Atmospheric Research 193 (2017) 50–59

Contents lists available at ScienceDirect

Atmospheric Research

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

Source apportionment and toxicity of atmospheric polycyclic aromatic hydrocarbons by PMF: Quantifying the influence of coal usage in Taiyuan, China

Yulong Yan[a], Qiusheng He[a,*], Lili Guo[a], Hongyan Li[a], Hefeng Zhang[b,*], Min Shao[c], Yuhang Wang[d]

[a] School of Environment and Safety, Taiyuan University of Science and Technology, Taiyuan, China
[b] Chinese Research Academy of Environmental Sciences (CRAES), Ministry of Environment Protection (MEP), Beijing, China
[c] College of Environmental Sciences and Engineering, Peking University, Beijing, China
[d] School of Earth and Atmospheric Science, Georgia Institute of Technology, Atlanta, GA, USA

ARTICLE INFO

Keywords:
PAHs
Meteorological factors
Phase partitioning
Source apportionment
Coke processing

ABSTRACT

Atmospheric polycyclic aromatic hydrocarbons (PAHs) were analyzed in the gas phase and total suspended particulate (TSP) from summer 2014 to spring 2015 in Taiyuan, northern China. Taiyuan is an area with some of the highest atmospheric PAH levels in the world, and the total PAHs was highest in winter, followed by autumn, spring and summer. Low air temperature and a southern wind with low speed often led to higher PAH levels in Taiyuan. Although less than a half fraction, the benzo[*a*]pyrene equivalent concentration (BEQ) of particulate PAHs was almost equal to that of the total PAHs. Four sources, coal combustion, vehicle emissions, coke processing and biomass burning, were determined by positive matrix factorization (PMF), with contributions of 41.36%, 24.74%, 19.71% and 14.18% to the total PAHs in Taiyuan, respectively. Compared with the total PAHs, the particulate PAH solution underestimated the contribution of the coke processing, especially in winter, and overestimated vehicle emissions. The coke processing had a greater contribution to atmospheric PAHs with a southern wind at low speeds in winter in Taiyuan. Ultimately, the coke plants distributed in the Taiyuan-Linfen-Yuncheng basin should receive greater attention for air quality improvement in Taiyuan.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), persistent toxic substances (PTS_S) formed from the incomplete combustion of fossil fuels and biomass burning, have received worldwide attention in past decades. With the similar properties to persistent organic pollutants (POPs) (Odabasi et al., 2015), PAHs occur in both the gas and particulate phases in the atmosphere and are transported regionally and globally (Sehili and Lammel, 2007). Almost all PAHs directly impact human health via carcinogenic, teratogenic and mutagenic effects and are included in the EPA's list of 188 hazardous air pollutants (IARC, 1983; USEPA, 1990).

China has suffered from severe atmospheric PAHs pollution resulting from massive fuel consumption, including coal combustion, vehicle exhaust, biomass burning and coke processing (Liu et al., 2008; Zhang et al., 2007). Based on an emission inventory, the main emission sources of PAHs in major cities with populations larger than 1 million were coke production, coal combustion and vehicular fuel, which accounted for 49%, 34% and 8% of the total emissions in 2003, respectively (Zhang et al., 2007). High levels of atmospheric PAHs have been reported in Chinese cities, especially in northern China, such as Harbin (100 ng/m^3, Ma et al., 2010), Beijing (222.8 ng/m^3, Ma et al., 2011; 508 ng/m^3, Tao et al., 2007), Xi'an (728.6 ng/m^3, Wei et al., 2015), and multiple cities in the North China Plain (752 ng/m^3, Liu et al., 2008). A recent study also showed that PAHs were much higher in China (115 ng/m^3) than in Japan (5.76 ng/m^3), South Korea (19.9 ng/m^3), Vietnam (42.8 ng/m^3), and India (62.3 ng/m^3) (Hong et al., 2016). Although PAH pollution in China has decreased in the past ten years due to the clean energy project and improvements in pollutant emission control technology (Li et al., 2006), atmospheric PAHs remain at high levels because of the coal-dominated energy consumption, especially in some northern cities in the winter (Zhang et al., 2007). For example, coal combustion was the largest contributor (60%), followed by traffic sources (34%), in the heating season, and diesel vehicle sources (59%), ground evaporation (18%) and coal (17%) were the largest contributors in the non-heating season in Harbin based on positive matrix factorization (PMF) (Ma et al., 2010).

Meteorological factors can also affect the PAH partitioning in the

---

* Corresponding authors.
E-mail addresses: heqs@tyust.edu.cn (Q. He), zhanghf@craes.org.cn (H. Zhang).

http://dx.doi.org/10.1016/j.atmosres.2017.04.001
Received 30 November 2016; Received in revised form 3 March 2017; Accepted 3 April 2017

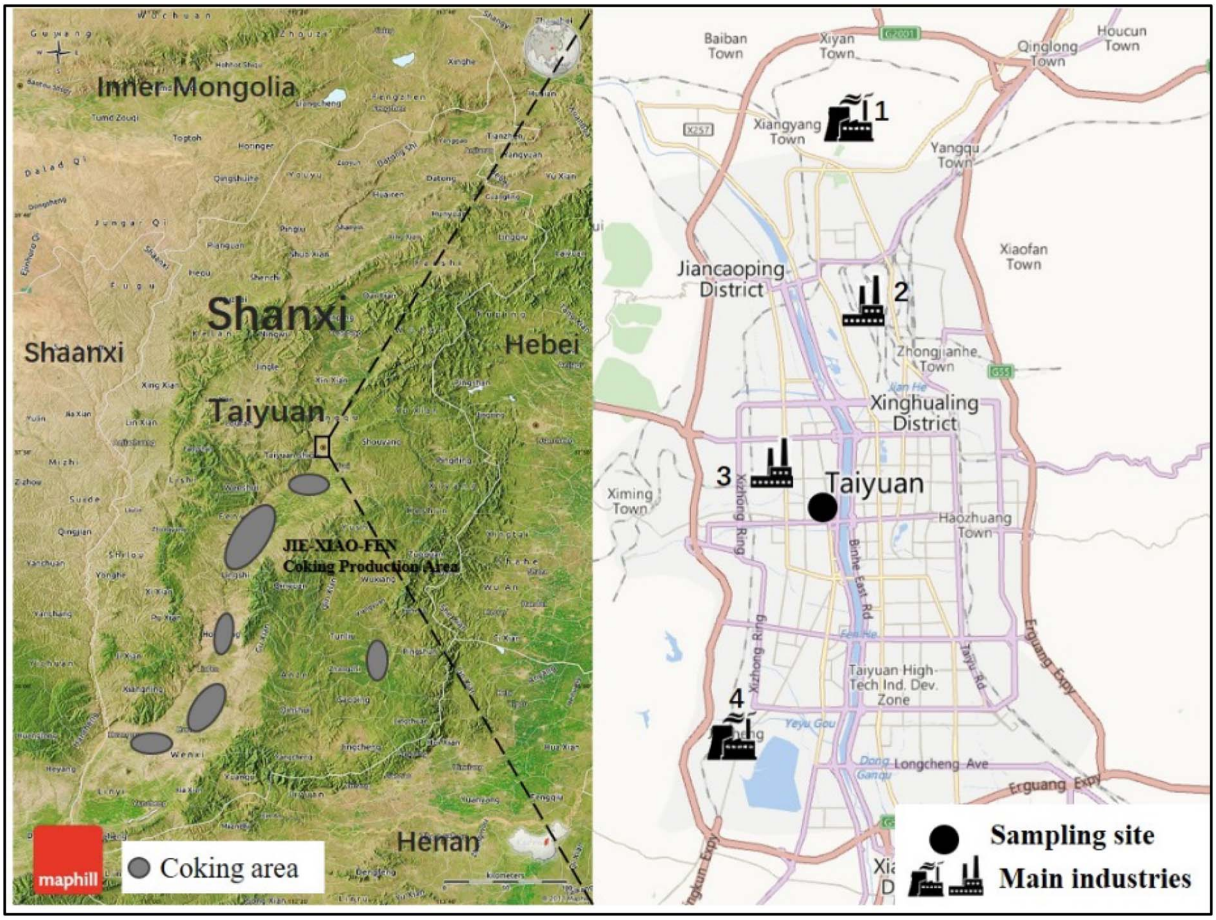

Fig. 1. Topography of Shanxi province and the location of the main industries, streets and the sampling site in Taiyuan (1, Second Thermal Power Plant of Taiyuan; 2, Taiyuan Iron and Steel Factory; 3, Taiyuan Heavy Machinery Factory; 4, First Thermal Power Plant of Taiyuan).

gas and particulate phases and the exposure levels induced by the strength of pollutant emissions in the atmosphere. In some regions, especially in cities where heating is required, high energy (such as coal, oil and gas) consumption could lead to strong PAH emissions and high atmospheric PAH levels (Ma et al., 2010). At the same time, air temperature can affect the partitioning of PAHs between the gas and particulate phases: low temperature facilitated the transfer of PAHs from the gas phase to the particulate phase and led to an increase in PAHs in the particulate phase (Tan et al., 2006). The partitioning of PAHs between gas and particulate is essential to understand the fate of PAHs and the characteristics of emission sources (Goss and Schwarzenbach, 1998; Mandalakis et al., 2002). The wind direction and speed, along with the air mass characteristics, could influence the transport, accumulation and diffusion of atmospheric PAHs (Lafontaine et al., 2015; Tan et al., 2006).

