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Influence of pollution control on lead inhalation bioaccessibility in $PM_{2.5}$: A case study of 2014 Youth Olympic Games in Nanjing

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ABSTRACT

Pollution controls were implemented to improve the air quality for the 2014 Youth Olympic Games (YOG) in Nanjing. To investigate the influence of pollution control on Pb inhalation bioaccessibility in $PM_{2.5}$, samples were collected before, during, and after YOG. The objectives were to identify Pb sources in $PM_{2.5}$ using stable isotope fingerprinting technique and compare Pb inhalation bioaccessibility in $PM_{2.5}$ using two simulated lung fluids. While artificial lysosomal fluid (ALF) simulates interstitial fluid at pH 7.4, Gamble's solution simulates fluid in alveolar macrophages at pH 4.5. The Pb concentration in $PM_{2.5}$ samples during YOG (88.2 ng m^{-3}) was 44–48% lower than that in non-YOG samples. Based on stable Pb isotope ratios, Pb in YOG samples was mainly from coal combustion while Pb in non-YOG samples was from coal combustion and smelting activities. While Pb bioaccessibility in YOG samples was lower than those in non-YOG samples (59–79% vs. 55–87%) by ALF, it was higher than those in non-YOG samples (11–29% vs. 5.3–21%) based on Gamble's solution, attributing to the lower pH and organic acids in ALF. Different Pb bioaccessibility in $PM_{2.5}$ between samples resulted from changes in Pb species due to pollution control. $PbSO_4$ was the main Pb species in $PM_{2.5}$ from coal combustion, which was less soluble in ALF than PbO from smelting activities, but more soluble in Gamble's solution. This study showed it is important to consider Pb bioaccessibility during pollution control as source control not only reduced Pb contamination in $PM_{2.5}$ but also influenced Pb bioaccessibility.

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1. Introduction

Due to its rapid industrialization, China has been experiencing severe haze events, with $PM_{2.5}$ as a main contributor (Guo et al., 2014; Huang et al., 2014). An increasing body of evidences has shown the correlation between exposure to $PM_{2.5}$ and many diseases including lung cancer (Cakmak et al., 2014; Richmond-Bryant et al., 2014). Lead (Pb) is one of the most enriched metals in $PM_{2.5}$ and has attracted much attention during the past few decades (Sun et al., 2006). Numerous studies have investigated Pb levels in $PM_{2.5}$, and significant correlation between $PM_{2.5}$ Pb levels and blood Pb levels in children has been observed (Liang et al., 2010; Richmond-Bryant et al., 2014). These results suggest that $PM_{2.5}$ inhalation is an important Pb exposure pathway for humans. It is therefore imperative to assess human health risks through Pb exposure in $PM_{2.5}$ via inhalation pathway.

Evidence shows that not all Pb in airborne particles can be absorbed into the systemic circulation (Boisa et al., 2014; Wiseman and Zereini, 2014). Accurate assessment of Pb exposure via $PM_{2.5}$ inhalation therefore requires the measurement of its bioavailability. Although in vivo assays using animals are more accurate to measure Pb inhalation bioavailability, they are still in the development phase. Consequently, in vitro assays using simulated lung fluid have been developed as they are simple and practical to use. There are two common artificial lung fluids, i.e., Gamble's solution and artificial lysosomal fluid (ALF), which simulate two different processes after $PM_{2.5}$ particles are inhaled into lungs. They have been used to measure metal bioaccessibility in $PM_{2.5}$. For example, inhalation bioaccessibility of platinum group elements in PM of Germany was measured using the two methods (Zereini et al., 2012). Similarly, Wiseman and Zereini (2014) reported Pb bioaccessibility in $PM_{2.5}$ at 84% (77–91%) by ALF and 4.0% (1.0–9.0%) by Gamble's solution. However, compared to the large number of studies investigating Pb levels in $PM_{2.5}$, there remains a knowledge gap regarding Pb inhalation bioaccessibility in $PM_{2.5}$.

