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Arsenic speciation in total contents and bioaccessible fractions in atmospheric particles related to human intakes

Minjuan Huang [a,c], Xunwen Chen [c], Yinge Zhao [c], Chuen Yu Chan [a], Wei Wang [c], Xuemei Wang [a], Ming Hung Wong [b,c,*]

[a] Faculty of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, PR China
[b] Department of Science and Environmental Studies, The Hong Kong Institute of Education, Tai Po, Hong Kong, China
[c] State Key Laboratory in Marine Pollution – Croucher Institute for Environmental Sciences, Hong Kong Baptist University and City University of Hong Kong, Hong Kong, China

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ABSTRACT

Speciation of inorganic trivalent arsenicals (iAs^{III}), inorganic pentavalent arsenicals (iAs^{V}), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) in total arsenic (As) content and its bioaccessible fractions contained in road dust, household air-conditioning (AC) filter dust and $PM_{2.5}$ was investigated. Inorganic As, especially iAs^{V}, was observed as the dominant species. Physiologically based extraction test (PBET), an *in-vitro* gastrointestinal method, was used to estimate the oral As bioaccessibility in coarse particles and the species present in the oral bioaccessible fraction. A composite lung simulating serum was used to mimic the pulmonary condition to extract the respiratory bioaccessible As and its species in $PM_{2.5}$. Reduction of iAs^{V} to iAs^{III} occurred in both *in-vitro* gastrointestinal and lung simulating extraction models. The inorganic As species was the exclusive species for absorption through ingestion and inhalation of atmospheric particles, which was an important exposure route to inorganic As, in addition to drinking water and food consumption.

1. Introduction

Arsenic (As) is a ubiquitously distributed metalloid in the earth's crust (Mandal and Suzuki, 2002). Volcanic activity is the major natural source. Human activities, such as fossil fuel combustion, metal smelting and pesticide use, account for most proportion of As emission to atmosphere (Wang and Mulligan, 2006; WHO, 2001). More than 90% of atmospheric As exist in particulate form, predominantly in fine airborne particles with diameter smaller than or equal to 3.5 μm (Šlejkovec et al., 2000). Arsenic concentration in the atmosphere has been reported to be significantly higher in urban and industrial districts compared with those in rural areas (EC, 2000; Putaud et al., 2004; Serbula et al., 2010).

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 numerous stationary and mobile pollution sources (power plants, factories and traffic emissions) (Shao et al., 2006; Zhang et al., 2008). In PRD region, the significant atmospheric point sources are concentrated in the central area and scattered in the south coastal area (Wang et al., 2013; Wong et al., 2003). On the other hand, the atmospheric As were also mainly contaminated in the central area of PRD region (Duan and Tan, 2013). Guangzhou (22″26′–23″56′N, 112″57′–114″03′E), the capital of Guangdong province and one of the largest cities in China, is located in the center of PRD region. The urban district of Guangzhou is one of the most typical areas with local industrial pollution and traffic emissions in China.

Around the world, the studies on atmospheric As mainly focused on the total contamination and its speciation in total content (Tsopelas et al., 2008; Yang et al., 2012), few have revealed detailed information on speciation in the bioaccessible As fraction in atmospheric particles, that is most likely to pose harmful effects on human health.

Inorganic As and its compounds have been classified as Group 1 human carcinogens by the International Agency for Research on Cancer (IARC) (IARC, 1987) and as dangerous substances for the environment by the European Union (EU, 1967). Furthermore, dimethylarsinic acid (DMA^{V}) is also identified as animal carcinogen (IARC, 2004). It has been known that the difference in As species exert varying toxicities to the human body. In general, it is recognized that the inorganic As species are more toxic than most organic ones (except

* Corresponding author.
E-mail address: mhwong@hkbu.edu.hk (M.H. Wong).

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for the trivalent organoarsenicals), and that iAs^{III} is more toxic than iAs^{V} (B'hymer and Caruso, 2004; Dopp et al., 2004; Duker et al., 2005).