Taiyuan, a typical basin city, is an important base of energy, chemical and heavy industries in China (Fig. 1). Air pollution has remained heavy in Taiyuan even though stack gas has been heavily cleaned before emission into the atmosphere since the last century (He et al., 2015). High PAHs levels have been reported in Taiyuan, such as 410 and 360 ng/m^3 in PM_{10} and $PM_{2.5}$, respectively (Fu et al., 2010), and 420.8–915.7 ng/m^3 in $PM_{2.5}$ in winter in 2009–2013 (Li et al., 2016a), 88.07, 10.36, 21.31 and 215.93 ng/m^3 in $PM_{2.5}$ in spring, summer, autumn and winter during 2012–2013, respectively (Zhang et al., 2016). Coal-related emissions such as coal combustion and coke production have been the main sources of atmospheric PAHs in Taiyuan, especially in winter (Jiang et al., 2013; Li et al., 2016a; Zhang et al., 2016). Compared with previous studies (Fu et al., 2010; Li et al., 2016a; Zhang et al., 2016), few studies have quantitatively analyzed the PAH sources in both the gas and particulate phases in various seasons in Taiyuan, especially the contribution of coal combustion and coking in different seasons. The present work aimed to investigate the atmospheric PAH levels and partitioning in the particulate and gas phases, discuss the seasonal variation and influence of meteorological factors, assess PAH exposure and quantify the source apportionment of coal usage for PAHs by PMF. The results of this study will provide valuable insights into air pollution abatement for other coal energy-dependent cities, especially those in northern China.

2. Materials and methods

2.1. Sampling site

Taiyuan, the capital of Shanxi Province, is located at an east longitude of 111°30′–113°09′ and a north latitude of 37°27′–38°25′, with a population of 4.2 million and a land area of approximately 1500 km^2. The terrain of Taiyuan is similar to a dustpan surrounded by mountains in the west, north and east, and a valley plain in the south (Fig. 1). Located in the continental interior, Taiyuan belongs to a warm temperate zone with a continental monsoon climate and an annual mean temperature of 9.5 °C, with the high in summer (23.5 °C) and the low in winter (− 6.8 °C). The prevailing wind direction is southeast in summer and northwest in winter.

The sampling site was located on the roof of a 15-story office building northwest of Yingze Bridge (Fig. 1), which is the central urban area of Taiyuan. Factories (such as the Taiyuan heavy machinery group, Taiyuan coal gasification factory, and thermal power plant), heavy traffic lines (Binhe Road and Yingze Street), and residential areas are

Table 1
Sampling period and statistics of meteorological factors.

Season	Sampling period	Number of samples	T (°C)	Wind speed (m/s)
Summer	Aug 7, 2014, to Aug 25, 2014	16	24.2[a] (23–27)[b]	2.15 (0.83–4.44)
Autumn	Oct 2, 2014, to Oct 29, 2014	25	13.1 (8–19)	2.23 (1.39–5.00)
Winter	Dec 1, 2014, to Dec 25, 2014	21	− 4.6 (− 10 ~ − 1)	2.23 (0.83–5.00)
Spring	Apr 3, 2015, to Apr 25, 2015	21	9.1 (3–16)	3.21 (2.22–5.28)

[a] Mean value.
[b] Min-max.

located around the sampling site. As shown on the map, two thermal power plants that supply electricity, two heavy industrial plants that are responsible for the largest stainless steel production in the world and one of the largest heavy machinery factories in China are located in this urban area. Because of the pollution reduction enforced by administrational orders beginning in 2000, SO_2 and PM_{10} concentrations have decreased steadily but still exceed the second threshold value of the China National Air Quality standards (TYEPB, 2015).

2.2. Sampling

Samples of PAHs in the particulate and gas phases were collected on quartz fiber filters (QFFs, 8″ × 11″, Whatman Ltd., Buckinghamshire, U.K.) and polyurethane foam (PUF, length of 8.0 cm, diameter of 6.5 cm and density of 0.035 g/cm^3) by a high-volume air sampler at a flow rate of 1.05 m^3/min (TH-1000F, Wuhan Tianhong Intelligent Instrument Co., Wuhan, China) in summer, autumn, winter and spring during 2014–2015 (Table 1). The sampler was carefully checked and calibrated by a flow calibrator before use in each campaign. All QFFs were pre-baked at 450 °C for 4 h before sampling to remove carbonaceous residues. Before and after sampling, all QFFs were balanced at constant temperature (25 °C) and relative humidity (50%) for 24 h in a climate chamber (KBF-150, Binder, Germany). The PUF samples were pre-extracted with dichloromethane for 48 h in a Soxhlet extractor, dried under vacuum, and sealed in pre-cleaned compacting bags prior to use. At least one field-blank (completely sampling process without sampling) and one laboratory-blank (completely sampling process without sampling and transportation) QFF and PUF per season was also prepared during the sampling to demonstrate interferences. After sampling, the QFF and PUF samples were sealed and stored in a freezer at − 10 °C for further analysis. During the sampling period, meteorological data, including the ambient temperature, wind speed and direction, were recorded from the Weather Underground website (http://www.wunderground.com/).

2.3. Analysis procedures

Some details of the analytical methods were similar with a previous study (Li et al., 2016a). The QFF and PUF samples were ultrasonically extracted and Soxhlet extracted, respectively. Before extraction, four PAH surrogates, acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12 (Dr. Ehrenstorfer GmbH, Germany), were added to the extraction solvent. One-eighth of the QFF samples were placed in 50 ml beakers and extracted by ultrasonic agitation with 30 ml of hexane, 30 ml of dichloromethane, and 30 ml of dichloromethane/methanol (1:1 v/v). The extraction consisted of two such cycles at 30 min per cycle. The PUF samples were Soxhlet extracted with dichloromethane for 24 h. The combined organic extract, including the QFF and PUF extracts, was concentrated to 1 ml on a rotary evaporator and then cleaned by liquid-solid chromatography using silica gel-aluminum oxide column with 70 ml of 1:1 hexane/dichloromethane to remove interfering polar compounds. An internal standard of hexamethylbenzene was added before instrumental analysis. The samples were analyzed on a gas chromatograph (Agilent 7890) with a mass spectrometer detector (Agilent 5975C) in electron impact mode. Separation of the compounds was carried out on an HP-5 capillary column (50 m × 0.32 mm × 0.17 μm). Helium (chromatographic grade) was used as the carrier gas at a total flow rate of 24.2 ml/min. The pressure in the column was maintained at 22 psi. The temperature conditions were as follows: initial temperature of 65 °C, holding for 2 min, ramping from 5 °C to 290 °C, and holding for 20 min.

The PAHs were confirmed based on their retention time and abundance of quantification/confirmation ions compared to authentic PAHs standards. Fifteen priority PAHs were quantified using the response factors related to the respective internal standards based on a five-point calibration curve for the individual compounds. The fifteen target compounds in this study including acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz[*a*]anthracene (BAA), chrysene (CHR), benzo[*b*]fluoranthene (BBF), benzo[*k*]fluoranthene (BKF), benzo[*a*]pyrene (BAP), indeno[1,2,3-*cd*]pyrene (INP), dibenz[*a*,*h*]anthracene (DAH) and benzo[*ghi*]perylene (BGP). All data were subject to strict quality control procedures. After the similarly treated, almost all PAH species in both the field-blank and laboratory-blank QFF and PUF samples were below the method detection limit (MDL). The surrogate recoveries of ACE-d10, PHE-d10, CHR-d12 and PYR-d12 were 53 ± 25%, 84 ± 17%, 92 ± 13%, 90 ± 17% and 88 ± 14%, respectively. The method detection limit (MDL) of individual PAHs species was shown in Table S1. The results of a parallel experiment showed that the relative differences for individual PAHs in paired duplicate samples were all < 15%.

2.4. Source apportionment with PMF

The US EPA PMF 5.0 model was applied to explore the sources of PAHs in the present study. The detailed method description can be found in previous literature (Norris et al., 2014). Briefly, Eq. (1) illustrates j chemical species in the ith sample as the concentrations from p independent sources.

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{ki} + e_{ij} \tag{1}$$

where x_{ij} is the j_{th} species concentration measured in the i_{th} sample, g_{ik} is the species contribution of the k_{th} source to the i_{th} sample, f_{kj} is the j_{th} species fraction from the k_{th} source, e_{ij} is the residual for each sample/species, and p is the total number of independent sources (Paatero, 1997). Data below detection limit can be retained for use in the model with the associated uncertainty adjusted because PMF allows each data point to be individually weighted such that these data points have less influence on the solution than the measurements above the detection limit (Paatero, 1997; Paatero and Tapper, 1994). Based on these uncertainties (μ), the object function Q (Eq. (2)) allows the analyst to review the distribution for each species in order to evaluate the stability of the solution.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{\mu_{ij}} \right]^2 \tag{2}$$

For the PMF input, data values below the MDL (Table S1) were substituted with MDL/2. Uncertainties (Unc) were treated with the method in the guidebook of the US EPA PMF 5.0 (Norris et al., 2014). If the concentration is less than or equal to the MDL, the uncertainty is calculated as Unc = 5/6 × MDL; if the concentration is greater than the MDL provided, the calculation is Unc = $[(\text{Error Fraction} \times \text{concentration})^2 + (\text{MDL})^2]^{1/2}$. In this study, we use 20% as error fraction of each PAHs species as suggested (Gao et al., 2013).

During the PMF analysis, the model was run with different number of factors ranging from 3 to 7, and the optimum solution with 4 factors is most explainable (Q(robust) / Q(true) = 0.93 in particulate PAH solution with the run times of 16 and Q(robust) / Q(true) = 0.96 in total PAH solution with the run times of 14), which implies a better model fitting (Norris et al., 2014). By examining the observed versus predicted scatter plots, it was found that the correlation coefficients (R^2) for all species were larger than 0.92, indicating the species were simulated well. Bootstrap method was used to estimate the stability and uncertainty of the solutions with block size of 6, number of bootstraps of 100 and minimum correlation R value of 0.6. Fpeak rotation with Fpeak values between − 1.5 and 1.5 gave the optimum convergent results of the minimum Q robust (2137.9), Q true (2163.4) with Fpeak values of − 0.5 for particulate PAH solution and the minimum Q robust (4315.7), Q true (4462.4) with Fpeak values of 0.5 for total PAH solution. Then, the Fpeak rotational result was used as the original source analysis data. A time series of the daily contributions of the four sources for the particulate PAH and total PAHs were calculated by the matrix analysis with the data of profiles and contributions in Fpeak rotational result and residuals in base run result. By examining the observed versus predicted data of individual PAH concentration in each day, correlation coefficients (R^2) for all species were larger than 0.83 both in particulate PAH solution and total PAH solution indicating that most of the species simulated nicely.

3. Results and discussion

3.1. General levels of PAHs

Table 2 presents the PAH levels in the TSP and the gas phase in Taiyuan and other cities. The total PAH levels (gas plus particulate phase) varied from 26.60 to 3240.97 ng/m^3, with a mean of 840.69 ng/m^3. The PAH levels in this study exceeded those in the gas and particulate phase reported by Xia et al. (2013) and were much higher than those reported in $PM_{2.5}$ and PM_{10} (Fu et al., 2010; Li et al., 2016a; Li et al., 2014). Li et al. (2016a) reported PAH levels in $PM_{2.5}$ of 826.2 ng/m^3 in winter 2009, with 92.36% of the PAHs in the particulate phase. As illustrated in Table 2, the mean total PAH concentration in Taiyuan was similar to that in Xi'an (a city in northwest China, Wei et al., 2015) and multiple cities in the North China Plain (region with serious haze pollution in China, Liu et al., 2008) and higher than that in Singapore (coastal city, He and Balasubramanian, 2009), Harbin (city in northeastern China, Ma et al., 2010), Beijing (sampled after the Olympic Games, Ma et al., 2011; vertical PAH distribution, Tao et al., 2007), Guangzhou (coastal city in northern China, Li et al., 2006), Ningbo (coastal city in southeastern China, Liu et al., 2014), Agra (a famous tourist city in Inida, Masih et al., 2012), Lumbini (a rural site in Nepal in Indo–Gangetic Plain, Chen et al., 2016) and multiple cities in China, Japan, South Korea, Vietnam and India (Hong et al., 2016). While the PAHs in particulate phase in Taiyuan was also higher than that in Xi'an and Guangzhou (two Chinese megacities, Ren et al., 2017), Guiyang (a city in southwest China with huge coal consumption, Hu et al., 2012). Similar to cities with pillar industries of energy, metallurgy and machinery in the North China Plain, heavy PAH pollution in Taiyuan comes primarily from industrial and domestic coal combustion and vehicle emissions (Liu et al., 2008; Ren et al., 2017).

The mean concentration of total PAHs was 463.95 ng/m^3 in the gas phase, with a range of 7.8–1772.85 ng/m^3, and 376.74 ng/m^3 in the particulate phase, with a range of 11.53–1772.83 ng/m^3. The main species of PAHs were PHE (186.86 ng/m^3), FLU (113.93 ng/m^3) and ACY (56.97 ng/m^3) in the gas phase and FLA (78.50 ng/m^3), PYR (54.82 ng/m^3) and CHR (38.80 ng/m^3) in the particulate phase (Fig. S1). Because of the physical properties and exchange of individual PAH compounds, significant compositional differences were found between the gas and particulate phases (Fig. S1). ACY, ACE, FLU, PHE, ANT and FLA (low molecular weight PAHs) were the most abundant species in the gas phase, whereas high molecular weight PAHs, including PYR, BAA, CHR, BBF, BKF, BAP, INP, DAH and BGP, were predominant in the particulate phase. PAHs can be divided into five categories based on the number of rings and their physiochemical properties: 2-ring (ACY, ACE and FLU), 3-ring (PHE, ANT and FLA), 4-ring (PYR, BAA, CHR, BBF and

Table 2
PAH levels in the gas and particle phases in Taiyuan and other cities (ng/m^3).

Sampling site	Gas phase	Particle phase	Total	Note
Taiyuan	463.95	376.74	840.69	Year, this study
	269.42	75.13	344.55	Summer, this study
	366.18	232.72	598.90	Autumn, this study
	919.32	894.35	1813.67	Winter, this study
	251.22	260.39	511.61	Spring, this study
Taiyuan	82.3	126	208.3	Passive sampling, Xia et al., 2013
Singapore	29.3	4.3	33.5	He and Balasubramanian, 2009
Harbin	54	45	100	Ma et al., 2010
Beijing	118.7	104.1	222.8	Ma et al., 2011
Beijing	354	154	508	Tao et al., 2007
Guangzhou	313	23.7	337	Tan et al., 2006
Ningbo	32.4	12.9	45.3	Liu et al., 2014
Xi'an (March)	621.6	107.0	728.6	Wei et al., 2015
Multiple cities in the North China Plain	584	267	752	Liu et al., 2008
Agra, India (Winter)			435.04[a]	Masih et al., 2012
Agra, India (Summer)			325.54[a]	
Lumbini, Nepal			94.48	Chen et al., 2016
Multiple cities in China			115	Hong et al., 2016
Multiple cities in Japan			5.76	
Multiple cities in South Korea			19.9	
Multiple cities in Vietnam			42.8	
Multiple cities in India			62.3	
Xi'an (Winter)		57		Ren et al., 2017
Xi'an (Summer)		6		
Guangzhou (Winter)		18		
Guangzhou (Summer)		2.8		
Guiyang		1.2–84.8		Hu et al., 2012

[a] The concentration of same compounds in this study.

BKF), 5-ring (BAP, INP and DAH) and 6-ring (BGP) (Tan et al., 2006). In the gas phase, PAHs with fewer rings (2–3 rings) accounted for 97.12% of the total PAHs, and PAHs with more rings (5–6 rings) accounted for 0.01–0.22% (Fig. S2). In the particulate phase, the 3-ring and 4-ring PAHs composed 33.25% and 46.23%, respectively, and 5–6-ring PAHs composed only 16.19% (Fig. S2). PAHs in the particulate phase accounted for 45.11% of the total PAHs, which was comparable to the proportions in Harbin (46.00%, Ma et al., 2010) and Beijing (46.72%, Ma et al., 2011) but higher than the proportions in Singapore (12.54%, He and Balasubramanian, 2009), Guangzhou (7.12%, Li et al., 2006), Ningbo (28.48%, Liu et al., 2014), Xi'an (14.69%, Wei et al., 2015) and the North China Plain (22.34%, Liu et al., 2008). Compared with coastal and warmer cities, the gas-particulate partitioning of PAHs in Taiyuan was mostly controlled by meteorological conditions (especially the air temperature), which will be analyzed in the next section.

