Polycyclic Aromatic Hydrocarbons in Atmospheric PM_{2.5} during Winter Haze in Huang-gang, Central China: Characteristics, Sources and Health Risk Assessment

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ABSTRACT

Levels, compositions, sources and health risk of PM_{2.5}-bound PAHs were measured at a regional monitoring site of Huang-gang in the winter of 2018. Samples were collected every morning, afternoon, evening and late night (LN). The average concentrations of PM_{2.5} and PAHs were $110.4 \pm 48.3 \mu\text{g m}^{-3}$ and $25.6 \pm 12.0 \text{ ng m}^{-3}$, respectively. The concentration of PM_{2.5} was in the order of evening > morning > afternoon > LN, while PAHs concentration was in the order of evening > LN > morning > afternoon. According to PM_{2.5} concentration and its changing trend, the haze can be divided into three stages: early (low concentration, January 13–15, EHZ), medium (high concentration, January 16–22, MHZ) and late (concentration decreased rapidly, January 23–24, LHZ). A positive correlation ($P < 0.01$) was observed between PM_{2.5} and $\sum_{16}\text{PAHs}$ concentration only in MHZ. Besides, PAHs concentration was positively related to NO_x concentration, CO concentration and temperature but negatively correlated with RH, independent of O₃ concentration. The ratios of OC/EC indicated that the secondary aerosol had a great influence on the formation of haze. Three sources of PAHs including traffic emission, coal combustion and biomass combustion were extracted and quantified, accounting for 54.4%, 13.3% and 32.3% of PAHs, respectively. Potential source contribution function (PSCF) and concentration weighted trajectory (CWT) indicated the transmission of PM_{2.5} from Wuhan and local pollutant emission were crucial to the formation of haze. BaP_{eq} concentration combined with ILCR values was used to evaluate health risk and the results showed this haze had potential health risk to both adults and children.

Keywords: PM_{2.5}, PAHs, Sources, Spatial distribution, Health risk assessment

1 INTRODUCTION

As one of the most serious atmospheric environmental problems, haze not only reduces visibility, affects people's daily life, but also has a negative impact on human health and global climate change (Chang *et al.*, 2009; Tan *et al.*, 2009). Aerodynamic equivalent diameter less than $2.5 \mu\text{m}$ (PM_{2.5}) has been proved to be directly related to the formation of haze (Cao *et al.*, 2012). Due to its small particle size, PM_{2.5} can be suspended in the air for a long time, and its chemical composition and distribution will constantly change in time and space (Kim *et al.*, 2015). PM_{2.5} is mainly composed of organic aerosol (OA), heavy metals, water-soluble ions and so on. As the main component of PM_{2.5}, OA accounts for 20–90% of PM_{2.5} mass (He *et al.*, 2001; Dan *et al.*, 2004). Organic carbon (OC) and elemental carbon (EC) are two main forms of OA. OC, is one of the main causes of visibility reduction, and its sources are primary organic carbon (POC) emitted directly from fuel combustion and secondary organic carbon (SOC) generated by chemical

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reaction of atmospheric organic matter. EC is mainly caused by incomplete combustion of biomass and fossil fuels, which is the main driving factor of regional climate change in China (Pandis *et al.*, 1992; Turpin and Huntzicker, 1995). It is generally considered that EC is a tracer of primary pollution source, and OC/EC ratio can be used to evaluate the secondary pollution degree of PM_{2.5} (Turpin and Huntzicker, 1995; Chow *et al.*, 1996). As important organic component of PM_{2.5}, polycyclic aromatic hydrocarbons (PAHs) have significant carcinogenic, teratogenic and mutagenic effects, and each individual PAH has different carcinogenic risk (Wang *et al.*, 2011). PAHs in the atmosphere are mainly released from human activities (Afshar-Mohajer *et al.*, 2016; Li *et al.*, 2017), and PAHs discharged into the air can be adsorbed on PM_{2.5}, increasing the harm to human health. Therefore, it is of great significance to study the PAHs bound to PM_{2.5} during haze.

Many studies have focused on the pollution levels, sources and meteorological conditions of PAHs bound to PM_{2.5} (Deng *et al.*, 2006; Akyuz and Cabuk, 2009; Martellini *et al.*, 2012). Isomer diagnosis ratio was used to trace the origin of PAHs qualitatively in case of less information and had much uncertainty to the source identification of PAHs (Yunker *et al.*, 2002), while diffusion model and receptor model were used to trace the origin of PAHs quantitatively. Receptor models, such as Principal Component Analysis-Multiple Linear Regression (PCA-MLR), can only explain the contribution rate of various pollution sources to samples, while diffusion models, such as Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT), potential source contribution function (PSCF), concentration weighted trajectory (CWT) can only judge regional pollution sources in space (Guo *et al.*, 2016; Zhang *et al.*, 2017). Previous studies has shown that coal/biomass combustion and vehicle emission were the major PAHs sources in PM_{2.5} by PCA (Zhang *et al.*, 2019a), and significant contribution regions of PAHs at Mount Tai were the north (Hebei Province) and southeast (Henan Province) directions by PSCF (Liu *et al.*, 2017). Few studies had analyzed the source of PAHs associated with PM_{2.5} by combining the two models. As for meteorological conditions, some studies reported that concentration of PAHs was significantly correlated with relative humidity (RH) (Hien *et al.*, 2007), wind speed (WS) (Li *et al.*, 2005) and temperature (T) (Wang *et al.*, 2016). However, other studies had shown no significant relationship between them (Yang *et al.*, 2018). In order to study the impact on PAHs, a large number of studies have been carried out in Beijing (Gao *et al.*, 2016), Shanghai (Wang *et al.*, 2014; Wang *et al.*, 2016), the Pearl River Delta (Wei *et al.*, 2012) and so on. These results showed that PAHs had certain potential hazards to human health. However, most of those studies mainly focused on a large time scale, and only limited researches pay attention to a sudden haze event in detail. As one of the important agricultural and economic province in central China, the study on atmospheric PAHs of Hubei Province is mainly concentrated in the capital of Wuhan, with a large time scale (Zhang *et al.*, 2019b). Less attention was paid to the sudden haze in surrounding medium cities.