It is well known that Pb speciation in soil is a main factor influencing its Pb bioaccessibility (Rasmussen et al., 2011; Smith et al., 2011). Different sources including industrial emission, vehicle exhaust, coal combustion and suspended soil particles contribute to Pb in $PM_{2.5}$ (Charlesworth et al., 2011; Cheng and Hu, 2010). For example, $PM_{2.5}$ from smelting activities are more enriched with PbO due to Pb vapor

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oxidization in the air (Batonneau et al., 2004) whereas more $PbSO_4$ is accumulated in $PM_{2.5}$ from coal combustion due to the sulfate enrichment in coal (Shah et al., 2009). Therefore, it can be expected that Pb inhalation bioaccessibility in $PM_{2.5}$ from different sources may vary greatly. The influence of Pb sources on its oral bioaccessibility in soils has been extensively studied (Bannon et al., 2009; Smith et al., 2011; Cao et al., 2003; Hardison Jr. et al., 2004). However, the influence of Pb source on its inhalation bioaccessibility in $PM_{2.5}$ has not been well elucidated. This knowledge gap is mainly due to the difficulty to identify the Pb sources in PM2.5 by conventional approaches including chemical mass balance, positive matrix factorization models and enrichment factor (Liang et al., 2016). In recent years, fingerprinting based on stable Pb isotope ratios has been successfully used to determine Pb sources in various environmental media including airborne PM (Widory et al., 2010). Here we hypothesized that the influence of contamination sources on Pb bioaccessibility in $PM_{2.5}$ can be effectively examined by coupling the stable Pb isotope ratio technique with simulated lung fluid extraction.

Nanjing is a mega city in eastern China with an area of 6587 km^2 and population of 8.2 million. It hosted the 2nd Summer Youth Olympic Games (YOG) during August 16th–28th, 2014. Considering the poor air quality in Nanjing, the local government implemented pollution controls during the YOG. Approximately 2630 construction sites were closed, and heavy-industry factories such as iron and steel industries and petrochemical enterprises were required to reduce manufacturing by 20%. Vehicles with high emissions such as trucks, engineered vehicles, and vehicle van transporting hazardous materials were banned in the city. In addition, 22 nearby cities were asked to cooperate with Nanjing to close industries with high pollution emission during the YOG (Ding et al., 2015; Pan et al., 2015). Significant improvement in air quality was expected with the pollution control, so were the changes in Pb contamination source in airborne PM during the YOG.

Therefore, the pollution control during the YOG provided us a unique opportunity to study the influences of Pb sources on its bioaccessibility in $PM_{2.5}$. To this end, $PM_{2.5}$ samples were collected before, during, and after the YOG in Nanjing. The overall objective of this study was to investigate the influence of pollution control on Pb inhalation bioaccessibility in $PM_{2.5}$ by 1) identifying Pb sources using the stable isotope ratio fingerprinting technique, and 2) measuring Pb inhalation bioaccessibility using two in vitro methods (ALF and Gamble's solution). The results from this study should provide us useful information for policy decision regarding pollution control and risk assessment for inhalation exposure to air-born Pb.

2. Materials and methods

2.1. Sampling of $PM_{2.5}$

Particulate matter ($PM_{2.5}$) sample was collected for ~12 h using a high volume air sampler (Model TE6070, Tisch Environmental Inc.) at a flow rate of 1.13 m^3 min^{-1} with quartz microfiber filters (Whatman, 203 mm × 254 mm). The sampling device was placed on the building roof (~30 m height) of the School of the Environment of Nanjing University on Xianlin campus. The campus is located in northeastern Nanjing, ~20 and 5 km away from industrial zone and Qixia lead–zinc mines.

A total of 32 $PM_{2.5}$ samples were collected before (10 samples, June 1st–July 31st), during (9 samples, August 1st–August 31st), and after (13 samples, September 1st–October 20th) YOG in 2014. Since the local government started source controls in early August, August samples were considered as the YOG period. Before sampling, quartz microfiber filters were heated at 500 °C for 5 h in a muffle furnace, and equilibrated in a desiccator for 48 h before being weighed using an analytical balance (Denver SI-234). After sampling, quartz microfiber filters were equilibrated in a desiccator before being weighed for $PM_{2.5}$ mass. The $PM_{2.5}$ mass was determined as the difference between the filter weights before and after sampling. The filters were encased in tinfoil and sealed in plastic bags and stored at −20 °C until analysis.

