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Fractionation of airborne particulate-bound elements in haze-fog episode and associated health risks in a megacity of southeast China

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ABSTRACT

Haze caused by high particulate matter loadings is an important environmental issue. $PM_{2.5}$ was collected in Nanjing, China, during a severe haze–fog event and clear periods. The particulate-bound elements were chemically fractionated using sequential extractions. The average $PM_{2.5}$ concentration was 3.4 times higher during haze–fog (96–518 μg/m^3) than non-haze fog periods (49–142 μg/m^3). Nearly all elements showed significantly higher concentrations during haze–fog than non-haze fog periods. Zn, As, Pb, Cd, Mo and Cu were considered to have higher bioavailability and enrichment degree in the atmosphere. Highly bioavailable fractions of elements were associated with high temperatures. The integrated carcinogenic risk for two possible scenarios to individuals exposed to metals was higher than the accepted criterion of 10^{-6}, whereas noncarcinogenic risk was lower than the safe level of 1. Residents of a city burdened with haze will incur health risks caused by exposure to airborne metals.

1. Introduction

Haze is defined as a phenomenon in which moisture, dust, smoke, or vapor in the atmosphere causes atmospheric visibility of <10 km (Sun et al., 2006). Haze–fog (HF) episodes, usually accompanied by high concentrations of particulate matter (PM), especially $PM_{2.5}$ (PM with aerodynamic particle diameters ≤2.5 μm), in the atmosphere have attracted increasing levels of concern over the past decade because of their adverse impacts on visibility, public health, ecological systems, and even the global climate (Tai et al., 2010; Cheng et al., 2013; Han et al., 2014; Pui et al., 2014). Severe haze pollution occurs in China because of high levels of atmospheric pollutant emissions, especially in city-clusters such as the Yangtze River Delta area (YRD), the Beijing–Tianjin–Hebei Province region, and the Pearl River Delta area (van Donkelaar et al., 2010; Cheng et al., 2013). Nanjing is one fast growing megacity in the YRD, however, the concentrations of $PM_{2.5}$ in Nanjing which are mainly from industrial emissions, vehicle exhausts, and construction activities are consistently higher than the new Chinese national ambient air quality standard (NAAQS), GB3095-2012.

Exposure to high $PM_{2.5}$ concentrations in ambient air can lead to lung diseases, heart diseases, and premature death in humans (WHO, 2006; Pui et al., 2014). Atmospheric particulates are classified as group 1 contaminants by the International Agency for Research on Cancer (Sun et al., 2014). Many elements, such as As, Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn, are widely present in PM and are therefore considered to be important airborne toxicants (Mohanral et al., 2004; Gerlofs-Nijland et al., 2009; Bollati et al., 2010; Loxham et al., 2013; Cakmak et al., 2014). Airborne metals can not only cause dysfunction and various diseases in humans but can also impose long-term burdens on biogeochemical cycling in ecosystems (Nriagu and Pacyna, 1988; Duan and Tan, 2013).

It is known that metals in different chemical fractions generally have different bioavailabilities and behaviors in the environment (Wang et al., 2007; Feng et al., 2009; Schleicher et al., 2011; Duan

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and Tan, 2013; Mukhtar et al., 2013; Rogula-Kozlowska et al., 2013; Witt et al., 2014). In general, highly soluble metallic fractions of PM are more readily bio-activated and bioavailable than less soluble components to lung tissues in the alveoli (Fernández-Espinosa and Ternero-Rodríguez, 2004; Smichowski et al., 2005). Bioavailability is the primary controller of toxicity, which means the degree and rate of absorption of a substance by a living system or the degree to which the substance is available to physiologically active sites (Smichowski et al., 2005; Mukhtar et al., 2013). The bioavailability of a metal depends on the surface properties of the PM, the strength of the intrinsic PM properties and PM–metal bonds, and the properties of the solutions the PM is in contact with (Smichowski et al., 2005). Studies on both the total amounts present and their chemical forms during HF episodes and non-HF days are required to gain a comprehensive understanding of particulate-bound metals and to estimate the potential health effects of these metals. However, much research has been focused on metal concentrations in PM, and in most studies the chemical fractionation of metals in particulate has not been determined.

A severe prolonged regional HF event with extremely high pollutant concentrations occurred in China from early December until the middle of December 2013. Almost all the cities in mid-eastern China were blanketed by heavy HF. In the present study we collected $PM_{2.5}$ samples from a typical megacity of Southeast China during this HF event and on days unaffected by haze in summer and fall. The main objectives were to characterize and compare the ways particulate-bound elements were chemically fractionated on HF and non-HF days. Meanwhile, the health risks posed by particulate-bound metals to residents because of $PM_{2.5}$ exposure were also evaluated.