Huang-gang is a prefecture-level light industrial city located on the bank of Yangtze River, which lies opposite to the industrial corridor (including Ezhou, Huangshi and Daye), and it belongs to the economic development of Wuhan City Circle. Huang-gang is located at the junction of Hubei Province, Henan Province, Anhui Province and Jiangxi Province. It has a long north-south span and is one of the important atmospheric transmission channels of the north to the south in China. Besides, Huang-gang was recommended as "National Hygienic City" in China in 2017 because of its good air quality. However, with the progress of urbanization and the development of large numbers of factories nearby, the organized and unorganized emission sources of surrounding have increased greatly, and because of the regional transport channel of air mass from north to south, the air quality has been declining day by day, which results in haze sometimes. This paper aims to study a winter haze event in Huang-gang City, analyze the diurnal variation of PAHs during the haze period, combine receptor model with diffusion model to analyze the pollution sources and spatial distribution of PAHs and PM_{2.5}, and evaluate the impact of haze on human health.

2 METHODS

2.1 Sampling Campaign

The sampling site is located on the roof of Huang-gang Environmental Protection Bureau, Huang-gang City, about 20 meters from the ground. There are schools, residential areas, commercial areas, no tall buildings, no large factories in the surroundings, and it is about 100 meters away

from the main road of this city. The sampling site is a representative sampling point and the surrounding environment of sampling site is shown in Fig. 1.

Samples were collected throughout the haze period (from January 13 to January 24). Four samples were obtained every day at 06:00–11:00, 11:30–16:30, 17:00–22:00 and 22:30–05:30, and totally 48 samples were obtained. A high-volume sampler (Wuhan Tianhong Environmental protection Industry, TH-1000C) with a flow rate of 1.05 m³ per minute was used to collect particulate matter and PAHs by quartz fiber filters. In order to reduce the experimental error, the quartz fiber filters were baked in a muffle oven at 550°C for 4 hours before using. Samples collected were sealed at –10°C for storage.

2.2 PM_{2.5} Measurement and PAHs Analysis

After baking (550°C for 4 hours), the quartz fiber filters were kept equilibrium at a temperature of 23 ± 1°C and a relative humidity of 40% ± 5%. After that, the quartz fiber filters were weighed by an electronic microbalance at least three times before sampling, and the weighing error did not exceed 0.05 mg. After that, the sampled quartz fiber filters were weighed under the same process. Thus, the mass difference of the filters before and after sampling is the mass of PM_{2.5} adsorbed on the filter membrane.

Concentrations of OC, EC were measured by an Organic/Elemental Carbon Analyzer (DRI model 2001, Atmoslytic Inc. USA) based on the Interagency Monitoring of Protected Visual Environments (IMPROVE) thermal/optical reflectance (TOR) protocol for pyrolysis correction. The analysis procedure of PAHs was the same as described in published paper (Zhang *et al.*, 2019b). Briefly, a half of the circular quartz fiber filter was put into the Soxhlet extractor for extraction. About 140 mL of dichloromethane (DCM) was added immediately after adding five deuterated PAHs (naphthalene-d₈, acenaphthene-d₁₀, phenanthrene-d₁₀, chrysene-d₁₂, perylene-d₁₀, o2si smart solutions, USA). The liquid was heated in a water bath at 45°C for 24 hours and then was concentrated to 5 mL on a rotating evaporator (Heidolph Laborota 4000, Germany). The glass column with silica gel and alumina (V:V = 6 mL:3 mL) was used to remove impurities in the extract with approximate 25 mL mixture of DCM and n-hexane (V:V = 2:3). The eluent was concentrated to about 1.5 mL on the rotating evaporator, and then transferred to a cell bottle for nitrogen blowing. The eluent was concentrated by nitrogen (purity ≥ 99.999%) to 200 µL. Finally, 5 µL internal standard substance hexamethylbenzene (HMB, 200 mg L⁻¹) was added before instrumental

Fig. 1. The geographic location and surrounding environment of sampling site.

analysis. Silica gel (100–200 mesh) and alumina (100–200 mesh) need to be baked at 180°C and 240°C for 24 hours to activate before experiment. After that, 3% pure water was added to silica gel and alumina to remove their activity.

Sixteen U.S. EPA priority PAHs (Table 1) were detected by gas chromatography–mass spectrometry (GC-MS, Agilent 6890N-5975). In order to ensure the accuracy of data and ensure samples are not contaminated during sampling and analysis, field blanks, process blanks and samples were detected together. The results showed that the concentration of blank PAHs was much lower than the detection limit of the method. The surrogate recoveries were in the range of 70%–120%, and the final results of PAHs concentration showed in Table 1.

2.3 Description of PCA-MLR

PCA-MLR has strong source analysis ability in the absence of source component spectrum. The main purpose of PCA is to explain most of the variation information in data with as few variables as possible. It is aimed to eliminate as much collinearity as possible through dimensionality reduction. A large amount of data information is simplified into a few representative influence factors by PCA. According to the load of the extracted factors on each component of PAHs, the sources of PAHs can be distinguished. Based on this, MLR is used to further determine the contribution rate of pollution sources. The equation for MLR analysis is

$$Y = \sum_{i=1}^n m_i \times X_i + b \quad (1)$$

In the formula, dependent variable Y denotes $\sum_{16}\text{PAHs}$, “ n ” denotes the number of factors, X_i denotes the factor score variable and m_i represents the coefficient of corresponding factor, the constant “ b ” denotes the unexplained residual variable information. Standardized the variable results and operate linear regression analysis again, the following equation is obtained

$$Y = \sum_{i=1}^n C_i \times X_i \quad (2)$$

Table 1. PM_{2.5} and PAHs concentrations in different periods of haze.