3.2. *Meteorological influence*

Taiyuan has a typical temperate monsoon climate characterized by significant seasonal changes and decreased air temperature in winter. Emissions and meteorological conditions were the most important factors influencing the levels of atmospheric PAH pollution (Tan et al., 2006). The highest total PAH concentration was observed in winter (1813.67 ng/m^3), followed by autumn (598.90 ng/m^3), spring (511.61 ng/m^3) and summer (344.55 ng/m^3) (Fig. 2). A negative correlation coefficient was obtained between PAHs and the daily air temperature ($r = -0.72$, $p < 0.05$) (Fig. S3). The data published by the media showed that the monthly average coal consumption in the heating season was about 1.7 million tons in the urban area of Taiyuan in 2012, which was nearly double of that in the non-heating season (http://news.cnr.cn/gnxw/201201/t20120107_509027129.shtml). In winter, PAHs remained at high levels due to the increased strength of source emissions from coal combustion for indoor heating (e.g., thermal power plants and domestic heating) (Liu et al., 2008; Ma et al., 2010; Zhang et al., 2007; Ren et al., 2017; Zhang et al., 2016). In contrast, the higher temperatures in summer led to reduce coal combustion, especially residential usage. The PAH concentrations were 1813.67 ng/m^3, 558.99 ng/m^3 and 344.55 ng/m^3 at temperatures < 0 °C (all in winter), from 0 to 20 °C and above 20 °C (all in summer) (Fig. S3), respectively, similar to a previous study in which PAHs were much higher at air temperatures below 20 °C compared to above 20 °C (Tan et al., 2006). On the other hand, atmospheric PAHs, especially in particulate phase, would be effectively removed by wet deposition, which is considered as a significant regulator in cleaning the PAHs in atmosphere (Wang et al., 2010). Due to the warm temperate zone with a continental monsoon climate, warm and humid monsoon winds from the southeast could bring most of its annual precipitation in summer, which was also a reason of low level PAHs in summer in Taiyuan. At the same time, temperature inversion could block vertical atmospheric motion at lower temperatures and wind speeds, along with higher atmospheric pressure, and concentrate pollutants near the surface (Li et al., 2006). Reportedly, this near-surface temperature inversion has frequently occurred in winter in Taiyuan (Meng et al., 2007). For example, during two inversion periods of Dec 3–7 and Dec 24–25, 2014, the daily temperature decreased from − 8 to − 10 °C and − 2 to − 4 °C, respectively, and the wind speed decreased from 5.00 to 1.67 m/s and 1.39 to 0.83 m/s, respectively (Fig. 1). As the temperature and wind speed decreased, the PAH levels increased to 2811.45 and 3178.35 ng/m^3 in these periods, compared with the mean concentration of 1813.67 ng/m^3 in winter.

Subject to the dustpan topography, the prevailing wind directions in Taiyuan were to the northwest and southeast with a high wind speed (> 2 m/s) (Fig. 2a and b). When the wind direction was to the south, southeast and northeast, the PAH concentrations were higher (1296.88 ng/m^3, 1276.98 ng/m^3 and 1054.36 ng/m^3, respectively) compared to the other directions (Fig. 2c). The largest coke production base is located in the Fenhe Valley, including the JIE-XIAO-FEN coke production area (Fig. 1), where the coke production was > 70% of the total production in Shanxi and almost 20% of the Chinese total coke production. The wind from the southeast and south could carry coke-related air pollutants to Taiyuan, and regional transport might be an important explanation for the high PAH levels in all air samples. Back trajectory clusters were analyzed for the days of each fluctuation using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model for discussing the regional transport of PAH in four seasons. The result (Fig. S4) showed that the trajectories coming from the southwest along with the center of Taiyuan basin with relatively slower moving speed were the important cluster during the sampling time, especial in summer and winter. These air masses passed the regions of Qingxu, Jinzhong, Lvliang and Linfen—the main polluted and developing areas in Shanxi, which would take the pollutants to affect the PAH level in Taiyuan. Compared to the influence of the northeast wind (325.49 ng/m^3) in this study, the mean PAH concentration was greatly enhanced to > 2200 ng/m^3 under the influence of the southern wind in winter.

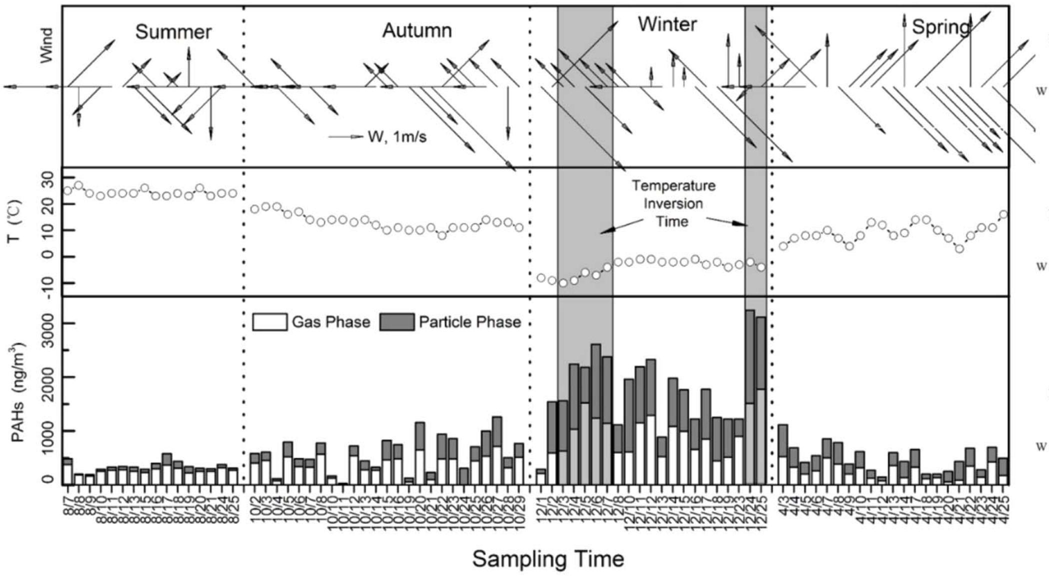

Fig. 2. Time series of the PAH distribution in the gas and particle phases, weather conditions, and wind rose map of the wind direction (%) (a), wind speed (m/s) (b) and PAH concentrations (ng/m^3) (c) during the sampling period.

PAHs had a good negative correlation with the wind speed classified as 0–1, 1–2, 2–3, 3–4, 4–5, and 5–6 m/s ($r = -0.88$, $p < 0.01$) (Fig. S5) (Lafontaine et al., 2015; Tan et al., 2006). The southern wind at low speed facilitated the accumulation of air pollutants and led to higher PAH levels in Taiyuan, whereas the north wind at high speed diluted the PAHs levels.

3.3. Phase partitioning

The gas–particulate partition coefficient is often calculated to evaluate the partitioning of PAH species between the gas and particulate phases. Pankow (1991) reported an Eq. (3) to parameterize gas/particulate partitioning.

$$K_P = (F/TSP)/A \tag{3}$$

where K_p ($m^3/\mu g$) is a partitioning constant; TSP ($\mu g/m^3$) is the TSP concentration; and F (ng/m^3) and A (ng/m^3) are the PAH concentrations in the gas and particulate phases, respectively. Eq. (4) was used to describe the equilibrium partitioning of semi-volatile organic compounds in the gas and particulate phases (Pankow, 1994).

$$\mathrm{Log}K_P = m_r \mathrm{Log}P_L^o + b_r \tag{4}$$

where $\log P_L{}^o$ is the sub-cooled liquid vapor pressure of the compound based on the temperature (Odabasi et al., 2006), and m_r and b_r are the slope and intercept of the linear equation.

In this study, seven individual PAHs, FLU, PHE, ANT, FLA, PYR, BAA and CHR, were chosen to calculate the slope of the linear relationship in the four seasons because these compounds were well distributed in both the particulate and gas phases. Fig. 3 shows a plot of the seasonal means of $\mathrm{Log}K_P$ against the temperature-dependent $\log P_L{}^o$ for these seven PAHs.

The selected individual PAHs were well correlated with each other in the four seasons ($r^2 = 0.76$–0.97, $p < 0.01$) (Fig. 3), indicating good data quality in this study. The seasonal m_r values decreased as spring > summer > -1 > winter > autumn because of the seasonal variation in gas-particulate partitioning of PAHs with low molecular mass, which agrees with the results obtained by Sofowote et al. (2010). Reportedly, the plot of $\mathrm{Log}K_P$ against $\log P_L{}^o$ is linear with a slope of m_r equal to -1 when the partitioning of SVOCs in the gas and particulate phases is in equilibrium (Pankow, 1987). The slopes of m_r in winter and autumn were closer to -1 than those in summer and spring, suggesting that the PAHs were well distributed between the gas and particulate phases in winter and autumn in contrast to in summer and spring. Mandalakis et al. (2002) reported that the distance away from the emission source and its strength influenced the equilibrium of some individual PAHs in the gas and particulate phases and that PAHs from fresh combustion stacks were not promptly mixed or distributed with the ambient air when the slope of the linear fit was greater than -1. The uneven phase partitioning indicates that atmospheric PAHs may be more influenced by the sources in the urban area and nearby areas in summer and spring than in other seasons.