2. Materials and methods

2.1. Sampling

Nanjing covers approximately 6600 km^2 and had a population of more than 8.2 million in 2013. Nanjing is in the north subtropical monsoon climate zone, and it has an annual mean temperature of 16 °C and a mean annual precipitation of 1106 mm. The prevailing wind normally blows from the southeast in summer and from the northwest in winter. Nanjing is an important comprehensive industrial production base and the main transportation hub in East China. $PM_{2.5}$ samples were collected from Xianlin campus of Nanjing University which is near the northern industrial zones. There are several important industrial point sources of pollutants near the sampling site and the air quality in Xianlin is mainly affected by the short-range transportation of industrial pollutants. More details can be found in Supporting Information, SI (Fig. S1). $PM_{2.5}$ samples were collected on quartz microfiber filters (Whatman, Maidstone, UK) using high-volume PM samplers (model TE-6070VFC; Tisch Environmental, Cleves, OH, USA) with a flow rate of 1.13 m^3/min. Each filter was conditioned for 48 h in a desiccator at 25 °C and 40% relative humidity before and after sampling, then weighed using a microbalance (Mettler-Toledo, Greifensee, Switzerland). Monitoring data from Nanjing Environmental Protection Bureau (http://www.njhb.gov.cn/), suggests PM pollution is less a concern during the summer and autumn seasons relative to the winter season. Thus, separate samples were collected during the day, from 0800 to 1800, and night, from 1900 to 0700, from 2 to 10 December 2013 (the HF event) and on non-HF days from 11 to 28 August (summer) and from 10 to 18 October (autumn). A total of 50 samples were collected. Meteorological data were recorded simultaneously at an air quality monitoring station set at the sampling site.

2.2. Sequential extraction procedure and analysis

A four-step sequential extraction procedure (SEP) was used. This SEP was used because this method can provide conditions similar to the deposition and solubilisation in the human lung (Fernández-Espinosa and Ternero-Rodríguez, 2004) and widely used previously (Fernández Espinosa et al., 2002; Feng et al., 2009; Schleicher et al., 2011; Li et al., 2015). The extraction procedure, reagents, and conditions used in each step were summarized in Table 1. The particulate-bound metals were fractionated into four fractions, operationally defined as soluble and exchangeable metals (F1); carbonate-bound, oxides, and reducible metals (F2); organic-matter-bound, oxidizable, and sulfidic metals (F3); and residual metals (F4). After each step, the extract was separated from the residue by centrifuging the mixture at 4200 rpm for 10 min. The supernatant was then transferred to a Teflon beaker and the filter was rinsed with fresh extraction solution, centrifuged again, and the supernatant decanted into the same Teflon beaker. The combined supernatants were heated until 1–2 mL of solution remained, then diluted with 2% HNO_3 for analysis.

The 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 (Perkin Elmer, Waltham, MA, USA) and by inductively coupled plasma-mass spectrometry (using an Elan 9000 instrument; Perkin Elmer). During the ICP-MS analysis, ^{115}In was used as internal standard at 20 μg/L in 2% HNO_3. Blank filters were analyzed simultaneously during SEP, and the concentration of each element in each $PM_{2.5}$ sample was corrected by subtracting the mean blank concentration. 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 element recovery percentage from the standard reference material was between 86% and 107%.

2.3. Internal check recovery of elements

The total metal concentrations of the $PM_{2.5}$ samples were separately determined by digestion with a mixture of $HClO_4$, HNO_3 and HF. An internal check of the recovery of each element by SEP was performed, 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 ranges were from 84% to 118% 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. Health risk assessment model

It is useful to perform a health risk assessment to estimate the potential adverse effects on residents caused by exposure to airborne metals (Taner et al., 2013; Sun et al., 2014; Zhou et al., 2014). The carcinogenic and noncarcinogenic risks posed by airborne metals via direct inhalation of $PM_{2.5}$ were calculated using US Environmental Protection Agency (US EPA) human health risk assessment models (US EPA, 1989, 2009), which mainly involve exposure assessment and risk characterization. No characteristic population parameters for local residents are found, thus sensitive residents were divided into children and adults. The inhalation exposure concentration (EC), hazard quotient (HQ) for non-cancer