Compounds	Abbreviation	Rings	EHZ (n = 12)	MHZ (n = 28)	LHZ (n = 8)
			Average ± standard deviation		
Fine particle matter	PM _{2.5}		60.3 ± 21.9	140 ± 34.6	80.2 ± 36.0
Naphthalene	Nap	2	2.13 ± 2.30	1.41 ± 2.04	0.33 ± 0.15
Acenaphthylene	Acy	3	0.22 ± 0.38	0.24 ± 0.37	0.21 ± 0.37
Acenaphthene	Ace	3	0.08 ± 0.08	0.07 ± 0.07	0.03 ± 0.03
Fluorene	Flu	3	0.31 ± 0.13	0.30 ± 0.26	0.22 ± 0.19
Phenanthrene	Phe	3	2.12 ± 0.57	2.31 ± 3.42	1.16 ± 0.39
Anthracene	Ant	3	0.26 ± 0.08	0.33 ± 0.75	0.14 ± 0.05
Fluoranthene	Fla	4	3.62 ± 0.90	3.48 ± 1.55	1.90 ± 0.76
Pyrene	Pyr	4	2.87 ± 0.87	2.46 ± 1.24	1.43 ± 0.63
Benz[a]anthracene	BaA	4	1.23 ± 0.87	0.87 ± 0.72	0.36 ± 0.22
Chrysene	Chr	4	3.08 ± 1.21	2.98 ± 1.23	1.91 ± 0.66
Benzo[b]fluoranthene	BbF	5	1.74 ± 0.87	2.12 ± 1.32	0.97 ± 0.49
Benzo[k]fluoranthene	BkF	5	4.38 ± 1.99	3.91 ± 1.84	1.54 ± 0.82
Benzo[a]pyrene	BaP	5	1.18 ± 0.77	1.06 ± 0.97	0.32 ± 0.14
Dibenz[a, h]anthracene	DBA	5	0.47 ± 0.16	0.41 ± 0.19	0.13 ± 0.10
Indeno[1,2,3-cd] pyrene	IcdP	6	3.06 ± 1.34	2.66 ± 1.42	0.98 ± 0.37
Benzo[ghi]perylene	BghiP	6	2.96 ± 1.07	2.76 ± 0.98	1.72 ± 0.51
Sum of PAHs	$\sum_{16}\text{PAHs}$		29.7 ± 10.2	27.4 ± 11.9	13.4 ± 4.79

PM_{2.5} concentration: μg m⁻³. PAH concentration: ng m⁻³.

EHZ, MHZ, LHZ represent early (January 13–15), middle (January 16–22) and late (January 23–24) stage of haze, respectively.

In the formula, C_i represents MLR coefficient. The average contribution rate (N_i) of pollution source factor “i” can be expressed by equation

$$N_i = C_i / \sum C_i \times 100\% \quad (3)$$

2.4 PSCF and CWT

HYSPLIT is a comprehensive model system developed by the US National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory (ARL) and the Australian Meteorological Agency to analyze trajectories of airflow, diffusion, and sedimentation. It can be used to diagnose the source and transmission velocity of air mass, but it cannot determine the distribution of potential pollution sources and the level of pollution. PSCF and CWT are grid-based statistical methods based on the HYSPLIT model. They can be used in the TrajStat model to obtain the distribution of potential source regions and pollution source concentrations semi-quantitatively.

The source of PM_{2.5} and PAHs during the haze period can be distinguished spatially by PSCF. PSCF analysis method is a probability function that infers the spatial distribution of the possible source area by backward trajectory. The mesh covering more than 90% of the track area is established by software, and the end point of the track segment terminated in each cell ($0.5^\circ \times 0.5^\circ$) is calculated to get the PSCF value of the mesh in the study area (Wei *et al.*, 2019). The PSCF value is defined as:

$$PSCF_{ij} = \frac{m_{ij}}{n_{ij}} \quad (4)$$

where i and j are on behalf of the latitude and longitude, respectively; n_{ij} is defined as the total number of endpoints that fall in the ij-th cell, and m_{ij} is the number of endpoints in the same cell that exceeded the threshold criterion. For PM_{2.5}, the threshold criterion is the second-grade level of National Ambient Air Quality Standards of China (NAAQS, GB 3095-2012, $75 \mu\text{g m}^{-3}$). The higher PSCF values, the greater probability that the concentration is higher. When the average number of each grid of the trajectory end point (n_{ave}) is three times that of n_{ij} , the uncertainty of each cell can be reduced by introducing a weight function $W(n_{ij})$:

$$WPSCF_{ij} = PSCF_{ij} \times W(n_{ij}) \quad (5)$$

$$W(n_{ij}) = \begin{cases} 1 & n_{ij} > 3n_{ave} \\ 0.7 & 3n_{ave} \geq n_{ij} > 1.5n_{ave} \\ 0.42 & 1.5n_{ave} \geq n_{ij} > n_{ave} \\ 0.15 & n_{ave} \geq n_{ij} \end{cases} \quad (6)$$

The PSCF value can only reflect the probability that the concentration of the pollutant is higher than the threshold criterion, and it is difficult to distinguish the pollution levels of different potential regions. The CWT analysis method refers to assigning a weighted concentration to each grid by averaging the sample concentrations having trajectories associated with the grid cells (Zhang *et al.*, 2017). CWT is expressed as follows:

$$C_{ij} = \frac{1}{\sum_{l=1}^M \tau_{ijl}} \sum_{l=1}^M C_l \tau_{ijl} \quad (7)$$

where C_{ij} represents the average weight concentrations in the ij-th cell, C_l is the measured PAHs concentration observed on the arrival of trajectory l , and τ_{ijl} is the number of trajectory end points in the ij-th cell associated with the C_l sample. The weighting function described in Eq. (6) can also be used in the CWT analyses.

2.5 Carcinogenic Risk Assessment

As semi-volatile organic pollutants, PAHs encounter gas-particle phase distribution after being discharged into the atmosphere. Both the gas and particle phase PAHs can reach the alveolar epithelium through inhalation exposure and enter the circulatory system rapidly, and cause harm to human (Liu *et al.*, 2019b). Because of the lack of gas-PAHs concentration data, the G/P distribution model is introduced to estimate PAHs in gas phase to assess the carcinogenic risk more accurately. The distribution model has been described in detail in previous study (Ma *et al.*, 2019), and the equation is as following:

$$K_p = \frac{C_p / PM}{C_g} \quad (8)$$

where K_p is G/P partitioning coefficient of each PAH, C_p and C_g are concentrations of each PAH in gas and particle phase (ng m^{-3}), PM is the concentration of particle matter ($\mu\text{g m}^{-3}$).

Individual PAH has different carcinogenic risk, and BaP is the most toxic and representative. The total carcinogenic concentration of PAHs can be assessed with BaP equivalent concentrations (BaPeq) (Gao *et al.*, 2015). Here, BaPeq can be calculated with the formula:

$$\text{BaPeq} = \sum_{i=1}^{16} \text{PAH}_i \times \text{TEF}_i \quad (9)$$

where PAH_i is the total PAH concentration (G+P phase), TEF_i is the toxic equivalency factor (TEF) for each PAH (Nisbet and Lagoy, 1992): 0.001 for Nap, Acy, Ace, Flu, Ant, Fla, Pyr, 0.01 for Phe, BghiP, 0.1 for BaA, Chr, BbF, BkF, IcdP, 1 for BaP, DBA. The incremental lifetime cancer risks (ILCRs) model was used to calculate the exposure risks of PAHs, and the pathways of exposure risks include inhalation, ingestion and dermal contact. Parameters of ILCRs are showed in (Table 2) and the equations for estimating ILCRs are as following (Wang *et al.*, 2011; Gong *et al.*, 2019; Ma *et al.*, 2020; Xing *et al.*, 2020):

$$\text{ILCR}_{\text{inh}} = \frac{\text{BaPeq} \times \text{CSF}_{\text{inh}} \times \text{IR}_{\text{inh}} \times \text{EF}_{\text{inh}}}{\text{BW} \times 10^6} \quad (10)$$

$$\text{ILCR}_{\text{ing}} = \frac{\text{BaPeq} \times \text{CSF}_{\text{ing}} \times \sqrt[3]{\text{BW}/70} \times \text{IR}_{\text{ing}} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 10^6} \quad (11)$$

Table 2. Parameters used to estimate the ILCRs.

Parameter	Meaning	Value	
		Adult	Children
BaPeq (ng m^{-3})	Concentration of PAHs		
CSF_{inh} ($\text{mg kg}^{-1} \text{day}^{-1}$)	Carcinogenic slope factor	3.14	3.14
CSF_{ing} ($\text{mg kg}^{-1} \text{day}^{-1}$)	Carcinogenic slope factor	7.30	7.30
CSF_{derm} ($\text{mg kg}^{-1} \text{day}^{-1}$)	Carcinogenic slope factor	3.85	3.85
BW (kg)	Body weight	61.5	15.0
IR_{inh} ($\text{m}^3 \text{day}^{-1}$)	Inhalation rate	15.9	8.3
IR_{ing} (mg day^{-1})	Ingestion rate	200	100
SA (cm^2)	Dermal exposure area	5700	2800
AF (mg/cm^2)	Dermal adherence factor	0.07	0.20
ABS (unitless)	Dermal adsorption fraction	0.13	0.13
EF (days year^{-1})	Exposure frequency	365	365
EF_{inh}	outdoor exposure fraction	0.208	0.127
ED (years)	Exposure duration	24.0	6.00
AT (days)	Average life span	25550	25550

$$ILCR_{derm} = \frac{Bap_{eq} \times CSF_{derm} \times \sqrt[3]{BW/70} \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^6} \quad (12)$$

$$TILCR = ILCR_{inh} + ILCR_{ing} + ILCR_{derm} \quad (13)$$

2.6 Meteorological Condition

Meteorological data, including temperature, relative humidity, wind speed and some other pollutants (CO, O₃, NO_x), come from the Air network (<https://www.zq12369.com>). The dates of backward trajectory analysis are from National Oceanic and Atmospheric Administration (NOAA) (<ftp://gus.arlhq.noaa.gov>).

3 RESULTS AND DISCUSSION

3.1 PM_{2.5} Levels and Composition

According to PM_{2.5} concentration and its variety trend (Fig. 2), the whole haze episode (WHZ) can be divided into three stages: early (low concentration, January 13–15, EHZ), medium (high concentration, January 16–22, MHZ) and late (concentration decreased rapidly, January 23–24, LHZ). PM_{2.5} concentration in MHZ was much higher than that in EHZ (about 2.33 times) and LHZ (around 1.75 times). Here, the sampling time period for obtaining four samples per day was specified as morning (06:00–11:00), afternoon (11:30–16:30), evening (17:00–22:00) and late night (LN, 22:30–05:30). The concentration of PM_{2.5} ranged from 30.7 μg m⁻³ to 196 μg m⁻³, with an average concentration of 110.4 ± 48.3 μg m⁻³ in WHZ, which was 11 times of the World Health Organization (WHO) safe level (10 μg m⁻³), and 1.47 times the severe pollution level (75 μg m⁻³, NAAQS, GB 3095–2012), indicating that Huang-gang was suffering from relatively serious air pollution. Compared with other cities, the concentration of PM_{2.5} was lower than those reported in northern China, such as Beijing (Cao *et al.*, 2018), Liaocheng in Shandong Province (Liu *et al.*, 2019a), whereas, higher than those in southern cities, like Guangzhou (Tan *et al.*, 2011), Wuhan (Zhang *et al.*, 2019b). The highest concentration of PM_{2.5} occurred in MHZ evening (16 January and 20 January). From the perspective of diurnal variation, the concentration of PM_{2.5} presented as evening > morning > afternoon > LN, and PM_{2.5} concentration at night was slightly higher than daytime, generally. Heavy traffic and coal combustion in the morning and evening might be the reasons for the high PM_{2.5} concentration (Yu *et al.*, 2009). In addition, the lower boundary layer at night made it difficult for pollutants to diffuse, thus further increasing the concentration of PM_{2.5} (Cao *et al.*, 2018). However, with the decrease of human activities at LN, the emission of pollutants would decrease, so the concentration of PM_{2.5} was lower in LN.

Fig. 2. Time series of PM_{2.5} (μg m⁻³) and associated PAHs (ng m⁻³) compositions concentration on daily scale.

The concentrations of OC and EC during the sampling period varied from 3.17 to 23.5 $\mu\text{g m}^{-3}$ and 1.70 to 10.5 $\mu\text{g m}^{-3}$ with the mean of $14.3 \pm 4.95 \mu\text{g m}^{-3}$ and $5.63 \pm 1.74 \mu\text{g m}^{-3}$, respectively. The concentrations of OC and EC were much lower than that in Xi'an, Taiyuan, Chongqing (Ni *et al.*, 2019) and were close to Tianjin (Wang *et al.*, 2019). OC and EC averagely accounted for 12.9% and 5.10% of total measured $\text{PM}_{2.5}$ concentration. Moreover, OC contributed 71.7% to total carbon (TC, sum of OC and EC), which indicated that OC was the predominant contributor to carbonaceous aerosols than EC. SOC can be calculated by the following formula (Grivas *et al.*, 2012):

$$\text{SOC} = \text{OC} - \text{EC} \times (\text{OC/EC})_{\min} \quad (14)$$

where $(\text{OC/EC})_{\min}$ was the minimum ratio of OC to EC in the entire sampling period. The OC/EC ratios can identify the contribution of primary and secondary sources to carbonaceous aerosols, and the formation of secondary aerosols can be characterized by higher OC/EC ratios (greater than 2) (Peng *et al.*, 2018; Wang *et al.*, 2019). During the haze period, a total of 85.4% of samples OC/EC exceeded this value, while 50.0% of samples exceeded this value in LHZ. The proportion of SOC in OC decreased significantly in LHZ (Table 3), which indicated that secondary aerosols played a key role to the formation of haze in MHZ. From the perspective of intraday changes, higher SOC concentrations and higher SOC/OC values occurred at afternoon and evening, which was related to the fact that more residential cooking and heavy traffic can promote the formation of SOC (Stone *et al.*, 2008; Yu *et al.*, 2009; Xu *et al.*, 2018).

The average concentration of $\sum_{16}\text{PAHs}$ during haze episode was $25.6 \pm 12.0 \text{ ng m}^{-3}$, which was similar to the annual average concentration of $\sum_{16}\text{PAHs}$ in Wuhan in 2014 (Zhang *et al.*, 2019a), and was much lower than those in northern China, such as Liaocheng (Liu *et al.*, 2019a), Jinan (Li *et al.*, 2017), higher than southern China cities, like Huangshi (Hu *et al.*, 2018), Shanghai (Wei *et al.*, 2019), Nanjing (Kong *et al.*, 2015a), Nanchang (Liu *et al.*, 2016). Furthermore, the concentration of carcinogenic PAHs (CARPAHs), including BaA, BbF, BkF, BaP, DBA, IcdP and BghiP, ranged from 1.59 to 38.4 ng m^{-3} , with a mean value of 12.8 ng m^{-3} , which was much higher than that in Shanghai (Wei *et al.*, 2019). The average concentration of PAHs in EHZ was slightly higher than that in MHZ, and both of which were about twice than that in LHZ. A positive correlation ($P < 0.05$, $R = 0.56$) was observed between $\text{PM}_{2.5}$ concentration and $\sum_{16}\text{PAHs}$ concentration only in MHZ, which suggested that PAHs and $\text{PM}_{2.5}$ might come from the same source in MHZ. The concentration of PAHs at night was about 1.20 times higher than that at daytime and both the highest and lowest concentrations of $\sum_{16}\text{PAHs}$ occurred at LN. Additionally, the concentrations of $\sum_{16}\text{PAHs}$ presented as follows: evening > LN > morning > afternoon, which was different from $\text{PM}_{2.5}$. The concentration of $\text{PM}_{2.5}$ and PAHs can be affected by the amount of pollutants, the way of emission and meteorological conditions. In addition, as one of the components of $\text{PM}_{2.5}$, PAHs accounts for only 0.2‰ of $\text{PM}_{2.5}$ mass in this study, so $\text{PM}_{2.5}$ is not the main factor causing the change of PAHs concentration. Moreover, PAHs concentration can be greatly affected by meteorological conditions. Wind speed, temperature and relative humidity can affect the gas-solid distribution of PAHs. Among the CARPAHs, BaP was the representative compound of PAHs, and was considered as a good index for the whole PAHs carcinogenicity (Shi *et al.*, 2010). The concentration of BaP was ranged from 0.09 to 5.18 ng m^{-3} , with a mean value of 0.96 ng m^{-3} . In all of the 48 samples, only 3 samples exceeded the daily limit (2.5 ng m^{-3} , NAAQS, GB 3095-2012).

Table 3. The concentration of OC, EC, TC, SOC ($\mu\text{g m}^{-3}$) and the ratio of related compounds.

	EHZ	MHZ	LHZ	Morning	Afternoon	Evening	LN
OC	14.9 ± 5.03	15.5 ± 4.03	9.00 ± 4.25	13.3 ± 3.12	14.0 ± 3.86	16.9 ± 5.27	12.9 ± 5.97
EC	5.53 ± 2.08	6.04 ± 1.26	4.32 ± 1.94	5.73 ± 1.31	5.56 ± 1.52	6.12 ± 2.15	5.10 ± 1.69
TC	20.4 ± 7.03	21.6 ± 4.77	13.3 ± 6.15	19.0 ± 4.16	19.6 ± 5.04	23.0 ± 7.15	18.0 ± 7.43
OC/EC	2.74 ± 0.28	2.61 ± 0.67	2.09 ± 0.27	2.36 ± 0.44	2.57 ± 0.55	2.82 ± 0.59	2.46 ± 0.63
OC/TC	0.73 ± 0.02	0.71 ± 0.05	0.67 ± 0.03	0.70 ± 0.04	0.71 ± 0.04	0.73 ± 0.03	0.70 ± 0.05
SOC	5.41 ± 2.02	5.21 ± 3.54	1.61 ± 1.29	3.50 ± 2.21	4.50 ± 2.76	6.45 ± 3.05	4.19 ± 3.91
SOC/OC	0.37 ± 0.07	0.31 ± 0.16	0.17 ± 0.10	0.25 ± 0.13	0.31 ± 0.13	0.37 ± 0.10	0.26 ± 0.18

According to the number of aromatic rings, the concentration of $\Sigma_{16}\text{PAHs}$ presented as 4-ring > 5-ring > 6-ring > 3-ring > 2-ring in each time periods (Fig. 3(a)), which suggested $\Sigma_{16}\text{PAHs}$ was mainly concentrated in the middle molecular weight (MMW, 4-ring) and heavy molecular weight (HMW, 5-ring and 6-ring). MMW and HMW of PAHs accounted for 36.5% and 45.6% of total PAHs concentration respectively, which suggested the haze was mainly composed of PAHs with high molecular weight and low volatility. A significant positive correlation ($P < 0.01$) was also perceived between the concentration of $\Sigma_{16}\text{PAHs}$ and 4,5,6-rings PAHs during monitoring period, which suggested 4,5,6-rings PAHs contributed to the accumulation of PAHs. The highest PAHs concentration occurred at night, and was mainly concentrated in HMW. Heavy traffic was the main cause of this phenomenon, because HMW-PAHs were significantly derived from the emission of vehicle exhaust (Kong *et al.*, 2015b; Li *et al.*, 2017). Compared with other time periods, the proportion of 4-ring PAHs increased at afternoon, which might be related to the combustion of coal and biomass during lunch (Lin *et al.*, 2015; Ren *et al.*, 2017). The concentrations of PAHs in the morning and LN were higher, because the lower temperature (5.50°C for morning and LN, 7.80°C for afternoon) was favorable for the transition of PAHs from the vapour phase to the particle phase (Li *et al.*, 2014) and weaker solar radiation inhibited the photochemical decomposition of PAHs at LN (Duan *et al.*, 2007). Compared to EHZ, the concentration of $\text{PM}_{2.5}$ increased sharply in MHZ, but the concentration of PAHs was basically the same as that in EHZ, which was manifested in each ring of PAHs (Fig. 3(b)). This may be due to that when $\text{PM}_{2.5}$ increased to a light pollution level ($\text{PM}_{2.5} > 75 \mu\text{g m}^{-3}$), organic matter fractions decreased probably during the transition and pollution (Zhang *et al.*, 2019b). Therefore, more factors should be studied further.

3.2 Relative to Meteorological Condition and Other Air Pollutants

During the WHZ, meteorological conditions and other air pollutants, including relative humidity (RH), wind speed (WS), carbon monoxide (CO), nitrogen oxide (NO_x) and so on, had a significant impact on $\text{PM}_{2.5}$ and PAHs concentration (Table 4). Generally speaking, WS had a significant negative correlation ($P < 0.01$) with $\text{PM}_{2.5}$ concentration and PAHs concentration, while RH had a significant positive correlation ($P < 0.01$) with $\text{PM}_{2.5}$ concentration. Intensive winds can lead to less inversion situation and better dilution of pollutant, while fine particles combined with water in the high humidity air result in particles suspended in the air and not easy to dissipate. Different from the whole monitoring period (Fig. 4), $\text{PM}_{2.5}$ concentration showed a significant negative correlation ($P < 0.05$, $R = -0.73$) with RH in LHZ, while the relation was not obvious in MHZ. When RH is low, the $\text{PM}_{2.5}$ concentration will increase with the rise of RH. But when RH increased to a high level (rainfall exceeded 1 mm per hour), $\text{PM}_{2.5}$ can be effectively removed from the air (Pu *et al.*, 2011). There was also a significant positive correlation between NO_x and CO and PAHs concentration, which indicated that PAHs mainly come from primary emission sources, such as

Fig. 3. Concentrations and percentages of PAHs with different aromatic rings in different periods.

Table 4. Pearson correlation coefficients between PM_{2.5}, PAHs and other factors.

	PM _{2.5}	PAHs	NO _x	CO	WS	RH
PM _{2.5}	1					
PAHs	0.354*	1				
NO _x	0.275	0.595**	1			
CO	0.653**	0.389**	0.678**	1		
WS	-0.462**	-0.461**	-0.719**	-0.587**	1	
RH	0.479**	-0.215	-0.008	0.496**	-0.109	1

** Significant at 0.01 level. * Significant at 0.05 level.

Fig. 4. Changes on meteorological conditions and pollutant concentrations in daily scale. The units of PM_{2.5}, NO_x, O₃ are $\mu\text{g m}^{-3}$, and CO is mg m^{-3} , T and RH are $^{\circ}\text{C}$ and %, WS is m s^{-1} , the unit of PAHs is ng m^{-3} .

combustion source and traffic emission source, since NO_x and CO were basically generated by primary emission sources (Ohara *et al.*, 2007). PAHs concentration showed no obvious correlation with O₃ during the whole monitoring period. Furthermore, PAHs concentration was positively correlated with T ($P < 0.01$) and negatively correlated with RH ($P < 0.05$) in LHZ. With the increasing of relative humidity ($> 80\%$) and rainfall in LHZ, PAHs were easier to deposit together with PM_{2.5}. In addition, the low temperature (0°C) caused by strong wind made it difficult for PAHs in the atmosphere to be adsorbed by PM_{2.5}.

3.3 Source of PAHs

In order to identify the sources of PAHs during haze episode, isomer diagnosis ratio was used firstly to explain sources qualitatively. BaA/(BaA+Chr), Fla/(Fla+Pyr), BaP/BghiP and IcdP/(IcdP+BghiP) can be used to preliminarily determine the possible origin of PAHs (Yunker *et al.*, 2002; Li *et al.*, 2006). In the WHZ, PAHs bound to PM_{2.5} in ambient air mainly come from petrogenic sources, traffic emissions (e.g., vehicular exhaust), tar/coal combustion and biomass (e.g., wood) combustion (Fig. 5). The sources of pollutants in EHZ and MHZ were relatively more complex than those in LHZ. BaA was considered to be more readily degradable than its isomers (Chr) during atmospheric transport, so the ratio of BaA to BaA+Chr can be used to determine whether the air mass was locally emitted or regionally transported (Ding *et al.*, 2007). The ratio of BaA to BaA+Chr greater than 0.50 indicated typical local emissions (Khalili *et al.*, 1995). The ratio of BaA to BaA+Chr was

concentrated in the range of less than 0.50 in this study, especially in LHZ, indicating that regional transport has an effect on haze episode.

