



Chemical partitioning of fine particle-bound metals on haze–fog and non-haze–fog days in Nanjing, China and its contribution to human health risks



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ABSTRACT

Information on chemical partitioning and associated risk of airborne metals, particularly during a haze–fog episode, is limited. Fine particulate matter (PM_{2.5}) was collected during a severe haze–fog event in winter and non-haze–fog periods in summer and fall from an urban region of a typical Chinese mega-city, Nanjing. The particulate-bound metals (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, Ti, V, and Zn) were chemically fractionated in a four-step sequential extraction procedure and human health risk was assessed. During the haze–fog episode, PM_{2.5} was extremely elevated with a mean concentration of 281 µg/m³ (range: 77–431 µg/m³), whereas the mean PM_{2.5} concentrations in summer and fall periods were 86 µg/m³ (range: 66–111 µg/m³) and 77 µg/m³ (range: 42–131 µg/m³), respectively. All elements had significantly higher concentrations and many metals exceeded relevant limits on haze–fog days. K, Na, Sr, Zn, Mo, Ca, Cd, Mg, Mn, Cu, Ba, Cr and As all showed relatively high proportions of the soluble and exchangeable fraction and strong bio-accessible potential. High temperature and humidity may increase the bio-accessible fraction of many airborne metals. The hazard index for potential toxic metals was 0.115, which was lower than the safe limit (1). However, the combined carcinogenic risk was 1.32×10^{-6} for children and 5.29×10^{-6} for adults, with both values being higher than the precautionary criterion (10^{-6}). Results of this study provide information for the behavior and risk mitigation of airborne metals.

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1. Introduction

Urban atmospheric pollution is considered one of the world's most serious environmental issues in the face of rapid economic development. Among types of atmospheric particulate matter (PM), fine particulate matter (PM_{2.5}, particles having an aerodynamic diameter of 2.5 µm or less) is of great concern owing to its adverse health effects and close association with haze (Pui et al., 2011; Yang et al., 2012; Ram et al., 2016). It has been reported that exposure to high PM_{2.5} concentrations in ambient air can cause lung diseases, heart diseases, and premature death in humans (WHO, 2006; Dominici et al., 2007; Janssen et al., 2013; Ostro et al., 2014). Compared with coarse PM, PM_{2.5} with increased surface area has more potential to absorb air pollutants, especially high concentrations of potentially toxic metals that can be incorporated into human

body through inhalation (Hu et al., 2012; Li et al., 2013). There is growing evidence, from toxicological and epidemiological studies, that toxic metals in PM are a major component of the toxicity of PM (Mohanral et al., 2004; Gerlofs-Nijland et al., 2009; Bollati et al., 2010; Zhai et al., 2014). Additionally, metals bound to fine PM are a long-term burden on biogeochemical cycling in the ecosystem (McConnell and Edwards, 2008; Li et al., 2013).

Studies have shown that for the evaluation of potential environmental and health effects, it is crucial to know not only the total metal amounts but also the chemical forms, which determine the behaviors of the metals in the environment (Fernández-Espinosa et al., 2002; Feng et al., 2009; Betha et al., 2014). The labile fraction of particle-bound metals is considered more readily available to environmental receptors than the resistant fraction (Feng et al., 2009). The easily released water-soluble metal fractions are assumed to be easily mobilized when interacting with human body fluid and are therefore regarded as bio-accessible trace metal fractions (Mukhtar and Limbeck, 2013). Previous studies conducted in vitro by simulating the respiratory

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environment, or in vivo using animal models, have implied that concentrations of water-soluble metals in airborne PM are correlated positively with observed pulmonary toxicity (Gavett et al., 1997; Dye et al., 2001; Li et al., 2003). After interaction with body fluid, bio-accessible trace metal fractions are released where they can be absorbed into human physiological systems and thereby exert adverse toxic effects (Mukhtar and Limbeck, 2013). There are several sequential chemical fractionation schemes available for PM (Tessier et al., 1979; Chester et al., 1989; Zatka et al., 1992; Ure et al., 1993). Generally, among fine PM-bound metals, the toxic and predominantly anthropogenic elements such as Zn, As and Cd have relative high mobile proportions, whereas the predominantly geogenic elements such as Ti and Fe always present high proportions in the residual fraction (Feng et al., 2009; Schleicher et al., 2011; Li et al., 2015). A four-step modified Tessier scheme was used in this study because it provided conditions similar to the deposition and solubilisation in the human lung (Fernández-Espinosa and Ternero-Rodríguez, 2004) and was widely used previously (Fernández-Espinosa et al., 2002; Feng et al., 2009; Schleicher et al., 2011; Li et al., 2015). Within this paper, the bio-accessible metal fractions estimated by the sequential fractionation steps and the possible influencing meteorological factors were discussed.

Haze is a phenomenon where moisture, dust, smoke, or vapor in the atmosphere results in atmospheric visibility of < 10 km, whereas fog is composed of fine droplets of water suspended in air near the Earth's surface (Han et al., 2014). Haze–fog (HF) is attracting increasing concern because of its adverse effects on visibility, public health, ecological systems, and even the global climate (Sun et al., 2006; Cheng et al., 2013; Han et al., 2014). High atmospheric PM loading is an indicator for the quantification of an HF episode (Chan and Yao, 2008; Tan et al., 2009; Hu et al., 2016). Several studies on chemical composition including metal elements of PM on haze days have recently been reported (Huang et al., 2011; Yin et al., 2012; Norela et al., 2013; Tian et al., 2014). However, to our knowledge, there are few reports on the chemical fractionation distribution of particulate-bound elements on HF days, which is important information for us to gain a comprehensive understanding of the pollution characteristics and health effects of airborne metals.

