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Trace elements in particulate matter from metropolitan regions of Northern China: Sources, concentrations and size distributions

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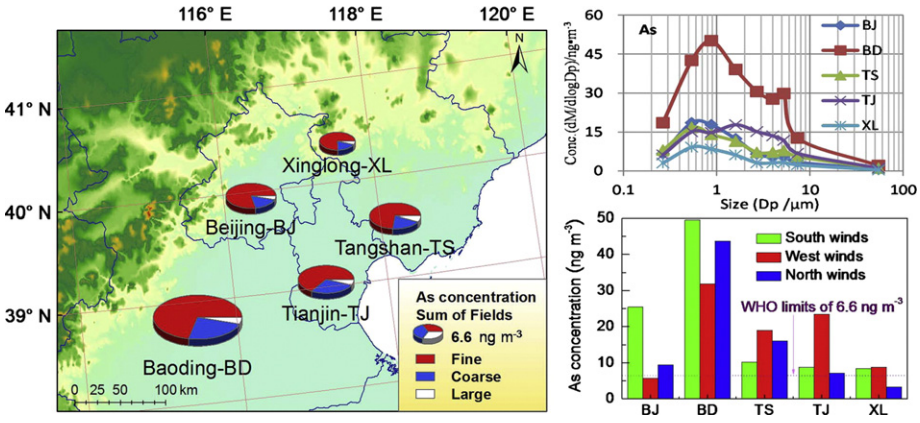
HIGHLIGHTS

- Trace elements of size-resolved aerosols were measured in an urban agglomeration.
- Aerosol heavy metals were enriched by over 100-fold relative to the Earth's crust.
- The annual mean As, Pb, Cd and Mn concentrations in the air exceeded the WHO limits.
- High levels of elements with westerly winds indicated that the major source is soil.
- Fossil fuel burning and industrial processes contributed to aerosol metal pollution.

GRAPHICAL ABSTRACT



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ABSTRACT

Public concerns over airborne trace elements (TEs) in metropolitan areas are increasing, but long-term and multi-site observations of size-resolved aerosol TEs in China are still lacking. Here, we identify highly elevated levels of atmospheric TEs in megacities and industrial sites in a Beijing–Tianjin–Hebei urban agglomeration relative to background areas, with the annual mean values of As, Pb, Ni, Cd and Mn exceeding the acceptable limits of the World Health Organization. Despite the spatial variability in concentrations, the size distribution pattern of each trace element was quite similar across the region. Crustal elements of Al and Fe were mainly found in coarse particles (2.1–9 μm), whereas the main fraction of toxic metals, such as Cu, Zn, As, Se, Cd and Pb, was found in submicron particles (<1.1 μm). These toxic metals were enriched by over 100-fold relative to the Earth's crust. The size distributions of Na, Mg, K, Ca, V, Cr, Mn, Ni, Mo and Ba were bimodal, with two peaks at 0.43–0.65 μm and 4.7–5.8 μm. The combination of the size distribution information, principal component analysis and air mass back trajectory model offered a robust technique for distinguishing the main sources for airborne TEs, e.g., soil dust, fossil fuel combustion and industrial emissions, at different sites. In addition, higher elemental concentrations coincided with westerly flow, indicating that polluted soil and fugitive dust were major sources of TEs on the regional scale. However, the contribution of coal burning, iron industry/oil combustion and non–ferrous smelters to atmospheric metal pollution in Northern China should be given more attention. Considering that

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the concentrations of heavy metals associated with fine particles in the target region were significantly higher than those in other Asian sites, the implementations of strict environmental standards in China are required to reduce the amounts of these hazardous pollutants released into the atmosphere.

1. Introduction

Trace elements (TEs) constitute a minor proportion of urban aerosols but contribute significantly to overall air pollution due to their toxicity (Kampa and Castanas, 2008; Pacyna and Pacyna, 2001). Airborne TEs include mineral elements and heavy metals, which originate mainly from natural and anthropogenic sources, respectively (Bilos et al., 2001; Karaca et al., 2009; Pancras et al., 2013). In addition, they are distributed among the wide aerodynamic size range of their constituent particles (Polidori et al., 2009). PM_{10} (particles with aerodynamic diameters less than 10 μm) deposit mainly in the upper respiratory tract, while fine (<2.5 μm) and ultra-fine (<100 nm) particles are able to reach lung alveoli (Kampa and Castanas, 2008). Thus, most heavy metals in the form of small particles are responsible for harmful effects on health and are designated as "hazardous air pollutants" due to their accumulation in the human body (Bilos et al., 2001). TEs in fine particulate matter can also be widely dispersed before being scavenged by rain. Meanwhile, TEs associated with coarse particles (2.5–10 μm) are primarily lost via dry deposition due to their high deposition velocities (Pan and Wang, 2015). After deposition on plants, soil or water through wet or dry deposition, TEs can enter the human body through the food chain and bioaccumulate (Järup, 2003). These effects on human health and the environment strongly depend on the size distribution of aerosols, a significant but variable property that determines the residence time and toxicity of TEs in the atmosphere (Besis et al., 2015; Samara and Voutsa, 2005). Moreover, the collection and analysis of particles in different size ranges provides insight into the sources and fate of the TEs, which is useful for characterizing the different types of aerosols in urban and rural environments.