Arsenic in atmospheric particles is mainly able to enter the human body via non-dietary ingestion and inhalation (Chou et al., 2009; Hu et al., 2012, 2011). Human health risks due to As intake depend on its bioaccessible fractions and the As species present for absorption. Physiologically based extraction test (PBET), an *in-vitro* gastrointestinal method, will be used to preliminarily estimate the oral bioaccessibility of total As in coarse particles and species in their bioaccessible fractions (Pouschat and Zagury, 2006; Rodriguez et al., 1999). Coarse particles are referred to as the road dust and AC dust particles with the diameter smaller than 100 μm in the present study, which can be directly swallowed or finally reach the gastrointestinal tract after a short stay in tracheal and bronchial region through inhalation (Butte and Heinzow, 2001).

Different from coarse particles, more than 80% of the airborne particles smaller than 2.5 μm can directly reach the pulmonary alveoli, where they can be deposited and stay for months to years (Falta et al., 2008). Accordingly, the lung serum stimulant will be selected in this study to extract the potential respiratory bioaccessible fraction of As in $PM_{2.5}$ (Hodgson et al., 2002; Voutsa and Samara, 2002).

Generally, reduction of iAs^{V} to iAs^{III} is considered as one of the initial steps for the detoxification of inorganic As (Pinyayev et al., 2011). The present study attempts to confirm the reduction of iAs^{V} using the *in-vitro* ingestion and inhalation models. It is hypothesized that reduction of iAs^{V} to iAs^{III} accompanied by further methylation processes of inorganic As may happen through gastrointestines and tracheobronchiol and pulmonary region ahead of absorption by the human body.

Accordingly, the major objectives of the present study are to (1) investigate As speciation (iAs^{III}, iAs^{V}, MMA and DMA) in total contents in road dust, household air-conditioning (AC) filter dust and $PM_{2.5}$ collected from Guangzhou urban area, south China; (2) preliminarily study the transformation of As species after intake via ingestion and inhalation of atmospheric particles; and (3) estimate the daily intakes (DIs) of different As species.

2. Materials and methodology

2.1. Sampling and sample preparation

A total of thirty road dust samples, seven household $PM_{2.5}$ samples and ten household AC filter dust samples were collected using plastic broom and shovel, in Guangzhou urban area from the middle of July to the end of August, 2010 (Fig. S1). The road dust samples were collected from different locations, including scenic park ($n = 3$), educational sites ($n = 6$), residential sites ($n = 9$), heavy traffic sites ($n = 6$), commercial sites ($n = 3$) and peri-urban district ($n = 3$). All of the dust samples were collected at the edge of the lane. The samples were placed in plastic seal bags. In each site, 4 subsamples (composited as one representative sample for each site) were collected randomly but areas around traffic lights, bus stops and soil around greenbelts were avoided. Ten out of thirty road dust samples were collected specific near the sampling houses for AC filter dust. In order to compare with the household coarse particles (AC filter dust), the $PM_{2.5}$ samples were additionally collected from seven out of the houses that were for AC filter dust sampling. The collection of each $PM_{2.5}$ sample lasted for at least three days consecutively to obtain enough amounts of particles for chemical analysis. The sampling program, weighing methods for $PM_{2.5}$ membrane and AC filter dust, and sampling quality controls had been described in detail in our previous paper (Huang et al., 2012), in which AC filter dust was mentioned as total suspended particulate matters (TSP) with the diameters less than 100 μm. Hence, the road dust samples were sieved to 100 μm ahead of analysis so as to compare with the AC filter dust samples.

2.2. Determination of pH values, total organic carbon (TOC) and dissolved organic carbon (DOC) in dust particles

The pH of dust particles was measured with a pH meter by taking 2.0 g of road dust sample or a strip of 1″ × 8″ of AC filter dust into 20 mL of ultra pure (>18 MΩ cm) deionized water. Total organic carbon (TOC) was analyzed using thermal partitioning method at 550 °C after pretreatment of aliquots of 10% HCl (USEPA, 1997). Dissolved organic carbon (DOC) was determined with Total Organic Carbon Analyzer (Shimadzu Co.) by extracting the dust particles with ultra pure deionized water. All of extracted solutions were filtered through 0.45 μm filter membrane ahead of determination of DOC.

2.3. Extraction of total contents, bioaccessible fraction and species of As

All samples of road dust, AC filter dust and $PM_{2.5}$ were determined for total As content and speciation in it. In order to estimate the mobility of As species, subsamples of road dust, AC filter dust and $PM_{2.5}$ were used for determination of the bioaccessible As fraction, and its speciation. Each $PM_{2.5}$ membrane was cut into three equal parts for the analysis of total content, speciation and respiratory bioaccessible fraction.