Thus, the main objectives of this study were to investigate the total amounts and the chemical partitioning of metal elements in PM_{2.5} collected from an urban region of Nanjing, a typical megacity of China, during a severe HF event and during non-HF periods, and to evaluate the carcinogenic and non-carcinogenic health risks via inhalation of PM_{2.5} based on the bio-accessible fractions of airborne toxic metals.

2. Materials and methods

2.1. Sampling

Nanjing (118°46' E, 32°03' N), the second largest city in the Yangtze River Delta region, is one of the fastest growing districts in China. It is the industrial production base and the main transport hub for south-eastern China. PM_{2.5} samples were collected from the Gulou campus of Nanjing University, which is located in the center of the city and near the central business area of Nanjing. The air quality in the study area is affected by emissions from high levels of traffic and industrial pollutants emitted from suburban areas. More details can be found in the Supporting Information (Supplemental Fig. S1).

PM_{2.5} samples were collected on Whatman quartz microfiber filters using high-volume PM samplers (model TE-6070VFC, Tisch Environmental, Inc.) at a flow rate of 1.13 m³/min. Daytime (8:00 a.m. to 6:00 p.m.) and nighttime (7:00 p.m. to 7:00 a.m.) sampling was conducted from December 2 to 10, 2013 (HF period), and on consecutive non-HF days from August 11 to 28 in summer and from October 10 to 18 in fall of 2013 (non-HF periods). All quartz microfiber filters were equilibrated in a desiccator for 48 h after sampling and then weighed to determine the aerosol mass. Hourly meteorological data and hourly atmospheric pollutant concentrations were recorded simultaneously at air-quality monitoring stations set near the sampling site.

2.2. Sequential extraction procedure (SEP)

The four-step SEP used in this study fractionates the particulate-bound metals into four fractions, which can be defined as soluble and exchangeable metals (F1), carbonates, oxides and reducible metals (F2), metals bound to organic matter and oxidizable and sulfidic metals (F3) and residual metals (F4). The reagents and operational conditions used in each step are summarized in Table 1. During each extraction step, separation was performed by centrifugation at 4500 rpm for 15 min and the supernatant was transferred to a Teflon beaker. The filters were then rinsed with fresh extracting reagent and centrifuged again, and the supernatant was decanted into the same Teflon beaker. The combined supernatants were heated until 1–2 mL of solution remained and diluted with 2% HNO₃ for analysis. A total of 50 samples were used for SEP. At least five blank filters were analyzed simultaneously during the SEP, and the concentration of each element in each PM_{2.5} sample was corrected by subtracting the mean blank concentration.

2.3. Analysis of elemental concentrations

Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sr, Ti, V, and Zn concentrations in each extract were determined by inductively coupled plasma atomic emission spectrometry (PerkinElmer, Waltham, MA, USA) and by inductively coupled plasma-mass spectrometry (using an Elan 9000 instrument; PerkinElmer). Inductively coupled plasma-mass spectrometry was optimized using 10 µg/L⁻¹ Mg, Rh, In, Ba, Ce, Pb and U solution in 2% HNO₃ and ¹¹⁵In was used as the internal standard at 20 µg/L in 2% HNO₃ during element analysis. The standardized reference materials SRM 1649a (urban particulate matter) from the National Institute of Standards and Technology was used to verify the precision and accuracy. The recoveries generally between 88% and 105% for the different metals studied in this study.

An internal recovery of each element as the sum of the four fractions (F1, F2, F3 and F4) was compared with the total metal concentrations separately determined as an internal check of the extraction process (Li et al., 2015), which was calculated as follows:

$$\text{Recovery}(\%) = \frac{F1 + F2 + F3 + F4}{TC} \times 100, \quad (1)$$

where, F1, F2, F3, F4 and TC refer to the concentration extracted in each fraction and the total concentration of elements, respectively. Generally, the recovery ranged from 86% to 112% for the studied elements, which indicates that the sums of the four fractions are in good agreement with the total concentrations and this SEP is reliable and repeatable.

2.4. Enrichment factors

The enrichment factor (EF), based on the normalization of a tested metal against a conservative reference element (Chen et al., 2008;

Table 1
Chemical fractions of metals, corresponding reagents and operating conditions used in the SEP.

Fraction	Reagents	Experimental conditions
Soluble and exchangeable metals (F1)	Milli-Q	3 h agitation on a shaker at room temperature
Carbonates, oxides, and reducible metals (F2)	0.25 M NH ₂ OH · HCl at pH 2.0	5 h agitation on a shaker at room temperature
Organic-matter-bound, oxidizable, and sulfidic metals (F3)	H ₂ O ₂ 30% and 2.5 M NH ₄ OAc at pH 3.0	Agitation on a shaker at 95 °C until nearly dry then agitation on a shaker for 90 min at room temperature
Residual metals (F4)	HNO ₃ , HCl, and HClO ₄	Agitation on a shaker for 5 h at 95 °C

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