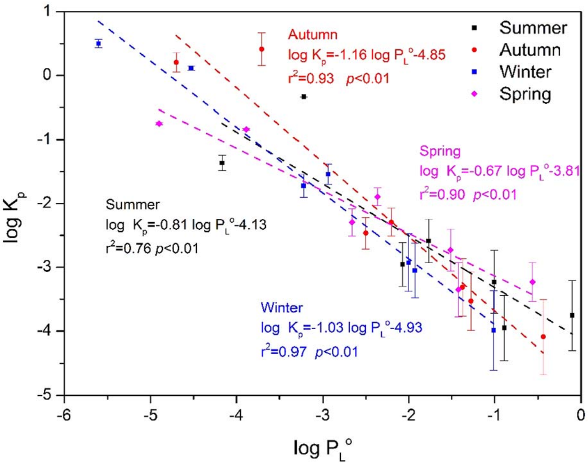

Fig. 3. Regressions of log K_P versus log $K_L{}^o$ for selected PAHs in the four seasons.

Furthermore, m_r could provide insights into the sorption process. Slopes steeper than -1 are characteristic of adsorption, and slopes shallower than -0.6 are suggestive of an absorption mechanism (Goss and Schwarzenbach, 1998). In this study, both absorption and adsorption mechanisms occurred in summer and spring because the slopes of the linear fit were between -0.6 and -1. In winter and autumn, an adsorption mechanism played a leading role because the slope was steeper than -1. Due to $PM_{2.5}$, with bigger specific surface area, takes a great proportion of TSP in Taiyuan, so adsorption mechanism could cause more SVOCs to absorb to particles, especially in $PM_{2.5}$, when an adsorption mechanism played a leading role during the phase partitioning (Li et al., 2016b; Goss and Schwarzenbach, 1998). That would lead PAHs were in higher abundance in winter and autumn than in summer and spring, which agrees with the seasonal variation in the PAH concentration.

3.4. Risk assessment

The BAP equivalent concentration (BEQ) was used to assess the carcinogenic risk of PAHs, and the toxic equivalency factors (TEFs) were obtained from previous studies (Table S2) (Malcolm and Dobson, 1994; Nisbet and LaGoy, 1992).

The BEQs of the PAHs in the gas and particulate phases were calculated according to Eq. (3):

$$BEQ_i = \sum_{i=1}^{n} C_i \times TEF_I \tag{3}$$

where C_i is the concentration of the individual PAH i in each sample and TEF_i is the TEF of the individual PAH i. The carcinogenic risk of the 15 PAHs was calculated as the sum of the individual BEQs.

During the sampling time, the BEQ was 28.96 ng/m^3 overall and 0.63 and 28.33 ng/m^3 in the gas and particulate phases, respectively. The seasonal values decreased as follows: winter (73.66 ng/m^3) > autumn (18.94 ng/m^3) > spring (17.16 ng/m^3) > summer (6.06 ng/m^3) (Fig. 4), which were all higher than the limit of the Chinese national standard (2.5 ng/m^3, GB 3095—2012). BEQ in Taiyuan was higher than many domestic and overseas cities of China, such as Kumasi in Xiamen (1.12–2.02 ng/m^3, Hong et al., 2015), Guangzhou (2.87 ng/m^3, Gao et al., 2015), and multi-cities in China (7.79 ng/m^3), Japan (0.288 ng/m^3), South Korea (1.21 ng/m^3), Vietnam (4.44 ng/m^3) and India (5.79 ng/m^3) (Hong et al., 2016). BAP, the PAH with the highest carcinogenic risk, contributed to 26.10% of the BEQ in summer, 60.78% in autumn, 60.46% in winter and 47.06% in spring. The daily BEQ was negatively correlated with the wind speed in summer ($r = -0.54$, $p < 0.05$) and winter ($r = -0.65$, $p < 0.05$) and negatively correlated with the temperature in autumn ($r = -0.45$, $p < 0.05$). Windless weather could increase the health risk posed by atmospheric PAHs in summer and winter, and wind could decrease this risk. Although a large fraction of the measured total PAHs consisted of low molecular weight species, which were mainly found in the gas phase, the BEQ of the PAHs in particulate phase was much higher because of the higher toxicities (manifested as higher TEFs in this study) of the high molecular weight congeners, which dominated the particulate phase (Gao et al., 2015). The health risk was high in winter, especially in terms of the high molecular weight congeners. The highest BEQs, 2.33 and 154.52 ng/m^3 in the gas and particulate phases, respectively, occurred on December 24, 2014, with the highest level of the high molecular weight PAHs (including FLA, PYR, BAA, CHR, BBF, BKF, BAP, INP, DAH and BGP). To some extent, high PAH levels in the particulate phase often meant a higher BEQ; therefore, simple methods to moderate the inhalation of particulate (using masks, for

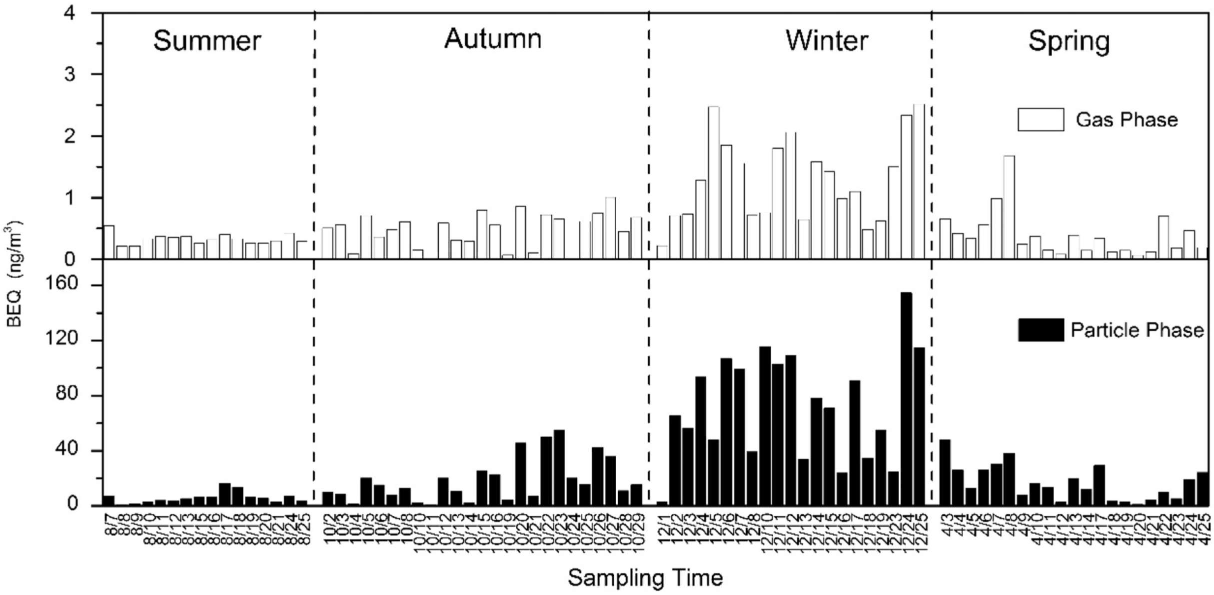

Fig. 4. BEQ in the gas and particle phases in the four seasons.

example) can substantially reduce the PAH exposure risk.

3.5. Source analysis

In this study, the sources of particulate PAHs and total PAHs (gas plus particulate phase) were analyzed by PMF 5.0. Four sources were identified in both the particulate PAHs and total PAHs (gas plus particulate phase): coal combustion, coke processing, vehicle emissions and biomass burning (Fig. 5).

The profile of factor 1 explained 41.99% of the particulate PAHs and 41.36% of the total PAHs, with FLU, PHE, ANT, FLA and BAA as the dominant species. Wang et al. (2009a) reported that FLU, PHE, ANT and FLA were the typical markers of coal combustion. Previous statistical data has indicated that the total coal consumption in Taiyuan in 2014 was 64.07 million tons, accounting for 20.00% of total province's coal consumption (Shanxi statistical yearbook, 2015). Withal, based on emission inventory, PAH emissions from coal combustion were approximately 81.3 t in Taiyuan, accounting for 43.28% of the total PAH emissions (Jiang et al., 2013), which agrees with the results in this study. Factor 2 was heavily loaded with BBF, BKF, INP and BGP

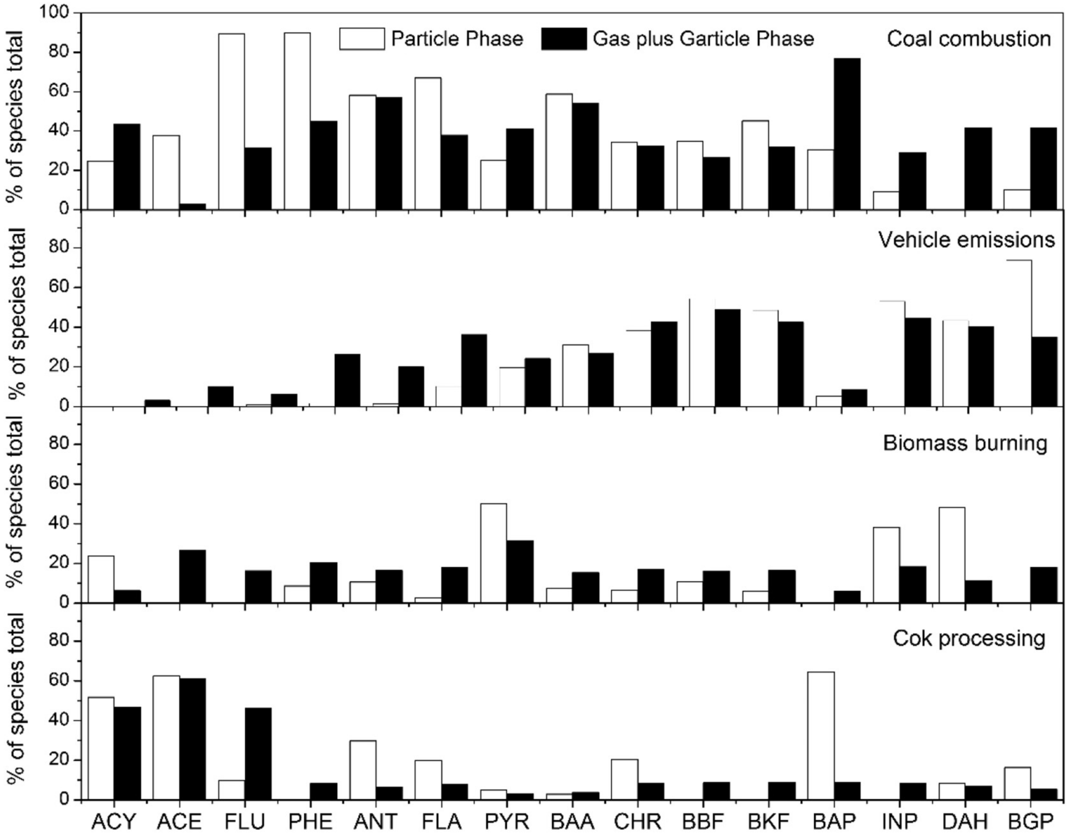

Fig. 5. Factor profiles of the individual sources.

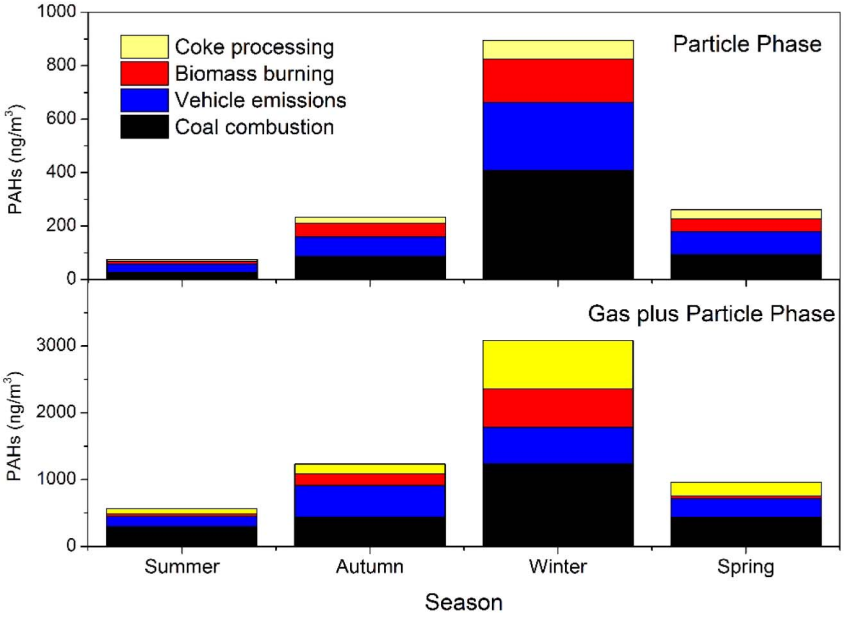

Fig. 6. Mass contributions of the four sources in the four seasons.

and explained 30.52% of the particulate PAHs and 24.75% of the total PAHs in Taiyuan. BBF, BKF, INP and BGP have often been used as tracers of liquid fossil fuel combustion (Harrison et al., 1996); therefore, factor 2 could be representative of vehicle emission. This representation is consistent with a previous study by Jiang et al., in which vehicle emissions were the third largest PAH source (Jiang et al., 2013). Factor 3 contributed 18.53% of the particulate PAHs and 14.18% of the total PAHs, with a high level of PYR, and could be considered as biomass burning (Wang et al., 2009b). This result agrees with the statistical results indicating that biomass burning, including firewood and straw burning, accounted for > 15% of the total PAH emissions (Jiang et al., 2013). Factor 4 accounted for 8.95% of the particulate PAHs and 19.71% of the total PAHs, with a high loading by ACY and ACE, which are tracers of the coke process (Mu et al., 2013; Wang et al., 2009a). This result was not unexpected since several coking industrial areas were located southwest of Taiyuan. Notably, the particulate PAH solution underestimated the contribution of the coke processing by 120.28% and overestimated the vehicle emission contribution by 18.92%, in contrast to the total PAH solution.

Fig. 6 shows the mass contribution of every source in the four seasons. Compared with the PAHs in particulate phase, the total PAHs better expressed the mass contribution of every source. The obvious difference was the contribution of the coke processing in winter, which was 7.73% and 23.62% to the particulate PAHs and total PAHs, respectively, because the major component in the stack gas from coke processing is low molecular weight PAHs (2–3 rings) (Mu et al., 2013). Li et al. (2016a) reported that coking was an important source of PAHs, with a contribution of 27.3% during winter in 2009–2013. The statistical data in Shanxi province showed that coking, an important industry of coal consumption rather than other industries, consumed about 119.71 billion tons coal in 2014, accounting for 37.34% of total province's coal consumption (Shanxi statistical yearbook, 2015). Although the main coke production was located in the Taiyuan basin, the regional transport of PAH from the northeast should affect pollution level of PAHs in Taiyuan (Li et al., 2016a). Therefore, the total PAH solution should be more realistic than the particulate PAHs solution.

Fig. 7 shows a time series of the daily contributions of the four sources to the total PAHs (gas plus particulate phase). Coal combustion was the major source of PAHs in every season due to high industrial and residential consumption in Taiyuan, which was also observed in many cities in northern China (Jiang et al., 2013; Liu et al., 2008; Ma et al., 2010). Biomass burning contributed 14.36% and 18.56% to the total PAHs in autumn and winter, respectively, which was much higher than the values in summer (5.75%) and spring (4.85%). Corn straw is often burned in the open air in September and October, and firewood is still used for heating in many rural areas in northern China in winter. The contribution of the coke processing was 23.62% in winter, much higher than in summer (14.62%) and autumn (11.58%). As mentioned above, the near-surface temperature inversion was a frequent occurrence in winter in Taiyuan. This would lead to the reduction of pollutants vertical diffusion, while the horizontal diffusion should be become the dominant way. At the same time, affected by the terrain of Taiyuan Basin, the south wind with low speed aided the diffusion and accumulation of coke-related air pollutants and resulted in the higher PAH levels in Taiyuan. The poor diffusion conditions, including weather and geographical conditions both in Taiyuan and nearby areas control regional atmospheric PAH accumulate, particularly in the winter. Based on a wind rose of the various PAH sources (Fig. 8), the southern, southeastern and southwestern source contribution of PAHs was approximately 2.85 times higher than the contributions from the other directions for the coke processing, 2.56 times for vehicle emissions, 2.03 times for coal combustion, and 2.02 times for biomass burning. The analysis of HYSPLIT in section 3.2 also showed that the trajectories from Taiyuan basin were the important cluster and the air mass moving could aggravate PAH pollution in Taiyuan. Combined with the dustpan terrain, the PAH levels in Taiyuan were easily influenced by the southern, southeastern and southwestern wind, and the coking industry is crucial to future air quality improvements in Taiyuan.

