Environmental Pollution 233 (2018) 714–724

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Temporal-spatial characteristics and source apportionment of $PM_{2.5}$ as well as its associated chemical species in the Beijing-Tianjin-Hebei region of China☆

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ARTICLE INFO

Article history:
Received 20 November 2016
Received in revised form
29 October 2017
Accepted 30 October 2017

Keywords:
Beijing-Tianjin-Hebei region
$PM_{2.5}$
Chemical composition
Spatial and temporal characteristics
Source apportionment

ABSTRACT

$PM_{2.5}$ and its major chemical compositions were sampled and analyzed in January, April, July and October of 2014 at Beijing (BJ), Tianjin (TJ), Langfang (LF) and Baoding (BD) in order to probe the temporal and spatial characteristics as well as source apportionment of $PM_{2.5}$ in the Beijing-Tianjin-Hebei (BTH) region. The results showed that $PM_{2.5}$ pollution was severe in the BTH region. The average annual concentrations of $PM_{2.5}$ at four sampling sites were in the range of 126–180 μg/m^3, with more than 95% of sampling days exceeding 35 μg/m^3, the limit ceiling of average annual concentration of $PM_{2.5}$ regulated in the Chinese National Ambient Air Quality Standards (GB3095-2012). Additionally, concentrations of $PM_{2.5}$ and its major chemical species were seasonally dependent and demonstrated spatially similar variation characteristics in the BTH region. Concentration of toxic heavy metals, such as As, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se, and Zn, were higher in winter and autumn. Secondary inorganic ions (SO_4^{2-}, NO_3^-, and NH_4^+) were the three-major water-soluble inorganic ions (WSIIs) of $PM_{2.5}$ and their mass ratios to $PM_{2.5}$ were higher in summer and autumn. The organic carbon (OC) and elemental carbon (EC) concentrations were lower in spring and summer than in autumn and winter. Five factors were selected in Positive Matrix Factorization (PMF) model analysis, and the results showed that $PM_{2.5}$ pollution was dominated by vehicle emissions in Beijing, combustion emissions including coal burning and biomass combustion in Langfang and Baoding, and soil and construction dust emissions in Tianjin, respectively. The air mass that were derived from the south and southeast local areas around BTH regions reflected the features of short-distant and small-scale air transport. Shandong, Henan, and Hebei were identified the major potential sources-areas of secondary aerosol emissions to $PM_{2.5}$.

1. Introduction

Nowadays, due to rapid economic, industrial expansion, and urbanization in China, haze or smog episodes occur frequently. There has been a growing concern about the air pollution impact in China, and the emphasis is shifting from pollution on a local scale to that on a regional scale. The BTH region is the largest and most dynamic economic region in northern China, accounting for 9.7% of national GDP and 8.1% of national population in 2014 (NBS, 2015), as well as 9.0% of national coal consumption and 22.6% of national steel production in 2013 (NBS, 2014). Numerous energy-intensive and highly polluting industries, such as coal-fired power plants, cement, iron and steel, oil refining, and petro-chemical manufacturing, are gathered in this region. Owing to the emissions from fossil fuel combustion, industrial production processes

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.

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https://doi.org/10.1016/j.envpol.2017.10.123
0269-7491/

as well as vehicle exhaust, more polluted and hazy days have appeared and become increasingly conspicuous (Wang et al., 2014; Xue et al., 2016). It has attracted wide attention from the government and public due to the adverse effects of fine particles pollution on human health and the ecological environment. Several studies have revealed the health effects from aerosols and the relationship between $PM_{2.5}$ pollution and morbidity and mortality (Wu et al., 2010; Li et al., 2015a; Feng et al., 2016). On February 29, 2012, the third revision of "the National Ambient Air Quality Standards" (NAAQS) (GB 3095-2012) was issued, in which daily and average annual ambient $PM_{2.5}$ concentrations were included in the NAAQS as one of six criterion pollutants for the first time.

In the BTH region, multiple studies about chemical species of $PM_{2.5}$ have been carried out in Beijing. Several studies have discussed the general characteristics of $PM_{2.5}$ chemical compositions and given their seasonal variations, correlations, or sources (Sun et al., 2014; Li et al., 2015b; Lv et al., 2016). Previous studies have focused mainly on the concentrations, formation, and sources of some specific chemical species of $PM_{2.5}$ in Beijing, such as elements (Schleicher et al., 2011a; Duan and Tan, 2013; Chen et al., 2016), water-soluble inorganic ions (Liu et al., 2015; Wang et al., 2015a), and carbonaceous species (Schleicher et al., 2013; Sun et al., 2016). Moreover, aerosol optical and radiative characteristics or mixing state (Zhao et al., 2011; Bi et al., 2014; Wang et al., 2015b) and new particle formation processes (Sun et al., 2013a, b; Wang et al., 2015c) have also been discussed for Beijing and its surrounding region. The results showed that $PM_{2.5}$ pollution not only came from local sources emissions but also was highly influenced by the surrounding cities in the BTH region. The introduced mitigation measures could reduce particle concentrations by 30–70% (Schleicher et al., 2011b, 2012; Chen et al., 2016). Chen et al. (2014) showed that some element concentrations in Beijing correlated to the restrictiveness of relative measures, especially during different traffic restrictions (including after the Olympic Games). However, most reductions were only temporary and particle concentrations in Beijing increased again back to pre-event levels already in the following year (Schleicher et al., 2011a).