2.2. Total Pb concentration in $PM_{2.5}$

Quantification of Pb in $PM_{2.5}$ was performed by digesting quartz microfiber filters using ultra-pure concentrated HNO_3 and 30% H_2O_2 according to USEPA Method 3050B with slight modifications. Briefly, 1/16 of quartz microfiber filters were cut into pieces of <2 mm^2 using acid-cleaned ceramic knife. The filters were digested with 10 mL concentrated HNO_3 (1:1) by immersing quartz filters in concentrated HNO_3 so all $PM_{2.5}$ particles were in contact with HNO_3. Since $PM_{2.5}$ and filter were digested together, the digestion process should measure all the Pb on the filters. The digestion was conducted on a HotBlock digestion system (Environmental Express, USA) at 105 °C for 5 h, and then 10 mL concentrated HNO_3 was added. After concentrated HNO_3 was evaporated to near dryness and cooled down, 1–2 mL 30% H_2O_2 was added. The digestion was continued to reach ~1 mL solution, which was diluted to 50 mL with Milli-Q water, and filtered through 0.22 μm filter before analysis. Concentrations of Pb in the solution were determined by inductively coupled plasma mass spectrometer (ICP-MS, NexIONTM300X, Perkin Elmer, USA) with detection limit of 0.008 μg L^{-1}. Standard Reference Material (SRM) D056–540 was performed for QA/QC during digestion process. The Pb recovery was of 99.4 ± 5.78%, which is within the ±10% recommended by USEPA (2013).

2.3. Stable isotope ratios in $PM_{2.5}$

Lead stable isotope ratios of $^{207/206}Pb$ and $^{208/206}Pb$ in digestion solution were determined using ICP-MS. Instrument parameters were set as 190 sweeps/reading, 1 reading/replicate, and 10 replicates/sample solution. Dwell time of 40 ms was set for ^{204}Pb and 25 ms for ^{206}Pb, ^{207}Pb, and ^{208}Pb. Prior to analysis, Pb concentration in solution was diluted to ~15 μg L^{-1} using 0.1 M high-purity HNO_3. Standard reference material (SRM) NIST 981 with concentration of 15 μg L^{-1} was measured every 5 samples to obtain ratio correction factors to compensate for mass discrimination. The analytical precision for samples was generally <0.5% for $^{207/206}Pb$ and $^{208/206}Pb$. Measured $^{204/206}Pb$ (0.0590 ± 0.0001), $^{207/206}Pb$ (0.9149 ± 0.0024), and $^{208/206}Pb$ (2.1688 ± 0.0029) in the SRM NIST 981 ($n = 10$) were in good agreement with the certified values of 0.0590, 0.9146, and 2.1681.

2.4. Pb bioaccessibility in $PM_{2.5}$

Two artificial lung fluids including artificial lysosomal fluid (ALF) and Gamble's solution were employed to measure Pb inhalation bioaccessibility in $PM_{2.5}$ (Boisa et al., 2014; Colombo et al., 2008; Zereini et al., 2012). Detailed compositions of the lung fluids can be found in support information as Table S1. The extraction procedure was performed according to Zereini et al. (2012). Briefly, 1/16 of quartz microfiber filters (<2 mm^2) were placed in 50 mL high density polyethylene tubes containing 30 mL of fluid. Based on the $PM_{2.5}$ mass, the solid and solution ratio was 1:2400 to 1:14,000, which was in the range of 1:500 to 1:50,000 suggested by Julien et al. (2011). The tubes were put in an incubator at 37 °C in dark. Samples were shaken for 10 min every 4 h on a shaker at 50 rpm. Once inhaled into lungs, part of $PM_{2.5}$ can be quickly dissolved in the interstitial fluid, but 10–15% of the initially deposited $PM_{2.5}$ can be present in lungs after 1 day and their clearance in human bronchial tree may last for several weeks (Hofmann and Asgharian, 2003; Lippmann et al., 1980). So the $PM_{2.5}$ particles deposited in lung are subject to both short and long retention with most studies using 1 day as the short term (Julien et al., 2011). For the long term, time variations of 4–30 days were reported (Boisa et al., 2014; Zereini et al., 2012). In our preliminary test, some fungi appeared in lung fluid after 15-day extraction. To avoid the analysis uncertainty caused by fungi,