Atmospheric Research 184 (2017) 48–55

Contents lists available at ScienceDirect

Atmospheric Research

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

Characterization and source analysis of water-soluble inorganic ionic species in $PM_{2.5}$ in Taiyuan city, China

Qiusheng He [a,*], Yulong Yan [a], Lili Guo [a], Yanli Zhang [b], Guixiang Zhang [a], Xinming Wang [b]

[a] School of Environment and Safety, Taiyuan University of Science and Technology, Taiyuan, China
[b] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China

ARTICLE INFO

Article history:
Received 11 January 2016
Received in revised form 11 September 2016
Accepted 12 October 2016
Available online 13 October 2016

Keywords:
$PM_{2.5}$
Water-soluble inorganic ions (WSI)
Seasonal variation
Acidic balance
Ratio analysis

ABSTRACT

$PM_{2.5}$ samples were collected in urban area in Taiyuan for four seasons from August 2009 to April 2010. The Water-soluble inorganic ions (WSI, including F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, and Ca^{2+}) were analyzed by ion chromatography. The daily $PM_{2.5}$ levels in the field samples varied from 49.90 to 477.93 μg/m^3 with the mean of 209.54 μg/m^3, which all largely exceeded the $PM_{2.5}$ 24-hour limitation value of 35 μg/m^3 in Environmental Protection Administration of United States and 75 μg/m^3 in Ministry of Environmental Protection of China. The WSI average concentration was 68.86 μg/m^3 and accounted for about 32.86% of $PM_{2.5}$. As the most abundant anion and cation, SO_4^{2-} and NH_4^+ were 43.53 and 14.78 percent of WSI, respectively. $PM_{2.5}$ in Taiyuan was acidic by the micro-equivalents concentration methods but nearly neutral in autumn, and the chemical forms of WSI were mainly NH_4HSO_4, $(NH_4)_2SO_4$ and NH_4NO_3. $PM_{2.5}$ and WSI levels showed obvious seasonal variation and were the highest in winter in all samples. $PM_{2.5}$, SO_4^{2-}, and some coal-related ions such as NH_4^+ and Cl^- were higher in winter than other seasons, which mainly attributed to more coal combustion for power and indoor heating supply. The ratio analysis showed that Mg^{2+} and Ca^{2+} were not only from soil dust, but also from coal combustion and industry emission. Biomass burning such as the cornstalk and tree branches led to the highest K^+ emission in autumn and summer. Wind had a regular influence on the $PM_{2.5}$ and WSI, and would transport the soil dust mainly from the northwest and also lead to re-suspension of dust in the air when the wind speed was high. Furthermore, the dustpan topography easily helped the pollutants to concentrate in Taiyuan city, and some coal coking industries might contribute to high $PM_{2.5}$ and WSI in Taiyuan.

1. Introduction

Particle matters <2.5 μm in aerodynamic diameter ($PM_{2.5}$) have been paid more attention in recent decades due to its distinct impacts on human health, air quality and global climate change. Being characterized by a higher surface/mass ratio, small particles were more likely to absorb toxic constituents, and cause many kinds of healthy effects (WHO, 1999; EPA, 2015). $PM_{2.5}$ could directly scatter and absorb the sunlight contributing to light extinction, and affect the atmosphere visibility (Yuan et al., 2006).

Many studies have reported the $PM_{2.5}$ levels were higher in Chinese cities than other countries because of excessive coal usage (Tan et al., 2014 & 2016; Qiu et al., 2013; Zhang et al., 2011). Compared with those reported in foreign countries (e.g. Khan et al., 2010; Aldabe et al., 2011), the high $PM_{2.5}$ pollutions were found in some Chinese cities and its levels exceeded the limit value of $PM_{2.5}$ issued by EPA (e.g. Tan et al., 2016; Tao et al., 2012; Zhang et al., 2011). Water-soluble inorganic ions (WSI), including NO_3^-, SO_4^{2-}, NH_4^+, Mg^{2+}, and Ca^{2+} species, accounted for about 20–45% or even >70% of the mass of $PM_{2.5}$ (Tan et al., 2016; Zhang et al., 2011; Li et al., 2010; Kulshrestha et al., 2009; Khan et al., 2010; Tao et al., 2012; Dai et al., 2013; Tao et al., 2013), and played a decisive role in the process of aerosol hygroscopicity which could exacerbate visibility impairment (Shen et al., 2009). SO_4^{2-}, NO_3^- and NH_4^+ were the major species of WSI and contributed 32% and 43% to $PM_{2.5}$ mass in Shanghai and Fuzhou, respectively (Wang et al., 2006; Xu et al., 2012). Compared with vehicle emission, the high level of SO_4^{2-} and NO_3^- in Chinese cities were mainly related to coal combustion, especially in winter in some northern cities (Xiao and Liu, 2004; Hu et al., 2002; Wang et al., 2005; Xu et al., 2012; Tan et al., 2016). In addition, WSI in particles were also affected by the variation of sources, such as industrial source, agricultural source and et al., which could lead to the variation of F^-, Cl^-, NH_4^+, K^+, Mg^{2+} and Ca^{2+} in particles (Nair et al., 2006; Rengarajan et al., 2011; Li et al., 2010). For example, fertilizer usage in agricultural activity may result in more formation of NH_4^+ in atmospheric particles (Zhang et al., 2011).

WSI in particles existed in some specific chemical forms, which can influence the characteristics of $PM_{2.5}$. $(NH_4)_2SO_4$, a typical chemical form of two important ions of SO_4^{2-} and NH_4^+, not only have hygroscopic effect on particulate matters, but also enhance the hygroscopic

* Corresponding author.
E-mail address: heqs@tyust.edu.cn (Q. He).

http://dx.doi.org/10.1016/j.atmosres.2016.10.008
0169-8095/© 2016 Published by Elsevier B.V.

growth of mixtures of organic salts with ammonium sulfate (Wu et al., 2011). Compared with abundant NH_4NO_3 of Beijing in 2001–2003 and Shanghai in 2001, the major ions were in the form of $(NH_4)_2SO_4$, $Ca(NO_3)_2$, $CaCl_2$, and $CaSO_4$ in aerosol particles in Shanghai in 2004 (Wang et al., 2005 & 2006; Yao et al., 2002). The fine mode NH_4NO_3 increased greatly in recent year in East Asia due to the increasing emissions of pollutants (both including NH_3 and NO_X emission from anthropogenic sources) and the decreasing concentration of coarse particles (Kim et al., 2006).

The ratio of NO_3^-/SO_4^{2-} could be reasonably used to evaluate the contribution of mobile and stationary sources to sulfur and nitrogen in the atmosphere. The ratio was higher in cities with heavy traffic density, such as Guangzhou (0.79, Tan et al., 2009), Shanghai (0.64, Wang et al., 2006), Beijing (0.58, Yao et al., 2002), Xiamen (0.52, Zhang et al., 2012a), and lower in coal-dominated cities, such as Guiyang (0.14; Xiao and Liu, 2004) and Qingdao (0.35; Hu et al., 2002). Previous studies have indicated that the major source of F^- in atmosphere in urban area was coal burning, while the main sources of Cl^- were coal burning, biomass burning and soil dust (Kulshrestha et al., 2009; Watson et al., 2001). Besides dust and coal combustion which were dominate contributor of Mg^{2+} and Ca^{2+} in atmosphere, industrial emission was another important source of Mg^{2+} in some magnesium production areas (Osada et al., 2002; Zhang et al., 2002). In general, NH_4^+ and K^+ were suggested as the main tracers of biomass burning (Nair et al., 2006), but Zhang et al. (2012a) reported that coal combustion was also an important source of NH_4^+, especially in urban area.

As the largest coal base of China, atmospheric SO_2, NO_X and particles in Taiyuan was one of the highest in China (MEP, 2015). SO_4^{2-}, NO_3^-, Ca^{2+} and NH_4^+ were the main components in wet precipitations in recent years, and high deposition flux of S and N should be concerned in Taiyuan (Guo et al., 2015). In spite of high atmospheric SO_2 and NO_X level, there were still few studies about the SO_4^{2-} and NO_3^- level and corresponding contribution in the related particle phase. The purpose of this paper was to discuss the $PM_{2.5}$ and WSI levels, and fully illustrate the key influence factors on its seasonal variation and chemical forms in Taiyuan.

2. Experiment

2.1. Site description

Taiyuan, with a population of 4.2 million and a land area of about 1500 km^2, is the capital of Shanxi Province. The terrain resembles a dustpan surrounded by mountains in its west, north and east directions, with valley plain in the south, which was conducive to the air pollutants confluent and accumulation in the city. Located in the continental interior, Taiyuan belongs to the warm temperate zone continental monsoon climate. The annual average temperature is 9.5 °C, with the highest in summer (23.5 °C) and the lowest in winter (−6.8 °C), and the prevailing wind direction is southeast in summer and northwest in winter.

As showed on the map, in the urban area there are two thermal power plants for electricity and heating supply, and two heavy industrial plants for the largest stainless steel production in the world and heavy machinery factory in China. Since 2004, some heavily polluted industries such as coking and chemical plants have been forced to shut down, and stack gas was cleaned before being emitted to the atmosphere by administrational orders. The SO_2 and PM_{10} concentrations decreased steadily, but still exceeded the second level values of the National Air Quality standards (TYEPB, 2011; Meng et al. 2007a & b).

The sampling site was located on the roof of a 15-storey office building at the northwest of Yingze Bridge, which is the central urban area of Taiyuan city without obvious pollution emission sources around (Fig. 1). Based on the on-line monitoring data in four atmospheric environmental monitoring stations located in the urban area of Taiyuan, the pollution level of SO_2, NO_2 and PM_{10} was quite close, which implicated that air pollutants dispersed steadily in the whole downtown area (TYEPB, 2011; Zhang et al., 2012b). Therefore, the confluent and accumulated air pollutants in the city can uniformly mix, and the sampling site could represent the urban air quality in Taiyuan.

2.2. Sampling

The $PM_{2.5}$ samples were collected on the quartz fiber filter (QFF, 8″ × 11″, Whatman L.td) by a high-volume air sampler with an impactor cutoff of 2.5 μm (aerodynamic diameter) at a flow rate of 1.05 m^3/min (TH-1000F, Wuhan Tianhong Intelligent Instrument company, China) during summer, 2009 – spring, 2010 (Table 1). The number of samples obtained in summer, autumn, winter and spring was 16, 25, 21 and 21, respectively. During the sampling period, field blank filters were also collected by exposing filters in the sampler without drawing air through, to account for any artifacts introduction during the sampling procedure. The sampler was checked and calibrated by a flow calibrator carefully before using. During the sampling periods, meteorological data in Fig. 2, including ambient temperature, relative humidity (RH), wind speed and direction were recorded from the website of Weather Underground (http://www.wunderground.com/). And the daily average level

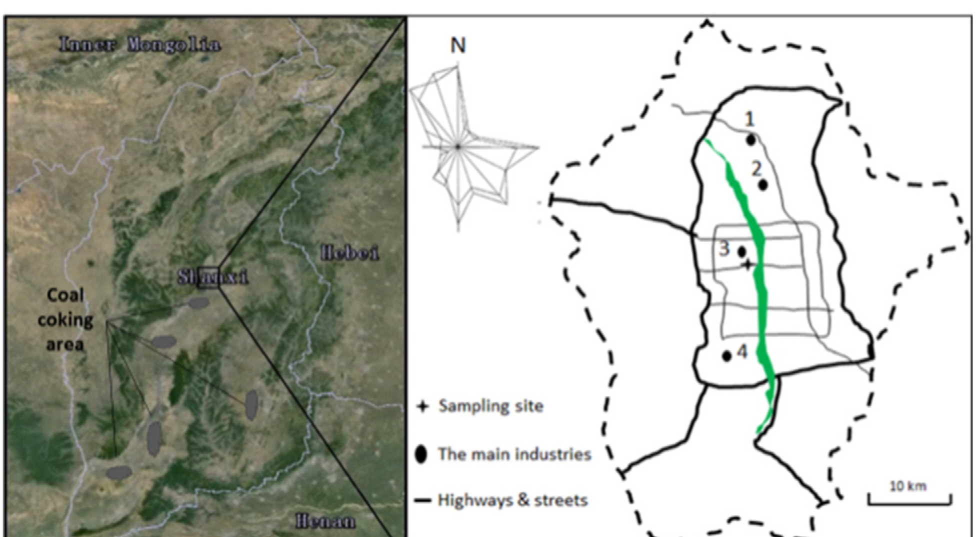

Fig. 1. Topography of Shanxi province, location of main industries, streets and the sampling site in Taiyuan (1, Second Thermal Power Plant of Taiyuan; 2, Taiyuan Iron and Steel Factory; 3, Taiyuan Heavy Machinery Factory; 4, First Thermal Power Plant of Taiyuan).