Atmospheric Research 216 (2019) 65–75

Contents lists available at ScienceDirect

Atmospheric Research

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

Sources and spatial distribution of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in Zhengzhou in 2016

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ARTICLE INFO

Keywords:
$PM_{2.5}$
PAHs
Health risk
Diagnostic ratios
PMF

ABSTRACT

Atmospheric polycyclic aromatic hydrocarbons (PAHs) in $PM_{2.5}$ were analyzed in 2016 at five representative sites in Zhengzhou, China to determine their seasonal and spatial characteristics. The annual $PM_{2.5}$ concentration of all sites (114 ± 85 μg/m^3) was 2.3 times higher than the Chinese National Ambient Air Quality Standard (NAAQS) (annual standard:35 μg/m^3). The total PAH level was highest at traffic site (46.2 ± 21.4 ng/m^3), followed by urban center site (40.1 ± 18.7 ng/m^3), industrial site (38.8 ± 17.2 ng/m^3), urban site (37.8 ± 10.3 ng/m^3) and background site (34.0 ± 19.4 ng/m^3) with an annual concentration of 39.1 ± 17.6 ng/m^3 for all sites. The seasonal variation was in the order of winter > autumn > spring > summer. Among 16 PAHs, BbF, Ind, BkF, Chry, and BghiP were more abundant species with an integral trend of 5–6 rings > 4 rings > 2–3 rings. The annual BaP concentration (2.1 ng/m^3) exceeded the limit of the annual average BaP (1.0 ng/m^3) given by the NAAQS, and the BaPeq concentration was at a high level, which indicated a severe health risk of PAHs. The incremental lifetime cancer risk results showed that the risk level was acceptable level in the study area. Diagnostic ratios analysis demonstrated that PAHs in the study area were produced by the common outcome of the fossil fuel, petroleum, biomass, and coal combustions. Four sources determined by positive matrix factorization were coal combustion, motor vehicles, biomass burning, and industry, which respectively accounted for 37.9%, 26.9%, 19.7% and 15.4% of the annual total PAHs in Zhengzhou. The contribution of motor vehicles/aircraft fuel source was the highest at the traffic site (29.7%) and the contribution of industry was higher at industrial site (21.4%). The contribution of biomass burning in autumn was greater than that in other seasons because open burning of straws increased during harvest season while the contribution of coal combustion increased in winter due to concentrated heating.

1. Introduction

Pollution caused by particulate matter (PM), especially $PM_{2.5}$, has become a serious environmental concern in most areas in China due to rapid industrialization and urbanization in recent years (Huang et al., 2014). As one group of the main pollutants in $PM_{2.5}$ that can adversely affect human health, polycyclic aromatic hydrocarbons (PAHs) have attracted attention due to its potential carcinogenic and mutagenic properties (Liu et al., 2016). PAHs are a group of chemicals that mainly derive from coal burning, motor vehicle exhausts, heat and power generation, and biomass burning (Bi et al., 2003; Rajput et al., 2011). As PAHs originate from various sources, the characteristics of PAH pollution in urban atmosphere must be investigated, and their sources must be apportioned to ameliorate air quality (Jin et al., 2012). Various methods, such as diagnostic ratio, principal component analysis, positive matrix factorization (PMF), and chemical mass balance model (Chen et al., 2009; Bravo-Linares et al., 2012; Wang et al., 2014b), have been used to analyze PAH sources in $PM_{2.5}$. Among these methods, diagnostic ratio, which only indicates a potential source without providing the distribution of each source, has been commonly used (e.g., Galarneau, 2008; Wu et al., 2014a). Furthermore, PMF, with advantages such as inclusion of uncertainties in the model and unnecessary acquisition of information on sources (Pindado and Perez, 2011), or emission inventory, is also widely applied to PAHs (Jang et al., 2013; Viana et al., 2008). Several studies have been conducted on atmospheric PAHs pollution in urban areas in China. For example, Guo et al. (2003) reported the concentration of PAHs in $PM_{2.5}$ and PM_{10} and identified vehicular emission as the predominant source of airborne PAHs in Hong Kong. Okuda et al. (2006) analyzed the PAHs concentration in the aerosol in Beijing and attributed the high concentrations of PAHs in winter to residential heating. Atmospheric levels and sources of particulate PAHs in an urban atmosphere have also been

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https://doi.org/10.1016/j.atmosres.2018.09.011
Received 12 March 2018; Received in revised form 13 September 2018; Accepted 17 September 2018
Available online 21 September 2018

studied in other Chinese cities, such as Qingdao (Guo et al., 2003), Tianjin (Shi et al., 2010), Ningbo (Liu et al., 2014), Nanjing (Wang et al., 2006; He et al., 2014), and five typical areas in Liaoning (i.e., Shenyang, Dalian, Anshan, Fushun, and Jinzhou) (Kong et al., 2010).

Zhengzhou, the capital of Henan Province, is in the heart of China; this city has a long-term coal-dominated energy structure and is one of the most polluted urban centers in China (Jiang et al., 2018a). Zhengzhou is a key area with a total population of over 9 million, thus, understanding the characteristics and sources of PAHs in this city is important. Several studies on the component concentration and source apportionment of $PM_{2.5}$ at a sampling site in Zhengzhou were conducted (Yu et al., 2016a; Jiang et al., 2017; Wang et al., 2017; Jiang et al., 2018c). However, few studies focus on PAHs in $PM_{2.5}$, e.g., long-term observations of $PM_{2.5}$-associated PAHs between normal and episode days from 2011 to 2013 (Wang et al., 2015) and seasonal variations and source apportionment of carbonaceous species in $PM_{2.5}$ and PM_{10} from October 2014 to July 2015 (Wang et al., 2017), not to mention multiple sampling-site studies. Previous studies that were limited to one sampling site were not comprehensive enough to explain the pollution situation in Zhengzhou. Moreover, research is lacking on different sampling sites that represent various characteristics, such as industrial and traffic conditions. In 2014, the Zhengzhou urban areas were divided into eight major functions, namely, one major urban district, three new town districts, and four peripheral group districts, to optimize the regional space resource plan in the city (Wu et al., 2014a). Thus, it is meaningful to select representative and comprehensive sampling sites in terms of functional districts to research the spatial and seasonal distribution characteristics of PAHs in Zhengzhou.

In this study, five representative sites were selected for $PM_{2.5}$ sampling in different seasons, and PAH concentrations were detected. Spatial and seasonal characteristics of PAHs were analyzed and a health risk assessment was conducted. Furthermore, qualitative (diagnostic ratios) and quantitative (PMF) analytical methods were used to determine PAHs pollution sources. Therefore, the primary goal of this study was to improve our understanding of the chemical characteristics, potential sources, and seasonal variations of atmospheric particulate PAHs on a city scale (specifically focusing on five sites) as well as investigate the spatial distribution of atmospheric particulate PAHs in different districts of Zhengzhou.

2. Materials and methods

2.1. Site description and sample collection

Considering the specific situation of Zhengzhou and the representativeness and differences of the sampling sites, five sampling sites were selected, namely, Zhongmoudong (ZMD), Hangkonggang (HKG), Gongyishi (GYS), Zhengfanfji (ZFJ), and Zhengzhou University (ZZU) (Fig. 1). Table S1 shows detailed information on each sampling site. HKG was classified as an external transportation area because it was the first national airport economic area with a comprehensive aviation hub, high–speed rail system, intercity railway, subway, and highway. HKG was an aviation economic and aviation metropolitan area where Xinzheng integrated free trade zone (near Zhengzhou Xinzheng International Airport, which accounts for 457,000 tons of annual cargo throughput and 20.763 million passenger throughputs) was the core that represents one of the characteristics of Zhengzhou (SBOZ, 2016). ZFJ was an inclusive region in an urban center. GYS, as one of the core cities in the Zhengzhou–Gongyi–Luoyang industrial corridor, was characterized by rapid economic development and convenient transportation. As an industrial development zone with 477 industries (SBOZ, 2016), GYS was mainly affected by the industrial production. ZZU was in a high–technology zone, and the sampling site was at Zhengzhou University, near some power plants and the West 4th Road with relatively heavy traffic. In ZMD, the road network was dense, and the agricultural development was rapid, covering 70,620 ha (SBOZ, 2016). Beyond these conditions, the industry was relatively slow and the population was scattered.

$PM_{2.5}$ was collected from April 2016 to December 2016 by using middle–volume sampling instruments (100 L/min; TH–150AII, Wuhan) with quartz microfiber filters (90 mm in diameter). All the samplers were calibrated before sampling. Sampling lasted for 23 h from 10:00 A.M. to 9:00 A.M. of the following morning with a 138 m^3 sample volume. The samples were not taken at certain times due to unstable weather conditions and logistical difficulties. A total of 224 filter samples (44 for ZMD, 39 for HKG, 42 for GYS, 42 for ZFJ, and 57 for ZZU) were collected for the PAH analysis.

Before sampling, quartz filters were baked at 450 °C in a muffle furnace for 5 h to remove the adsorbed organic materials and then stabilized in a clean room (temperature of 25 ± 5 °C; relative humidity of 50 ± 5%) for 48 h. Each filter was weighed twice with a difference of not > 0.03 mg by using a microbalance with a resolution of 10 μg (Mettler Toledo XS205, Switzerland). After sampling, all filters were stabilized in the clean room for 48 h and weighed before storage at −20 °C in a freezer for further analysis.

2.2. PAH analysis

Each quartz filter was cut into two pieces with the same area; one piece was extracted through pressurized liquid extraction (dichloromethane) using an accelerated solvent extractor (ASE350, Dionex, USA). The extract was transferred to a fully automatic nitrogen–blowing instrument (QZDJT-12S, Jutong, Hangzhou) that is concentrated below 1 mL and then 20 μL of five deuterated–PAH standard mixtures (naphthalene-D8, acenaphthene-D10, phenanthrene-D10, chrysene-D12, and perylene-D12). Furthermore, dichloromethane was added to the extract to guarantee a capacity of 1 mL prior to the gas chromatography–mass spectrometry (GC–MS) analysis. A total of 16 PAHs, which are classified as priority pollutants by the United States Environmental Protection Agency (US EPA) and the European Union (Manoli et al., 2004), were detected by using a 7890A GC with a 5975C mass selective detector (Agilent Technology with a DB-5 capillary column 30 m × 0.25 mm × 0.25 μm) in this study. These PAHs were naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acp), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[*a*]anthracene (BaA), chrysene (Chry), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3–cd]pyrene (Ind), dibenz[*a,h*]anthracene (DahA), and benzo[*ghi*]perylene (BghiP). The oven temperature was initially set at 70 °C for 2 min and then increased to 320 °C at a rate of 10 °C/min holding for 5 min. The PAH concentrations were quantified using an internal standard by injecting seven standard solutions namely 50, 100, 200, 500, 1000, 2000 and 5000 μg/L to make the working standard curves of PAHs.

All analytical procedures were monitored with strict quality assurance and quality control measures. The laboratory blank and blank standard addition was analyzed in experiments of every 20 samples. PAHs were not detected in the laboratory blank samples. A whole procedure blank was performed during the sampling period to eliminate the influence of the whole analysis process from the sampling and an insignificant amount of PAHs was found in the blanks (< 5%). Laboratory analysis of 16 PAH calibration curves was suitable with a correlation coefficient of > 0.993. The blank filter with a standard addition was repeated seven times to estimate the precision of the analysis. The relative standard deviation was between 1% and 7%, and the blank standard addition recovery rate was between 78% and 103%. A method detection limit (MDL) is defined as three times the mean of the standard deviation obtained from the seven consecutive analyses of the lowest point of the curve (Jiang et al., 2018b). The MDLs for the target PAHs were 0.07–0.91 ng/m^3.