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Size-resolved aerosol trace elements at a rural mountainous site in Northern China: Importance of regional transport

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HIGHLIGHTS

- Trace elements of size-resolved aerosols were measured at a rural site in North China.
- Measured heavy metals in fine particles increased significantly in the past 30 years.
- Meteorology and emissions affected the day-to-day variations of trace elements.
- Episodes of heavy metals were observed with south flows from upwind industrial areas.
- Elevated concentrations of heavy metals in potential source regions were identified.

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ABSTRACT

This paper presents an intensive field measurement campaign carried out at the rural mountainous site of Xinglong (960 m a.s.l.) in Northern China during Sep. 3–20 2008. Size-segregated samples were collected daily and analyzed for 25 trace elements (TEs). The majority of the TEs showed comparable concentrations in fine (<2.1 μm) and coarse particles (2.1–9 μm). In addition, elements like K, Mn, Cu, Se, Mo, Ag, Cd, Tl and Pb were accumulated in fine mode whereas Al, Co and Sb were concentrated in a coarse mode. For most of the TEs, their enrichment factor (EF) increased with decreasing particle size from large (>9 μm) to coarse, and to fine, signifying influences by anthropogenic emissions. The observed concentrations of heavy metals in fine particles, with EF values higher than 100, were significantly higher than the historical data recorded in the 1980s and 1990s, reflecting the increasing emissions in the target area. One pronounced event occurred on Sep. 14 when all of the TEs showed a peak, which was associated with regional emissions from both southeast (SE) and southwest (SW) indicated by backward trajectory analysis. This is further supported by the measurements in upwind sites where the concentrations of TEs were several times higher than those in Xinglong, suggesting potential source regions. Episodes of heavy metals were generally characterized by significant enhancements of fine mode and air mass trajectories from SE or SW alone. Taking this finding and factor analysis results together, the metallic episodes were attributable to the long-range transport of regional plumes from coal consumption and nonferrous metal smelting. With the rapid urbanization and industrialization in Northern China, the increasing emissions of TEs will place a great strain on human health and the environment in the downwind regions, thus long-term and multi-site observation with high time resolution are necessary.

1. Introduction

Atmospheric particulate matter is a mixture of organic and inorganic constituents originated from both natural and anthropogenic sources (Kim and Hopke, 2006; Schwarz et al., 2012). There is a specific interest in trace elements (TEs) which, although low in mass concentrations, are ubiquitous in airborne particles over large regions of the Earth because of their impacts on human health and the environment (Bao et al., 2012; Shevchenko et al., 2003). Most of toxic TEs in the troposphere are concentrated in fine particles (X. Li et al., 2012; Yang et al., 2009), which have a lifetime of days or weeks and can travel hundreds to thousands of kilometers (Moreno et al., 2012; Raes et al., 2000). They are therefore widely dispersed throughout the atmosphere before they finally deposit through wet and dry deposition (Duce et al., 1975; Yi et al., 2006). Fine particles were also removed from the atmosphere when they impact with a rough surface like vegetation (Beckett et al., 1998). As a result, forest areas tend to receive more input of TEs compared with regions where vegetative cover was little, arousing great concern of potential ecological impacts. Moreover, particles in the mountain atmosphere are suggested to be more significantly influenced by long-range transport, thus provide the atmospheric pollution information on a large-scale (Decesari et al., 2005).

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In the past decades, measurement information of size-resolved aerosol chemistry was carried out at many mountainous/rural/remote regions around the world (Boman et al., 2009; Khare and Baruah, 2010; Kim et al., 2007; Mooibroek et al., 2011; Pakkanen et al., 2001). Relevant studies in China have focused on the impact of dust storms on the downwind urban air quality and most of them are interested in reactive components that are non-conservative, including organic carbon, inorganic ions and their precursors (Wang et al., 2011). Only a few works considered the regional influences of the anthropogenic emissions on the downwind rural areas (Wong et al., 2003; Zhao et al., 2013). Compared to the aforementioned reactive species, TEs in fine particles can be served as a stable tracer for long-range transport since most of them were found to be more conservative and depositional loss could be neglecting.

As a result of rapid industrialization and urbanization, Northern China is becoming a hotspot subject to anthropogenic emissions of TEs such as Pb, Cd and Cr (Q. Li et al., 2012; Tian et al., 2012a), thus prompting great concern of regional influences. However, previous observations on aerosol TEs in the target area were mostly collected from ground level, and limited knowledge has been acquired in mountainous sites (Deng et al., 2011; Zhao et al., 2013). To date, few measurements with a high time (e.g., daily or few hours interval) and size resolution have been conducted in background Northern China to provide a better insight on processes such as formation, transport, removal, deposition and chemical reactions in the atmosphere, though the importance of such data has been emphasized in the source apportionment studies (Dall'Osto et al., 2012; Pancras et al., 2013; Vecchi et al., 2009).

The mountainous Xinglong (XL) station, by virtue of its location on the boundary area between North China Plain and Mt. Yanshan, is an ideal transport site capable of obtaining a regional signature of pollutants. The first report in the international literature regarding the impacts of long-range transport on the aerosol composition at this site appeared in 1980 (Winchester et al., 1981). The increase in regional background of atmospheric TEs due to anthropogenic emissions was recorded 15 years later by Yang et al. (2000). However, few up-to-date studies have been conducted in the past decade to determine the specific aerosol components at this location (Pan et al., 2010). In particular, temporal variations of the elemental composition in size-resolved aerosols are still not well understood, due to the paucity of fast-response chemical measurements (tens of minutes) that are commonly available currently.

In the current study, we present size-resolved elemental composition of aerosols from an intensive field campaign conducted at the XL site in autumn 2008, during which several pollution events were recorded. The objective of the study is to recognize the historical evolution of the fine particles by comparison with the elemental composition reported in the 1980s and 1990s, and to investigate the impact of long-range transport of regional emissions on the metallic episodes in downwind rural atmospheres. The results presented are important to inform policy-makers on abatement of pollutant emissions in the target area, and also help in predicting the impact of human activities on the downwind ecosystems in other countries now contemplating regional air pollution.

2. Materials and methods

2.1. Site description

The aerosol samples were consecutively collected from Sep. 3 to 20 during 2008 at the XL site (40.38°N, 117.57°E) (Fig. 1). Details of the sampling site can be found elsewhere (Pan et al., 2012) and are briefly described here. The site is located on a peak of Mt. Yanshan (north of Hebei province) with an elevation of 960 m a.s.l. It is a typical forest area over 100 km NE of downtown Beijing (BJ) and 100 km SW of Tangshan (TS). Since there are no serious local emissions except for a few villages at the foot of the mountain, the XL site is characterized by its background-like nature. The sampler was located on the rooftop of a building (8 m above the ground) at the site. Meteorological parameters were recorded concurrently (Fig. 2). To understand the episodes of air pollution, the concentrations of $PM_{2.5}$ at the site derived from Wu et al. (2010) are also shown in Fig. 2. Air mass backward trajectories were generated using the HYSPLIT Model (Draxler and Rolph, 2012).

2.2. Sampling and pre-treatment of samples

During the experiment, size-resolved particulate matter samples were collected daily using a cascade impactor (Anderson Series 20-800, USA) at a flow rate of 28.3 l min^{-1}. The sampling frequency was 24 h from 08:00 LST in the morning to 08:00 the following day. The sampler had 9 size stages with nominal cut-off set >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. During the period of study, 18 consecutive sampling days were carried out. In total, 162 samples were collected and analyzed.

Since a detailed description of the sampling equipment, procedures and analytical techniques has been published elsewhere in a series of data reports (X. Li et al., 2012; Yang et al., 2009), a brief description is presented here. The substrates used in the sampler were mixed cellulose ester filters that were each 81 mm in diameter (Thermo-Electron Co., USA). The filters were individually placed into plastic bags and frozen at −20 °C immediately after collection and were delivered in iceboxes to the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC, in Beijing). All sample-handing processes were conducted using gloves to avoid pollution.

2.3. Chemical analysis by ICP-MS

Microwave digestion has been applied for the destructions of mineral and metallic species in environmental samples using a variety of chemical reagents (Bettinelli et al., 1989; Karthikeyan et al., 2006). The extraction method applied here has been briefly introduced in previous work (Yang et al., 2009) and described in detail here. Upon returning to the laboratory of LAPC, half of the filters were acid digested in a mixture of concentrated HNO_3 (5 ml), HCl (2 ml) and HF (1 ml) by using a closed vessel microwave digestion system (MARS 5, CEM Corporation, Matthews, NC, USA). The addition of HF strongly affects the recovery of target TEs since this acid breaks down silicates and minerals better than HNO_3/HCl acid combinations (Melaku et al., 2005). However, HF can give rise to problems in glassware and torch damage of ICP-MS. After the final digestion of the samples, the clear dissolved solutions were warmed to 150 °C first in order to remove the excess acids, and then the residue is dissolved in 50 ml PET bottles with 2% HNO_3. All samples were stored in the dark at 4 °C prior to analysis.

The concentrations of Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Tl, Pb, Th and U in the digests were determined by using Agilent 7500a inductively coupled plasma mass spectrometry (ICP-MS, Agilent Technologies, Tokyo, Japan). The instrument was optimized daily according to the standard optimization procedures and criteria specified in the manufacturer's manual. Calibration was carried out using the reference of external standards (Agilent Technologies, Environmental Calibration Standard, Part 5183-4688) and the internal standard (^{45}Sc, ^{115}In and ^{209}Bi at 20 μg l^{-1} in 2% HNO_3) was added online during elements analysis.

2.4. Quality assurance and quality control

Two certified materials of soil (GBW07401) and fly ash (GBW08401) were prepared in parallel to ensure the analysis quality of the results obtained. Table 1 shows the recoveries of selected elements in GBW07401 and GBW08401, using the aforementioned digestion and analysis procedure. Some elements are not listed on the column of GBW08041 in Table 1 due to the absence of certified values (Na, Ni, Mo, Sb and Tl) or extremely low target levels (Be and Cd). Data for Ag,