4. Conclusions

As a typical city in northern China, Taiyuan has suffered from heavy air pollution from excessive coal usage during the past 20 years. The total PAH (gas plus particulate phase) concentrations in Taiyuan in this work varied from 26.60 to 3240.97 ng/m^3, with a mean of 840.69 ng/m^3. PAHs in the particulate phase accounted for 45.11% of the total PAHs, which is substantially lower than those in gas phase for all samples. Compared with the main components of 2- and 3-ring PAHs in the gas phase, 3- and 4-ring PAHs composed 79.48% of total PAHs in the particulate phase, respectively. The highest PAH levels were observed in winter, followed by autumn, spring and summer. The daily

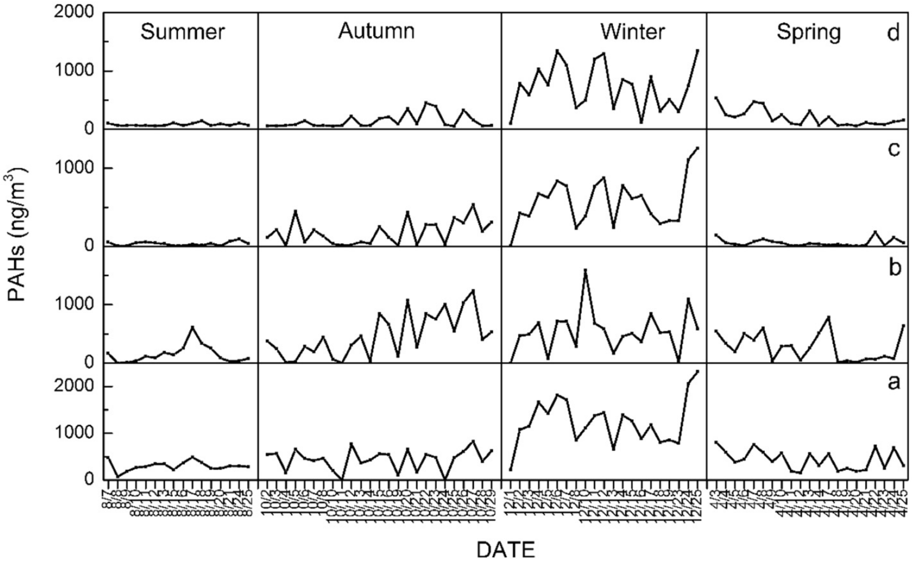

Fig. 7. Time series of the daily contributions of the four sources to PAH mass concentrations (a, coal combustion; b, vehicle emissions; c, biomass burning; d, coke processing).

PAH levels were negatively correlated with the air temperature and wind speed, and low air temperature and a southern wind with low speed often led to higher PAH levels in Taiyuan. Although smaller than a half fraction, the BEQ of particulate PAHs was almost equal to those of the total PAHs for the high molecular weight compounds were in the particulate phase and with higher TEFs. Four sources, coal combustion, vehicle emissions, coke processing and biomass burning, were determined by PMF, with contributions of 41.36%, 24.74%, 19.71% and 14.18% to the total PAHs in Taiyuan, respectively. Compared with the total PAHs, the particulate PAH solution underestimated the contribution of the coke processing and overestimated the vehicle emission contribution. Coal combustion was the major PAH source in the four seasons because of high industrial and residential consumption. The coke processing had a greater contribution to atmospheric PAHs in Taiyuan, especially in winter, because the low molecular weight PAHs (2–3 rings) are the major component of coking stack gas. In the end, the coke plants distributed in the Taiyuan-Linfen-Yuncheng basin and south Taiyuan should receive attention for air quality improvement in Taiyuan.

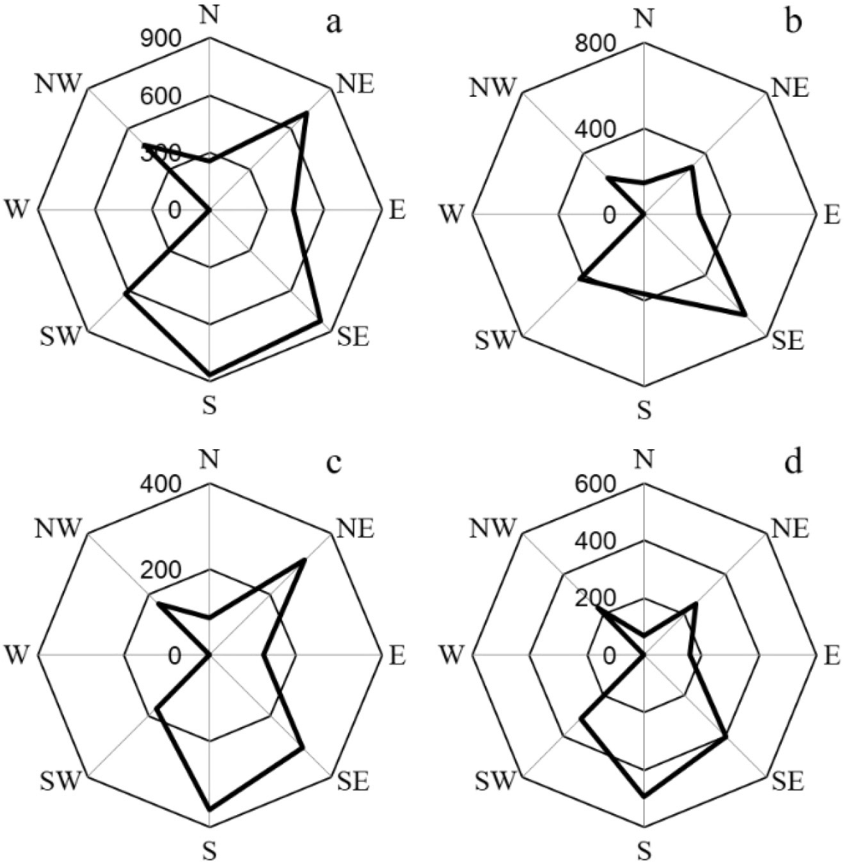

Fig. 8. Wind rose of the four PAH sources (ng/m^3) (a, coal combustion; b, vehicle emissions; c, biomass burning; d, coke processing).

Acknowledgments

This study was funded by the National Natural Science Foundation of China (nos. 41501543 and 41472311), the key project of the national Ministry of Education of China (no. 211026) and the Shanxi Province Science Foundation for Youths (2015021059). We gratefully acknowledge partial support from the One-hundred talent program supported by The Organization Department of Shanxi Province Committee.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.atmosres.2017.04.001.

References

Chen, P., Li, C., Kang, S., Yan, F., Zhang, Q., Ji, Z., Ji, Z., Tripathee, L., Rupakheti, D., Rupakheti, M., Qu, B., Sillanpää, M., 2016. Source apportionment of particle-bound polycyclic aromatic hydrocarbons in Lumbini, Nepal by using the positive matrix factorization receptor model. Atmos. Res. 182, 46–53.

Fu, S., Yang, Z., Li, K., Xu, X., 2010. Spatial characteristics and major sources of polycyclic aromatic hydrocarbons from soil and respirable particulate matter in a mega-city, China. Bull. Environ. Contam. Toxicol. 85, 15–21.

Gao, B., Guo, H., Wang, X., Zhao, X., Ling, Z.H., Zhang, Z., Liu, T., 2013. Tracer-based source apportionment of polycyclic aromatic hydrocarbons in $PM_{2.5}$, in Guangzhou, southern China, using positive matrix factorization (PMF). Environ. Sci. Pollut. Res. 20, 2398–2409.

Gao, B., Wang, X., Zhao, X., Ding, X., Fu, X., Zhang, Y., He, Q., Zhang, Z., Liu, T., Huang, Z.-Z., 2015. Source apportionment of atmospheric PAHs and their toxicity using PMF: impact of gas/particle partitioning. Atmos. Environ. 103, 114–120.

Goss, K.U., Schwarzenbach, R.P., 1998. Gas/solid and gas/liquid partitioning of organic compounds: critical evaluation of the interpretation of equilibrium constants. Environ. Sci. Technol. 32, 2025–2032.

Harrison, R.M., Smith, D., Luhana, L., 1996. Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. Environ. Sci. Technol. 30, 825–832.

He, J., Balasubramanian, R., 2009. A study of gas/particle partitioning of SVOCs in the tropical atmosphere of Southeast Asia. Atmos. Environ. 43, 4375–4383.

He, Q., Guo, W., Zhang, G., Yan, Y., Chen, L., 2015. Characteristics and seasonal variations of carbonaceous species in $PM_{2.5}$ in Taiyuan, China. Atmosphere 6, 850–862.

Hong, Y., Chen, J., Zhang, F., Zhang, H., Xu, L., Yin, L., Chen, Y., 2015. Effects of urbanization on gaseous and particulate polycyclic aromatic hydrocarbons and polychlorinated biphenyls in a coastal city, china: levels, sources, and health risks. Environ. Sci. Pollut. Res. 22, 14919–14931.

Hong, W., Jia, H., Ma, W.-L., Sinha, R.K., Moon, H.-B., Nakata, H., Minh, N.H., Chi, K.H., Li, W.-L., Kannan, K., 2016. Distribution, fate, inhalation exposure and lung cancer risk of atmospheric polycyclic aromatic hydrocarbons in some Asian countries. Environ. Sci. Technol. 50.

Hu, J., Liu, C., Zhang, G., Zhang, Y., 2012. Seasonal variation and source apportionment of PAHs in TSP in the atmosphere of Guiyang, Southwest China. Atmos. Res. 118, 271–279.