To date, $PM_{2.5}$ seldom has been simultaneously sampled and chemically analyzed at several sites in different cities of the BTH region. Comprehensive investigations of $PM_{2.5}$ chemical species for the BTH region outside Beijing are still quite limited. To control regional $PM_{2.5}$ pollution and conduct further related investigations about the BTH region, it is necessary to obtain detailed information about regional concentrations of $PM_{2.5}$ as well as its chemical compositions and to know their spatial and temporal variation characteristics and sources origination. In this study, $PM_{2.5}$ samples were collected simultaneously at four sites in the BTH region over four seasons. We focused on characterizing the seasonal and spatial variations in $PM_{2.5}$ mass concentrations and compositions. Results on chemical mass balance and source apportionment of $PM_{2.5}$ are presented and commented.

2. Experimental section

2.1. Field observation and meteorological conditions

The detailed location of each sampling site is illustrated in Fig. 1. As shown in Fig. 1, $PM_{2.5}$ samples were collected simultaneously at each sampling site for 15 consecutive days during four selected months (January, April, July, and October of 2014), which represented four seasons of four typical cities in the BTH region. (A) Beijing Normal University campus in Beijing (BJ), (B) Nankai University in Tianjin (TJ), (C) North China Institute of Science and Technology in Langfang (LF), and (D) North China Electric Power University in Baoding (BD). Four sampling sites were separately located in the urban areas of four cities. The details of location and characteristics of each sampling site were given in Table S1 in the appendix. It should be noted that only three groups of data (spring, summer, and autumn season) were obtained from TJ sites because of problems with the samplers. The collection and preservation methods of $PM_{2.5}$ samples were described in detail in our previous study (Gao et al., 2014, 2015). $PM_{2.5}$ were collected on quartz filters (Pallflex Tissuquartz™, 90 mm, USA) over a period of about 24 h each day with TH-150C medium volume air samplers (Wuhan Tianhong Instruments Co., Ltd., flow rate: 100 L/min). For each season, in each sampling site located in the four cities, 15 valid daily samples were collected consecutively and simultaneously. In total, 225 samples were collected and analyzed. All the procedures were strictly quality-controlled to avoid any possible contamination of the samples.

In BTH region, wind mainly blows from the south in the summer and from the north in the winter (Zhao et al., 2013). The topography not only governs the wind directions but also decides the regional transportation of air pollutants. In this study, meteorological parameters (temperature, relative humidity, wind speed, observed visibility, etc.) during sampling were obtained from Wunderground website (www.wunderground.com) and Langfang Municipal Environmental Protection Bureau website (http://www.lfhbj.gov.cn/). The average values of meteorological data for four sampling periods at the four sites were listed in Table S2 in the appendix, and the seasonal wind roses of four sampling periods at each site were illustrated in Fig. S1 in the appendix. In most cases, the four considered cities of BTH region are controlled under same weather system and the meteorological conditions showed an overall similar variation pattern, with some advance and lag in daily evolution among cities along with the direction of prevailing winds. For the four sites, temperature was highest at TJ, and wind speed was lowest in at BD; for the four seasons, temperature ranked in the order of winter < autumn < spring < summer, wind speed was highest in the spring, relative humidity was higher and visibility was lower in autumn and winter than in spring and summer.

2.2. Chemical composition analysis

After weighing, half of the aerosol-loaded filters were placed in Teflon tubes and each filter was digested with a 3:1:1 mixture of HNO_3-$HClO_4$-HF in Teflon vessels and heated in a microwave system. Blank filers, which was brought to the sampling site and installed in the sampler without sampling, were randomly inserted for quality control and elemental concentrations of the blank filter were subtracted from the samples. Then, the digested solution was diluted to 10 mL. In total, 18 elements (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Na, Ni, Pb, S, Sb, Se, V, and Zn) were measured by using inductively coupled plasma atomic emission spectrometry (ICP-AES, SPECTRO Analytical Instruments GmbH, SPECTRO ARCOS EOP) (Zhao et al., 2013; Gao et al., 2015). An external calibration method was used to calibrate ICP-AES. Calibrants were prepared from multi-element standard solution (50 μg/L, Teknolab A/S, Norway). Standard Reference Material, SRM 1648 'Urban Particulate Matter', from the National Institute of Standards and Technology (Gaithersburg, MD, USA) was used to validate the methods. The SRM was treated in the same manner as the samples. Reagent blanks were also routinely analyzed in between samples to check for contamination. Determination of each sample was repeated three times, the relative standard deviation (RSD) was less than 3%. The detection limits (units: μg/L) were Al (5.6), Ca (6.6), Fe (0.83), K (5.4), Mg (0.37), Na (1.9), S (3.4), Mn (0.32), As (6.3), Cd (1.3), Co (9.9), Cr (6.7), Cu (0.92), Ni (1.3), Pb (11), Sb (21), Se (18), V (0.76) and Zn (4.7).

One fourth of each quartz fiber filter was put into a glass tube, to