Because of the uncertainty of isomer diagnosis ratio, PCA-MLR was used to analyze the types of PAHs pollution sources and their contribution rates more accurately (Yunker *et al.*, 2002; Zhang *et al.*, 2019a). PCA factors for EHZ, MHZ, LHZ and WHZ are presented with four, four, two and three factors, totally explaining 90.7%, 89.3%, 89.4% and 82.2% of the data variance, respectively (Table 5).

In EHZ, principal component 1 (PC1) explained 47.6% of the data variance with high loadings of BaA, Chr, BbF, BkF, BaP, IcdP, BghiP. Among those compounds, BbF, BaP, IcdP, BghiP were considered as indicators of gasoline vehicle emissions (Miguel and Pereira, 1989), and BaA, Chr,

Fig. 5. Four sources of PAHs, including petrogenic sources, traffic emissions, tar/coal combustion and biomass combustion, were identified using isomers diagnostic ratios.

Table 5. Pollution sources and contribution rates of PAHs by PCA-MLR.

	EHZ				MHZ				LHZ	
	PC1	PC2	PC3	PC4	PC1	PC2	PC3	PC4	PC1	PC2
Nap	0.474	-0.120	0.366	-0.487	-0.054	0.028	0.099	0.972	0.152	-0.840
Acy	-0.123	0.336	0.866	0.058	-0.095	-0.052	0.946	-0.046	-0.024	0.996
Ace	0.149	0.134	0.971	0.016	0.030	0.014	0.860	0.271	0.041	0.993
Flu	0.018	0.566	0.775	0.222	-0.034	0.273	0.894	-0.041	0.107	0.982
Phe	-0.169	0.901	0.097	0.142	-0.043	0.985	-0.004	-0.063	0.954	0.113
Ant	0.055	0.922	0.232	0.106	-0.084	0.971	-0.001	-0.065	0.916	0.229
Fla	0.328	0.768	0.443	0.145	0.528	0.728	0.181	0.219	0.775	0.620
Pyr	0.522	0.716	0.273	-0.251	0.451	0.807	0.246	0.169	0.736	0.666
BaA	0.960	0.005	0.080	0.141	0.875	0.260	0.229	0.112	0.659	0.706
Chr	0.907	0.214	-0.076	0.090	0.950	-0.011	-0.179	-0.038	0.977	-0.058
BbF	0.974	-0.039	0.011	0.050	0.951	0.114	-0.108	-0.046	0.984	0.003
BkF	0.982	0.025	0.079	-0.034	0.942	0.131	0.029	0.003	0.961	-0.097
BaP	0.963	-0.071	0.049	-0.016	0.944	0.122	-0.043	-0.014	0.782	0.445
DBA	0.185	0.105	0.053	0.882	0.717	-0.092	-0.169	-0.076	0.631	-0.312
IcdP	0.977	0.068	0.108	-0.008	0.937	0.132	0.188	0.024	0.797	0.443
BghiP	0.925	0.301	-0.008	-0.090	0.947	-0.008	-0.019	0.033	0.948	-0.045
Variance (%)	47.6	26.6	10.1	6.40	47.0	21.7	14.1	6.48	61.0	28.4
Sources	traffic	coal	biomass	coal	traffic	coal	biomass	petroleum	mixed	biomass
Contribution Rate (%)	68.1	14.1	13.4	4.4	42.1	31.1	10.2	16.6	80.0	20.0

Factor loadings higher than 0.85 were shown in bold.

BkF were emitted from diesel exhaust (Rogge *et al.*, 1993). Therefore, PC1 can be considered as a source of traffic emissions. Principal component 2 (PC2) explained 26.6% of the data variance with high loadings of Phe, Ant, which were markers for coal combustion source (Kong *et al.*, 2010). Ant had been identified in coal combustion and coke production (Sofowote *et al.*, 2008). Thus, PC2 was identified as coal combustion source. Principal component 3 (PC3) explained 10.1% of the data variance with high loadings of Acy and Ace. These LMW-PAHs were mainly generated at a relatively low combustion temperature of biomass, such as wood, grass (Yunker *et al.*, 2002). Principal component 4 (PC4) explains 6.40% of the data variance with high loadings of DBA, which was related to thermal power plant that using coal as fuel (Fang *et al.*, 2004). In addition, MLR was used to analyze the contribution rate of each principal component. It suggested that the main sources of PAHs in EHZ were traffic emissions (68.1%), coal combustion (18.5%) and biomass combustion (13.4%).

The sources of PAHs in MHZ were similar to EHZ. PC1, PC2, PC3 and PC4 explain 47.1%, 21.7%, 14.1% and 6.48% of the data variance, respectively. PC4 has high loading of Nap, which can be regarded as petroleum source (Wang *et al.*, 2008). Thus, the main sources of PAHs in MHZ were traffic emissions (42.1%), coal combustion (31.1%), biomass combustion (10.2%) and petroleum source (16.6%).

Furthermore, only two principal components were extracted at LHZ, PC1 and PC2 explain 61.0% and 28.4% of the data variance, respectively. PC1, with high loadings of Phe, Ant, Chr, BbF, BkF and BghiP, suggested that it was mainly from mixed sources of traffic emissions and coal combustion (Li *et al.*, 2012). Therefore, the main sources of PAHs in LHZ were traffic emissions/coal combustion (80.0%) and biomass combustion (20.0%).

As can be seen from the above analysis, traffic emissions (TE), coal combustion (CC) and biomass combustion (BB) were the main sources of PAHs bound to PM_{2.5} throughout the haze period. PCA-MLR analysis of PAHs sources during the whole haze period also showed that TE (54.4%), CC (13.3%) and BB (32.3%) were the main sources. Compared with the EHZ, the contribution rate of TE decreased in MHZ, while the contribution rate of CC increased significantly. Therefore, the use of coal was one of the main factors for the aggravation of haze.