The particle size distributions of TEs have been widely studied in several areas around the world (Allen et al., 2001; Silva et al., 1999; Zereini et al., 2005). In Asia, however, previous reports mainly focused on a single fraction (e.g., PM_{10} or $PM_{2.5}$), as reviewed by Fang et al. (2010). To date, a paucity of measurement data is still a major challenge in China, especially in urban areas, where the air quality is usually poor. To make things worse, the national emissions of TEs in China are among the highest in the world (Wu et al., 2012). These emissions are mainly linked to fossil fuel combustion and industrial smelters (Tian et al., 2012). Northern China generates the highest anthropogenic metal emissions, such as Cr, Cd and Pb, in the country due to its rapid industrialization and urbanization (Li et al., 2012; Tian et al., 2012). Although efforts have been invested in characterizing the physical, chemical and optical properties of particulate matter in the target region (Zhang et al., 2007), most previous studies were short-term or limited to a single site (Jing et al., 2014). In a recent report, Pan et al. (2013a) analyzed the pollution episodes of heavy metals observed through daily measurements of size-resolved aerosols at a mountainous site in Northern China to understand the influences of regional transport. However, that study was limited to 18 days in autumn. Because the concentrations of TEs have large spatial and temporal variability, long-term and multi-site observations are needed (Zhao et al., 2013). In addition, measurements performed for single size fractions were not enough for the mitigation of measurements (Tian et al., 2015); thus, detailed size-resolved information should be the focus of future monitoring activities.

This study presents a one-year observation of the size distributions of TEs in airborne particles collected during an intensive field campaign at four selected cities with varying urban geographies, energy structures and human populations and a rural background site. The distinctive features of the study are (i) the multi-site and long-term sampling approach, (ii) the discrimination of size-resolved particles, and (iii) the uniform observation protocol used at the five sites. Using this approach, it was possible to clarify the sources, size distributions and spatial variations of aerosols in Northern China. The information presented in this article will advance our current understanding of the regional nature of airborne TEs and can be used to evaluate changes in anthropogenic versus natural emissions, which in turn can be used to inform policy-makers on reducing toxic metal emissions in metropolitan areas.

2. Materials and methods

2.1. Field sampling

Field sampling was conducted bi-weekly between Sep. 2009 and Aug. 2010 synchronously at the five sites, i.e. two urban sites located in urban agglomerations of Beijing (BJ) and Tianjin (TJ), two industrial cities of Baoding (BD) and Tangshan (TS) located in Hebei Province and a regional background site (Xinglong—XL) located on the Mountain Yan (the northeast border of North China Plain). These sites were selected to represent the typical air pollutant gradients across the industrial–urban–rural sprawl in the Beijing–Tianjin–Hebei urban agglomeration, with a total population of approximately 0.1 billion. This hotspot experiences some of the most serious air pollution in the world. Fig. 1 shows locations of five sampling sites, with detailed description in previous studies (Pan et al., 2012).

At each site, the size-resolved particles were collected on 81-mm mixed cellulose ester filters (Thermo-Electron Co., USA) using an 8-stage cascade impactor operating at 28.3 L min^{-1} (Anderson Series 20–800, USA). The sampler segregates particles based on their aerodynamic diameters (Dp) in the following 9 size ranges: >9.0, 9.0–5.8, 5.8–4.7, 4.7–3.3, 3.3–2.1, 2.1–1.1, 1.1–0.65, 0.65–0.43 and <0.43 μm. The sampling period was 24 h at 4 urban and industrial sites, but for 48 h at the XL site to collect enough particles accumulation for analysis. Due to the malfunctions of the sampler during the experiment period, in total 23, 23, 23, 22 and 18 sets of size-resolved filter samples were collected finally at BJ, BD, TS, TJ and XL, respectively. Because each sample set has 9 filters according to the aforementioned size ranges, in total 207, 207, 207, 198 and 162 filter samples were collected at BJ, BD, TS, TJ and XL, respectively. All of the filters were prepared and analyzed at the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC, Beijing).

2.2. Elemental analysis

A quarter of each filter was acid digested to dissolve the total TEs fraction in particles loaded on the filters. The digestion method was optimized with different acid mixtures and described in detail in our previous report (Pan et al., 2010). Briefly, a combination of concentrated HNO_3 (5 ml), H_2O_2 (2 ml) and HF (0.2 ml) was employed for microwave-assisted digestion (MARS 5, CEM Corporation, Matthews, NC, USA), with temperature-controlled procedure shown in Fig. 2. To ensure the analysis quality, reference materials of fly ash (GBW08401) and soil (GBW07401) were acid digested and measured in parallel with the filters. The recoveries of the TEs were within the allowable ranges of the certified values (100 ± 15%), with the exception of Se (Table 1).

Chemical analyses were performed with an Agilent 7500a inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies,