JOURNAL OF ENVIRONMENTAL SCIENCES XX (2017) XXX–XXX

Available online at www.sciencedirect.com

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JES JOURNAL OF ENVIRONMENTAL SCIENCES www.jesc.ac.cn

Chemical characteristics and source apportionment of $PM_{2.5}$ between heavily polluted days and other days in Zhengzhou, China

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ARTICLE INFO

Article history:
Received 17 January 2017
Revised 29 March 2017
Accepted 3 May 2017
Available online xxxx

Keywords:
$PM_{2.5}$
Water soluble inorganic ions
Secondary organic carbon
CMB
Back trajectory analysis

ABSTRACT

$PM_{2.5}$ samples were collected in Zhengzhou during 3 years of observation (2013–2015), and chemical characteristics and source contribution were analyzed. Approximately 96% of the daily $PM_{2.5}$ concentrations and annual average values exceeded the Chinese National Ambient Air Quality Daily and Annual Standards, indicating serious $PM_{2.5}$ pollution. The average concentration of water soluble inorganic ions was 2.4 times higher in heavily polluted days (daily $PM_{2.5}$ concentrations > 250 μg/m^3 and visibility < 3 km) than that in other days, with sulfate, nitrate, and ammonium as major ions. According to the ratio of NO_3^-/SO_4^{2-}, stationary sources are still the dominant source of $PM_{2.5}$ and vehicle emission could not be ignored. The ratio of secondary organic carbon to organic carbon indicated that photochemical reactivity in heavily polluted days was more intense than in other days. Crustal elements were the most abundant elements, accounting for more than 60% of 23 elements. Chemical mass balance results indicated that the contributions of major sources (*i.e.*, nitrate, sulfate, biomass, carbon and refractory material, coal combustion, soil dust, vehicle, and industry) of $PM_{2.5}$ were 13%, 16%, 12%, 2%, 14%, 8%, 7%, and 8% in heavily polluted days and 20%, 18%, 9%, 2%, 27%, 14%, 15%, and 9% in other days, respectively. Extensive combustion activities were the main sources of polycyclic aromatic hydrocarbons during the episode (January 1–9, 2015) and the total benzo[a]pyrene equivalency concentrations in heavily polluted days present significant health threat. Because of the effect of regional transport, the pollution level of $PM_{2.5}$ in the study area was aggravated.

Introduction

In recent years, China has experienced unprecedented economic developments along with a substantial quantity of energy consumption, which results in serious air pollution problems, especially extreme haze episodes (Wang et al., 2015). A haze comprising suspended solids, liquid particles, smoke, and vapor in the atmosphere which is defined as a weather phenomenon with the horizontal visibility less than 10 km and the relative humidity (RH) less than 80% (Tan et al., 2009; Yang et al., 2015). Haze episodes have frequently occurred in China along with the characteristics of large polluted areas, long duration, and high concentration level (Wang et al., 2014b). Recently, the occurrence of haze has

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http://dx.doi.org/10.1016/j.jes.2017.05.006
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rapidly increased in the Yangtze River Delta region and other regions (Wang et al., 2014a). Five heavy pollution episodes, whose frequencies were far greater than those in other years, were recorded in January 2013 in northern China (Ji et al., 2014).

Particular matter (PM) played a major role in the formation and evolution of haze (Tan et al., 2009). PM not only affects climate, environment, and visibility but also has a severe effect on human health (Pope et al., 2002). PM can be classified by size into PM_{10} (aerodynamic diameter < 10 μm) and $PM_{2.5}$ (aerodynamic diameter < 2.5 μm). As $PM_{2.5}$ is associated with more adverse health effects and influences on haze than larger particles (Zhao et al., 2009), numerous analyses of the haze mainly concentrate around chemistry compositions and the source appointment of $PM_{2.5}$ (Pateraki et al., 2012; F. Zhang et al., 2013; Zhou et al., 2016). Sulfate, nitrate, and ammonium (secondary inorganic aerosols, SIAs) were found to be the major components of water soluble inorganic ions (WSIIs), which accounted for one-third or more of $PM_{2.5}$ (Kim et al., 2006; Cao et al., 2012; Kong et al., 2014). Organic carbon (OC) and elemental carbon (EC) are also important constituents of $PM_{2.5}$, particularly in highly industrialized and urbanized areas (X.H.H. Huang et al., 2014). Elements were divided into crustal elements and anthropogenic pollution elements, including trace heavy metals harmful to the human body (Gao et al., 2015). Although polycyclic aromatic hydrocarbons (PAHs) constitute a small part of $PM_{2.5}$, they are well known to be carcinogenic and mutagenic (Hu et al., 2007).

Zhengzhou, which is the capital of Henan province, is faced with severe air pollution accompanied by the rapid development of the economy and a substantial number of people living demand, with a long-term coal-dominated energy structure (http://tongji.cnki.net/kns55/Navi/YearBook.aspx?id=N2016010114&floor=1###). According to satellite remote sensing data, China is the most serious global PM polluted area. Moreover, most of the Henan Province experienced high aerosol optical depth problems, particularly Zhengzhou (Tao et al., 2014), which is similar to the report by Luo et al. (2014). According to the data from the Ministry of Environmental Protection of the People's Republic of China (MEPPRC, http://www.mep.gov.cn/), Zhengzhou is among the 10 Chinese cities with the worst air quality in 2013–2015 and the primary pollutant was $PM_{2.5}$ (http://www.zzepb.gov.cn/Information/Content/?id=32853). Several studies have been reported on the chemical composition and source apportionment of $PM_{2.5}$ in Zhengzhou; however, only one year of data was available in most of the literature. For example, F.H. Geng et al. (2013) and N.B. Geng et al. (2013) determined that soil dust, secondary aerosol, coal combustion, biomass burning/oil combustion/incineration, vehicle emissions, and industrial emissions contributed approximately 26%, 24%, 23%, 13%, 10%, and 4%, respectively, to $PM_{2.5}$ mass by positive matrix factorization in Zhengzhou in 2010. A few studies on the long-term observation of $PM_{2.5}$ in Zhengzhou, such as the WSIIs, carbonaceous components (J. Wang et al., 2016), and PAHs (Wang et al., 2015) of $PM_{2.5}$ were investigated in Zhengzhou from 2011 to 2013. However, the source contribution percentages were obtained during normal days excluding episodes. There was no report on source apportionment of $PM_{2.5}$ during heavily polluted days in Zhengzhou, as well as the research in long-term episode days.

In this study, 174 $PM_{2.5}$ samples were collected and WSIIs, OC, EC, and elements of the samples were detected. Chemistry characteristics and potential source percentage contribution of $PM_{2.5}$ were contrasted between heavily polluted days and other days during 2013–2015 (including a typical haze episode).

1. Materials and methods

1.1. Site description and sample collection

Zhengzhou belongs to the warm temperate zone continental climate, which has four distinctive seasons with an average temperature of approximately 15°C (http://tongji.cnki.net/kns55/Navi/YearBook.aspx?id=N2014120113&floor=1). The sampling site is located on the roof of the Collaborative Innovation Center of Henan Resources and Materials Industry in Zhengzhou University in Zhengzhou High-tech Zone (34°48′ N, 113°31′ E) (Fig. 1). The sampling height is approximately 13 m above the ground and there is no tall building around.

One hundred seventy-four samples were collected by using quartz microfiber filters (20.3 cm × 25.4 cm, Pall, USA) with a high-volume $PM_{2.5}$ sampler (TE-6070D Tisch Environmental, USA), which was accompanied by the flow rate 1.13 m^3/min during the periods from 8 December 2012 to 24 October 2015. Sampling was conducted from 9:00 am to 8:00 am of the following day.

Before each sampling, the quartz filters were wrapped in aluminum foil and baked at 450°C for 4.5 hr in a Muffle furnace. All filters were then placed in a super clean room (temperature: 25 ± 5°C; RH: 50% ± 5%) for at least 48 hr and weighed in a micro-balance (Mettler Toledo XS205, Switzerland) before and after each sampling. All filters were stored in a freezer at −20°C before analysis.

1.2. Chemical analysis

1.2.1. WSIIs analysis

Two pieces of circular membranes (each piece 10.9 cm^2) were cut from each sample filter and dipped in 25 mL ultra-pure water in 100 mL bottles. WSIIs from the samples were extracted by the ultrasonic bath for 30 min (bath temperature < 30°C). The extracted solutions were filtered with hydrophilic membranes (0.22 μm) before determination. Four anion species (F^-, Cl^-, NO_3^-, and SO_4^{2-}) were analyzed by using an ion chromatography (ICS-900, Dionex, USA) with an IonPacASll-HC4 mm anion separation column and an IonPacAGll-HC4 mm guard column. The eluents were 8.0 mmol/L Na_2CO_3 and 1.0 mmol/L $NaHCO_3$ mixtures with 0.8 mL/min flow rate. Five cation species (Na^+, K^+, NH_4^+, Ca^{2+}, and Mg^{2+}) were detected by ion chromatography (ICS-90, Dionex, USA) with an IonPacCS12A cation separation column and an IonPacCG12A guard column. The eluents were 20 mmol/L of methane sulfonic acid with 1.0 mL/min flow rate.

1.2.2. EC and OC analysis

Two 2.0 cm^2 membranes were punched from each filter and used for analysis using a carbon analyzer (Sunset Laboratory, USA). The analysis proceeds essentially in two stages. In the first, OC is volatilized from the sample in a pure helium

Please cite this article as: Jiang, N., et al., Chemical characteristics and source apportionment of $PM_{2.5}$ between heavily polluted days and other days in Zhengzhou, China..., J. Environ. Sci. (2017), http://dx.doi.org/10.1016/j.jes.2017.05.006