Research article

Monitoring and source apportionment of trace elements in PM$_{2.5}$: Implications for local air quality management

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Abstract

Fine particulate matter (PM$_{2.5}$) samples were collected simultaneously every hour in Beijing between April 2014 and April 2015 at five sites. Thirteen trace elements (TEs) in PM$_{2.5}$ were analyzed by online X-ray fluorescence (XRF). The annual average PM$_{2.5}$ concentrations ranged from 76.8 to 102.7 µg m$^{-3}$. TEs accounted for 5.9%–8.7% of the total PM$_{2.5}$ mass with Cl, S, K, and Si as the most dominant elements. Spearman correlation coefficients of PM$_{2.5}$ or TE concentrations between the background site and other sites showed that PM$_{2.5}$ and some element loadings were affected by regional and local sources, whereas Cr, Si, and Ni were attributed to substantial local emissions. Temporal variations of TEs in PM$_{2.5}$ were significant and provided information on source profiles. The PM$_{2.5}$ concentrations were highest in autumn and lowest in summer. Mn and Cr showed similar variation. Fe, Ca, Si, and Ti tended to show higher concentrations in spring, whereas concentrations of S peaked in summer. Concentrations of Cl, K, Pb, Zn, Cu, and Ni peaked in winter. PM$_{2.5}$ and TE median concentrations were higher on Saturdays than on weekdays. The diurnal pattern of PM$_{2.5}$ and TE median concentrations yielded similar bimodal patterns. Five dominant sources of PM$_{2.5}$ mass were identified via positive matrix factorization (PMF). These sources included the regional and local secondary aerosols, traffic, coal burning, soil dust, and metal processing. Air quality management strategies, including regional environmental coordination and collaboration, reduction in secondary aerosol precursors, restrictive vehicle emission standards, promotion of public transport, and adoption of clean energy, should be strictly implemented. High time-resolution measurements of TEs provided detailed source profiles, which can greatly improve precision in interpreting source apportionment calculations; the PMF analysis of online XRF data is a powerful tool for local air quality management.

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1. Introduction

Beijing is the capital city of China with a population of over 21.7 million in 2015 (BJSTATS, 2016). With rapid economic development and urbanization, Beijing has experienced serious air quality problems characterized by high concentrations of fine particulate matter (PM$_{2.5}$) (Cheng et al., 2013). The annual average PM$_{2.5}$ concentration was 85.9 µg m$^{-3}$ (BJEPB, 2016), which was considerably higher than the National Ambient Air Quality Standard (NAAQS) of 35 µg m$^{-3}$ (Class II Annual Average Level). High PM$_{2.5}$ masses significantly influence air quality and urban visibility and adversely affect human health (Pui et al., 2014). In response to the severity of particulate air pollution, a series of air quality control measures have been proposed, including the reduction of emission sources, regulations on vehicular emission standards, improvements to industrial and energy structures, and reductions in coal burning. The design and assessment of air quality control strategies require a thorough understanding of major sources of PM$_{2.5}$.

Numerous source apportionment (SA) methods, such as positive matrix factorization (PMF) (Gao et al., 2014; Zhang et al., 2013), enrichment factor (Li et al., 2012), principal component analysis (Li et al., 2013), and chemical mass balance (Wang et al., 2009b), have been implemented to identify the main sources that emit PM$_{2.5}$ or its precursors. Over the last decade, extensive studies of particulate matter (PM) in Beijing have revealed that major sources include coal burning, vehicular emissions, biomass burning, secondary...
aerosols, soil dust, and industrial emissions (Song et al., 2006, 2012; Zhang et al., 2013). Minor sources, including Chinese cooking emissions (Wang et al., 2009b), cigarette smoke, and vegetative detritus (Zheng et al., 2005), also contribute to total PM concentrations. Previous PM$_{2.5}$ chemical profiles have been typically based on offline filter collections of 12–24 h periods, which involves labor-intensive and time-consuming sampling collection and chemical analysis processes. Small-scale fluctuations in emissions or incursions of polluted air masses (e.g., plume events) cannot be identified as well, and thus additional information on source profiles cannot be acquired. These limitations restrict the application of SA to air quality strategies.

To overcome these limitations, automatic observation instruments have provided alternative methods to obtain high time-resolution measurements of air samples by collecting a large volume of data with quick and easy processes and providing data at sampling intervals similar to meteorological variations. Data from these instruments can provide temporal variations of contributing sources and meteorology (Lioy et al., 1989). A large number of samples is vital for multivariate models to produce reliable receptor model results (Kim Oanh et al., 2009). Among various online measurements of PM chemical profiles, measurements of trace elements (TEs) cover a large proportion. Although TEs generally account for a few percent of the total mass of PM$_{2.5}$, they are characteristic chemical species associated with PM emissions from both anthropogenic and natural sources. Given their high source specificity and atmospheric stability, TEs have been employed as effective tracers and used in numerous SA calculations for identifying and apportioning the source contributions to ambient aerosol (Visser et al., 2015; Yu et al., 2013). Despite their practicability, simultaneous online measurements and SA analyses of TEs at multiple sites in Beijing have been seldom reported.

This work primarily aimed to develop a procedure for capturing spatiotemporal variations across a range of environments to gather precise information on PM$_{2.5}$ source profiles and provide appropriate data-based policy recommendations for local air quality measures. In this study, the concentrations of PM$_{2.5}$ mass and its chemical species of 13 TEs were detected at five sites in Beijing between April 2014 and April 2015. Online X-ray fluorescence (XRF) analysis was utilized for elemental analysis. Information on spatial and temporal (seasonal, weekly, and diurnal) variations of PM$_{2.5}$ and TEs is reported together with an evaluation of the likely SA of PM$_{2.5}$ using PMF modeling. The results are important in assessing long- and short-term air quality, applying PMF analysis of online XRF data to capture different PM$_{2.5}$ sources, and establishing effective air quality measures.

2. Material and methods

2.1. Sampling sites

Beijing is located at 39°56′N and 116°20′E on the northwestern edge of the Great North China Plain and surrounded by the Taibai Mountains in the west and Yan Mountains in the north and northeast, approximately 100 and 50 km far from the urban region (Guinot et al., 2007). The city is 180 km away from the Bohai Sea via Tianjin in the southeast. This region is affected by predominant westerly wind and Asian monsoon climate featuring warm and humid southern winds in summer and cold and dry northern winds in winter. Fig. 1 depicts the five sampling sites, and details of each site are provided in Table 1.

2.2. Sampling and analysis

PM$_{2.5}$ samples were collected continuously over a 24 h period from 0:00 a.m. to 11:00 p.m. the following day at five sites for one year from April 2014 to April 2015. Hourly PM$_{2.5}$ mass and elemental concentrations of Pb, Zn, Cu, Cl, S, Fe, Mn, Cr, K, Ca, Ti, Si, and Ni were measured with an online XRF (PX-375 Horiba, Japan). The online PX-375 monitor uses reel-to-reel filter tape sampling, with beta attenuation analysis to ascertain PM$_{2.5}$ mass and non-destructive XRF analysis to identify ambient particle elements. Air was drawn through a PM$_{2.5}$ inlet and filter tape at a flow rate of 16.7 L min$^{-1}$, providing a deposit of approximately 11.1 mm in diameter. NIST certified standard material, SRM 2783 (air particulate matter on filter media), was used to evaluate the elemental quantification of X-ray spectra and provide a quality control measure. In addition, the lowest detection limits (double the standard deviation of blank analyzed) were S (4.6 ng m$^{-3}$), Ti (3.5 ng m$^{-3}$), Cr (0.3 ng m$^{-3}$), Mn (1.6 ng m$^{-3}$), Cu (6.1 ng m$^{-3}$), Zn (4.5 ng m$^{-3}$), and Pb (1.7 ng m$^{-3}$). Each sample was analyzed for 1000 s. Non-woven PTFE fabric blanks ($n = 10$) were analyzed for elements by XRF, providing high blank levels within the range of 0.1–0.2 μg cm$^{-2}$ for S, Fe, and Ti. The remaining elements possessed considerably lower blank values ranging from 0.05 to 0.003 μg cm$^{-2}$. All results reported in this paper were blank corrected. Sites 1 to 5 acquired total effective samples numbering 8986, 8382, 8548, 8595, and 7048, respectively.

2.3. PMF analysis

SA was performed using EPA PMF5.0 software (USEPA, 2014). PMF is a multivariate factor analysis tool that solves the general receptor modeling problem given by

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij},$$

(1)

where $X_{ij}$ is the $j$th species concentration measured in the $i$th sample, $g_{ik}$ is the emitted mass concentration of the $k$th source contributing to the $i$th sample, $f_{kj}$ is the $j$th species mass fraction from the $k$th source, $e_{ij}$ is the residual associated with $X_{ij}$, and $p$ is the number of factors contributing to PM$_{2.5}$ at the sampling site.
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