; Wang, 2012). Investigation of As concentrations in saliva and urine samples collected from populations of West Bengal, India having been previously exposed to high As levels in their drinking water showed that saliva is a useful biomarker of As exposure in the studied population (Bhowmick et al., 2013). Arsenic species in saliva can be a useful tool to predict the individual susceptibility of high As exposure (Bhowmick et al., 2014). Therefore, saliva would be an efficient biomarker of chronic As exposure, which deserves further investigation, especially in high-As groundwater areas.

Normally, the major pathways of As exposure include ingestion of high As drinking water and digestion of As-containing foods (WHO, 2001; Carbonell-Barrachina et al., 2009; EFSA, 2009). Drinking high As water is an important pathway of As uptake by human. Irrigation with high-As groundwater led to high As contents of crops, which entered the food chain and human body (Panaullah et al., 2008; Tong et al., 2014).

In the Hetao basin, high As groundwater has been observed in 1990s, with the highest concentration up to 1350 μg/L (Guo et al., 2001; Yu et al., 2006). High As groundwater has caused chronic arsenicosis in thousands of residents (Ni et al., 2016), via pathways of drinking water and food crops (Guo et al., 2003; Tong et al., 2014). In 2000s, the major pathway was drinking water ingestion, with >300,000 people potentially exposed to As poisoning in drinking water (Guo et al., 2003). After high As drinking water has been replaced by low As drinking water since 2000s in most villages, drinking water pathway would be potentially minimized. In groundwater-irrigation areas, chronic As exposure to crops was expected to be another important pathway (Tong et al., 2014; Guo et al., 2014), which however needs to be quantified with respect to daily food consumption. In previous epidemiological studies, nail, urine and hair have been used to reveal a series of adverse health effects induced by high As groundwater (Guo et al., 2003; Xia et al., 2009; Yu et al., 2006; Wei et al., 2017). However, no any data are available on As in human saliva, which would reveal the suitability of saliva as a biomarker for As exposure by assessing the relationship between salivary As and uptake As.

The objectives of this study are to (1) investigate As contents and species in saliva, urine, nail and hair samples from residents, (2) reveal the major pathways of chronic As exposure with regard to As contents of grains, fruits, vegetables and drinking water used by the residents, and (3) evaluate the suitable biomarkers for chronic As exposure in As-affected areas.

2. Materials and methods

2.1. The study area

The study area lies in the northwestern margin of the Hetao Basin (HB). The Hetao basin, between the Langshan Mountain Ranges and the Yellow River, is known as one of the Chinese oldest crop-producing areas, where artificial irrigation systems are widely distributed to divert water from the Yellow river into the basin for agricultural irrigation (Guo et al., 2011). High As groundwater mainly occurs in both shallow aquifers and deep aquifers in the flat plain near the mountains (Guo et al., 2008; Guo et al., 2016). A number of deep wells have been used for agricultural irrigation near the Langshan Mountains due to the unavailability of diverted-river water. Drinking water resource has been shifted from local shallow wells to deep wells in alluvial fans, which usually has low As concentrations. Therefore, the study area which included four typical villages (Fengchan Wudui; Hongqi Erdui; Jianshe Yishe; Wuxing Ershe) was selected in the flat plain near the mountains to investigate pathways of environmental As into human body and biomarkers of chronic As exposure (Fig. 1), due to the high incidence of arsenic chronic poisoning.

2.2. Study population and sample collection

A total of 70 residents (male, 35; female, 35) were selected for this study from the four typical villages in March 2015. A questionnaire survey on residents was conducted prior to sample collection, for a detailed understanding of each resident, including height, age, gender, and smoking habits. Diagnosis for skin keratosis, depigmentation, and hyperpigmentation was based on the Chinese national standards for arsenicosis diagnosis by trained interviewers (Standards for Diagnosis of Endemic Arsenism, 2001).

Following the interview, the participants, who were asked not to eat or drink for 1 h prior to saliva collection, rinsed their mouths with ultrapure water and discarded the saliva. After 2–3 min, the participants were given 50 mL low density polyethylene (LDPE) bottles, and saliva samples were collected. Due to no significant difference in As species of urine throughout the day (Cui et al., 2013), single spot urine was collected in disposable plastic cups, and then filtered into 2 mL brown glass bottles. The surveyed participants supplying urine samples did not eat seafood in the recent 3 days. All saliva and urine samples were stored in −20 °C and kept frozen until analysis in the laboratory. Hair samples from scalp at different positions and nail clippings from all fingers were collected using stainless-steel scissors and a ceramic blade, and preserved in sealed bags.

Drinking water samples were collected from the tap water in the participant houses and acidified with HNO_3 (pH < 2). Since every village has the same drinking water source for their tap water, two drinking water samples were taken in each village. Different crops samples (n = 93) were collected from the nearby gardens of each surveyed household in four villages, including grains (wheat and corn), fruits and vegetables (beans, cucumbers, tomatoes, watermelons, etc.). They were preserved in sealed bags, and kept at 4 °C. All samples were analyzed within one week after sampled from the field sites.

2.3. Sample preparation

The frozen saliva samples were thawed at room temperature and filtered through a 0.45 μm filter for total As and As species analysis. The frozen urine samples were melted at room temperature and filtered through a 0.45 μm membrane before analyzed.

Hair and nail samples were pretreated with a reported method (Hinwood et al., 2003). Briefly, they were washed in three steps, deionized (DI) water-methanol-DI water. Vegetables were washed with tap water to remove soil and dust particles, rinsed with DI water. The