The total As was extracted based on EPA Method 3051 (USEPA, 1994). Orthophosphoric acid (H_3PO_4) (Sigma–Aldrich Chemical Co) microwave assistant method was applied (Chen et al., 2008; Gallardo et al., 2001; Oliveira et al., 2005) to speciate As in atmospheric particles. Briefly, a mass of 0.5 g of dry road dust, a strip of 1″ × 8″ of AC filter dust and a part of $PM_{2.5}$ membrane were introduced to the digestion tubes with 10–25 mL of 100 mM H_3PO_4 solution and submitted to microwave irradiation at 40 W to each tube for 20 min. After cooling down, the extracts obtained were centrifuged at 3000 rpm for 20 min. The supernatant was diluted by a factor of 10–50, and filtered through the 0.45 μm membrane before chromatographic analysis.

Physiologically based extraction test (PBET) was employed to evaluate the oral bioaccessibility of total As and the speciation of the bioaccessible As fraction, which simulating the chemical conditions of the gastrointestinal tract. The procedure adopted in this study was based on the earlier protocols (Pouschat and Zagury, 2006; Ruby et al., 1996), with slight modification. In brief, gastric solution was prepared immediately before use (Table S1). About 0.25 g of road dust and a strip of 1″ × 8″ strip from the 8″ × 10″ AC filter were respectively added to 50 mL polyethylene tubes with 40 mL gastric solution and end to end shaken at 37 °C. After 1 h, 10 mL of the mixtures (stomach phase, SP) were abstracted, centrifuged (37 °C, 2000 rpm, for 10 min) and filtered with 5C Whatman filter paper and 0.45 μm syringe filter successively. The remaining contents in the reaction tubes were added with 70.0 mg of bile salts and 20.0 mg of pancreatin and titrated with a few aliquots of saturated $NaHCO_3$ to pH 7.0 and continued to be digested. Another 10 mL of mixtures after 4 h (intestinal phase, IP) was abstracted and followed the rest of the procedure as mentioned above.

The lung simulating serum was also prepared immediately before use (Table S1) (Hodgson et al., 2002; Voutsa and Samara, 2002). Another part of $PM_{2.5}$ membrane was extracted with 10 mL serum by shaking at 37 °C. After filtrations with 5C Whatman filter paper and 0.45 μm syringe filter. The entire process of PBET and extraction with lung simulating serum were performed in sealed and dark condition.

2.4. Determination of As and its species

The total content and the bioaccessible fraction of total As were determined with ICP-MS (Perkin Elmer Elan 9000). All the extracts for As speciation analysis were stored at −80 °C before determination. The separation of different As species was conducted with Agilent 1100 series HPLC system (Agilent Technologies, Santa Clara, CA, USA) according to their retention times. The HPLC system was described as in the study by Wu et al. (2011). Injection volume was set at 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 outlet of the HPLC column was connected directly to a concentric nebulizer of ICP-MS, allowing continuous transportation of the determinants to the argon plasma of ICP-MS.

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 comparison with the retention times of individual standard compounds The detection limit was 1 μg/l for iAs^{III} DMA, MMA and iAs^{V}. The extractability using H_3PO_4 microwave assistant method (sum of As species) compared with US EPA Method 3051 (total As) varied between 70.2% and 113.9%.

2.5. Quality control

Standard reference material (SRM) of dust (NIST 2584, USA), matrix spike/matrix spike duplicates (MS/MSD), filter blanks and method blanks were processed and analyzed in parallel with the samples. MS/MSD is specific for the samples of AC filter dust and $PM_{2.5}$ by determining the added SRM (NIST 2584) with known As concentration. In addition, standard spikes (50 μg/l) were also performed in triplicate respectively for PBET and lung simulating extraction, to control the loss of solutions during shaking and transfer. The QA/QC results are summarized in Table S2.

2.6. Calculation of bioaccessibility, mobility and daily intakes (DIs)

2.6.1. Bioaccessibility

Oral bioaccessibility of total As was calculated as the percentages of the soluble concentrations sequentially in stomach phase (SP) and intestinal phases (IP)