3.4 Geographic Origin

The mesoscale transport of pollutants in the atmospheric boundary layer is generally within 1000 meters, and the transport time is 2–3 days. Therefore, the HYSPLIT model was used to simulate the movement of air mass at an altitude of 500-meter in the past 72 hours (Xing *et al.*, 2020), and each trajectory was obtained every 6 hours. TrajStat model was used to cluster the air mass trajectories to track the regional sources of air pollutants during haze. Cluster analysis of air mass trajectories during WHZ showed that four types of trajectories were obtained, of which 22.9% came from Kazakhstan and northwest China, 18.8% came from southwest China and 58.3% came from Hubei Province. Air masses trajectories in different periods of haze were also clustered (Fig. 6). The results showed that, on the one hand, the long-distance transport air masses from northwest China occupied 41.7% in EHZ, and decreased significantly in MHZ (7.14%), raised to 25.0% in LHZ, which indicated that the air masses from Northwest China had an obvious dilution effect on pollutants. On the other hand, the proportion of air masses from south Hubei Province was more than 60.0%, and the contribution rate of air masses from southwest China was more than 30.0% in MHZ, which indicated that air mass from south Hubei Province and southwest China had an aggravating effect on haze.

PSCF and CWT analysis results were shown in Fig. 7. PSCF analysis results of PM_{2.5} and PAHs showed that PSCF values were low in northwest and southwest China, which were far away from the sampling point, indicating that these regions were less likely to contribute to the haze. The higher PSCF values appeared in southern Henan Province, eastern Hubei Province and the junction of Hunan Province and Jiangxi Province, showing a north-south belt distribution. This phenomenon indicated that air masses from the south and the north played a key role in the formation and dissipation of haze in this region. Likewise, CWT analysis results were highly consistent with PSCF results. The concentration of PM_{2.5} and PAHs showed strip-shaped distribution in the region. The maximum value of CWT corresponding to PM_{2.5} appeared in Huanggang City and Wuhan City, indicating that the transmission of PM_{2.5} from Wuhan and the emission of local pollutants had a great effect on the formation of haze.

Fig. 6. Cluster analysis of air mass trajectories in different periods of haze by TrajStat model. The red dot represents the sampling site, and blue lines represent trajectories obtained every 6 hours.

Fig. 7. PSCF analysis results of $PM_{2.5}$ (a) and PAHs (b) and CWT analysis results of $PM_{2.5}$ (c) and PAHs (d). The red dot represents the sampling point.

3.5 Health Risk Assessment

Gas-phase PAHs were estimated to assess the carcinogenic risk more accurately, and the BaP_{eq} concentration determined by TETs was showed in Fig. 8(a). The average concentration of BaP_{eq} was $4.08 \pm 2.22 \text{ ng m}^{-3}$, which was higher than the daily limit (2.5 ng m^{-3} , GB3095-2012). The maximum BaP_{eq} concentration (10.2 ng m^{-3}) appeared at evening, while the minimum (1.16 ng m^{-3}) appeared at LN, and about 77.0% of the samples exceeded the daily limit. From the perspective of time series, BaP_{eq} concentration followed descending order: evening > LN > morning > afternoon in the WHZ, whereas, the lowest temperature led to the lowest concentration of gas-phase PAHs at evening. On the whole, BaP_{eq} concentration was at a relative risk level.

The ILCR analysis result was shown in Fig. 8(b). The average TILCR value of adult was $3.69 \pm 2.01 \times 10^{-5}$ and $15.0 \pm 8.16 \times 10^{-6}$ for children, which indicated potential carcinogenic risk according to USEPA. From the perspective of time series, ILCR results were shown as evening > LN > morning > afternoon for both adults and children, and adults have a higher cancer risk during

Fig. 8. BaPeq concentration (a) and ILCR value for adult and children (b) on time series.

haze. Besides, as compared with inhalation, the carcinogenic risk of exposure to PM_{2.5} mainly came from ingestion.

4 CONCLUSIONS

In this study, 48 samples, collected during haze in Huang-gang, were analyzed to explain levels, compositions, sources and cancer risk of PM_{2.5}-bound PAHs. The average concentrations of PM_{2.5}, OC, EC and PAHs were $110 \pm 48.3 \mu\text{g m}^{-3}$, $14.3 \pm 4.95 \mu\text{g m}^{-3}$, $5.63 \pm 1.74 \mu\text{g m}^{-3}$ and $25.6 \pm 12.0 \text{ ng m}^{-3}$, indicating that Huang-gang was suffering from relatively serious air pollution. The concentration of PM_{2.5} presented as: evening > morning > afternoon > LN, while PAHs concentration showed evening > LN > morning > afternoon. A positive correlation ($P < 0.05$) was observed between PM_{2.5} concentration and $\sum_{16}\text{PAHs}$ concentration only in MHZ, which suggested PAHs and PM_{2.5} had the same sources in MHZ. The SOC concentration was higher at afternoon and evening, indicated that more residential cooking and heavy traffic can promote the formation of haze. The proportion of SOC in OC was significantly lower in LHZ than in EHZ and MHZ, which indicated that secondary aerosols had greatly influence to the formation of haze. Furthermore, MMW and HMW of PAHs accounted for 36.5% and 45.6% of total PAHs concentration respectively, which suggested that the haze was mainly composed of PAHs with high molecular

weight and low volatility. $PM_{2.5}$ concentration was negatively correlated with WS, and was positively correlated with RH in EHZ, negatively in LHZ. Additionally, PAHs concentration was positively correlated with NO_x , CO and T, negatively correlated with RH, but showed no correlation with O_3 . Besides this, the main sources of PAHs in WHZ were traffic emission (54.4%), coal combustion (13.3%) and biomass combustion (32.3%), also the increase in the use of coal had an aggravating effect on haze in MHZ. Air masses from the south and the north played a key role in the formation and dissipation of haze in this region. Moreover, the transmission of $PM_{2.5}$ from Wuhan and the emission of local pollutants had a great effect on the formation of haze. Gas-phase PAHs were estimated to assess the carcinogenic risk more accurately, and the ILCR assessment showed this haze had potential health risks to both adults and children, the carcinogenic risk of exposure to $PM_{2.5}$ mainly came from ingestion.

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DISCLAIMER

Reference to any companies or specific commercial products does not constitute an interest.

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