IARC, 1983. IARC monographs on the evaluation of carcinogenic risk of chemicals to man: polycyclic aromatic compounds. In: Part 1, Chemical and Environmental Data. vol. 32. World Health Organization, pp. 409.

Jiang, Q., Li, Y., Hu, X., Lu, B., Tao, S., Wang, R., 2013. Estimation of annual emission and distribution characteristics of polycyclic aromatic hydrocarbons(PAHs) in Taiyuan. China Environ. Sci. 33, 14–20.

Lafontaine, S., Schrlau, J., Butler, J., Jia, Y., Harper, B., Harris, S., Bramer, L.M., Waters, K.M., Harding, A., Simonich, S.L.M., 2015. Relative influence of trans-Pacific and regional atmospheric transport of PAHs in the Pacific Northwest, US. Environ. Sci. Technol. 49, 13807–13816.

Li, J., Zhang, G., Li, X., Qi, S., Liu, G., Peng, X., 2006. Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China. Sci. Total Environ. 355, 145–155.

Li, R., Kou, X., Geng, H., Dong, C., Cai, Z., 2014. Pollution characteristics of ambient $PM_{2.5}$-bound PAHs and NPAHs in a typical winter time period in Taiyuan. Chin. Chem. Lett. 25, 663–666.

Li, H., Guo, L., Cao, R., Gao, B., Yan, Y., He, Q., 2016a. A wintertime study of $PM_{2.5}$-bound polycyclic aromatic hydrocarbons in Taiyuan during 2009–2013: assessment of pollution control strategy in a typical basin region. Atmos. Environ. 404–414.

Li, W., Shen, G., Yuan, C., Wang, C., Shen, H., Jiang, H., Zhang, Y., Chen, Y., Su, S., Lin, N., Tao, S., 2016b. The gas/particle partitioning of nitro- and oxy-polycyclic aromatic hydrocarbons in the atmosphere of northern china. Atmos. Res. 172, 66–73.

Liu, S., Tao, S., Liu, W., Dou, H., Liu, Y., Zhao, J., Little, M.G., Tian, Z., Wang, J., Wang, L., 2008. Seasonal and spatial occurrence and distribution of atmospheric polycyclic aromatic hydrocarbons (PAHs) in rural and urban areas of the North Chinese Plain. Environ. Pollut. 156, 651–656.

Liu, D., Xu, Y., Chaemfa, C., Tian, C., Li, J., Luo, C., Zhang, G., 2014. Concentrations, seasonal variations, and outflow of atmospheric polycyclic aromatic hydrocarbons (PAHs) at Ningbo site, Eastern China. Atmos. Pollut. Res. 5, 203–209.

Ma, W., Li, Y., Qi, H., Sun, D., Liu, L., Wang, D., 2010. Seasonal variations of sources of polycyclic aromatic hydrocarbons (PAHs) to a northeastern urban city, China. Chemosphere 79, 441–447.

Ma, W., Sun, D., Shen, W., Yang, M., Qi, H., Liu, L., Shen, J., Li, Y., 2011. Atmospheric concentrations, sources and gas-particle partitioning of PAHs in Beijing after the 29th Olympic Games. Environ. Pollut. 159, 1794–1801.

Malcolm, H., Dobson, S., 1994. The calculation of the environmental assessment level (EAL) for atmospheric PAHs using relative potencies. In: Great Britain, Her Majesty's Inspectorate of Pollution, .

Mandalakis, M., Tsapakis, M., Tsoga, A., Stephanou, E.G., 2002. Gas–particle concentrations and distribution of aliphatic hydrocarbons, PAHs, PCBs and PCDD/Fs in the atmosphere of Athens (Greece). Atmos. Environ. 36, 4023–4035.

Masih, J., Singhvi, R., Taneja, A., Kumar, K., Masih, H., 2012. Gaseous/particulate bound polycyclic aromatic hydrocarbons (PAHs), seasonal variation in north central part of rural India. Sustain. City Soc. 3 (1), 30–36.

Meng, Z., Jiang, X., Yan, P., Lin, W., Zhang, H., Wang, Y., 2007. Characteristics and sources of $PM_{2.5}$ and carbonaceous species during winter in Taiyuan, China. Atmos. Environ. 41, 6901–6908.

Mu, L., Peng, L., Cao, J., He, Q., Li, F., Zhang, J., Liu, X., Bai, H., 2013. Emissions of polycyclic aromatic hydrocarbons from coking industries in China. Particuology 11, 86–93.

Nisbet, I.C., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300.

Norris, G., Duvall, R., Brown, S., Bai, S., 2014. EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide Prepared for the US Environmental Protection Agency Office of Research and Development, Washington, DC. DC EPA/600/R-14/108 .

Odabasi, M., Cetin, E., Sofuoglu, A., 2006. Determination of octanol–air partition coefficients and supercooled liquid vapor pressures of PAHs as a function of temperature: application to gas–particle partitioning in an urban atmosphere. Atmos. Environ. 40, 6615–6625.

Odabasi, M., Cetin, B., Bayram, A., 2015. Persistent organic pollutants (POPs) on fine and coarse atmospheric particles measured at two (urban and industrial) sites. Aerosol Air Qual. Res. 15 (5), 1894–1905.

Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. Chemom. Intell. Lab. Syst. 37, 23–35.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. Environmetrics 5, 111–126.

Pankow, J.F., 1987. Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. Atmos. Environ. 21, 2275–2283.

Pankow, J.F., 1991. Common y-intercept and single compound regressions of gas-particle partitioning data vs 1/T. Atmos. Environ. 25, 2229–2239.

Pankow, J.F., 1994. An absorption model of gas/particle partitioning of organic compounds in the atmosphere. Atmos. Environ. 28, 185–188.

Ren, Y., Zhou, B., Tao, J., Cao, J., Zhang, Z., Wu, C., Wang, J., Li, J., Zhang, L., Han, Y., Liu, L., Cao, C., Wang, G., 2017. Composition and size distribution of airborne particulate PAHs and oxygenated PAHs in two Chinese megacities. Atmos. Res. 183, 322–330.

Sehili, A.M., Lammel, G., 2007. Global fate and distribution of polycyclic aromatic hydrocarbons emitted from Europe and Russia. Atmos. Environ. 41, 8301–8315.

Shanxi statistical yearbook, 2015. China Statistical Publishing House, Beijing.

Sofowote, U.M., Hung, H., Rastogi, A.K., Westgate, J.N., Su, Y., Sverko, E., D'Sa, I., Roach, P., Fellin, P., McCarry, B.E., 2010. The gas/particle partitioning of polycyclic aromatic hydrocarbons collected at a sub-Arctic site in Canada. Atmos. Environ. 44, 4919–4926.

Tan, J., Bi, X., Duan, J., Rahn, K.A., Sheng, G., Fu, J., 2006. Seasonal variation of particulate polycyclic aromatic hydrocarbons associated with PM_{10} in Guangzhou, China. Atmos. Res. 80, 250–262.

Tao, S., Wang, Y., Wu, S., Liu, S., Dou, H., Liu, Y., Lang, C., Hu, F., Xing, B., 2007. Vertical distribution of polycyclic aromatic hydrocarbons in atmospheric boundary layer of Beijing in winter. Atmos. Environ. 41, 9594–9602.

TYEPB (Taiyuan Environment Protection Bureau), 2015. Real-time System of Atmospheric Environment Quality in Taiyuan .

USEPA, 1990. Clean Air Act, Sec 112: Hazardous Air Pollutants .

Wang, K., Shen, Y., Zhang, S., Ye, Y., Shen, Q., Hu, J., Wang, X., 2009a. Application of spatial analysis and multivariate analysis techniques in distribution and source study of polycyclic aromatic hydrocarbons in the topsoil of Beijing, China. Environ. Geol. 56, 1041–1050.

Wang, Z., Bi, X., Sheng, G., Fu, J., 2009b. Characterization of organic compounds and molecular tracers from biomass burning smoke in South China I: broad-leaf trees and shrubs. Atmos. Environ. 43, 3096–3102.

Wang, Y., Li, P., Li, H., Liu, X., Wang, W., 2010. Pahs distribution in precipitation at mount taishan: China. Identification of sources and meteorological influences. Atmos. Res. 95, 1–7.

Wei, C., Han, Y., Bandowe, B.A.M., Cao, J., Huang, R.-J., Ni, H., Tian, J., Wilcke, W., 2015. Occurrence, gas/particle partitioning and carcinogenic risk of polycyclic aromatic hydrocarbons and their oxygen and nitrogen containing derivatives in Xi'an, central China. Sci. Total Environ. 505, 814–822.

Xia, Z., Duan, X., Tao, S., Qiu, W., Liu, D., Wang, Y., Wei, S., Wang, B., Jiang, Q., Lu, B., 2013. Pollution level, inhalation exposure and lung cancer risk of ambient atmospheric polycyclic aromatic hydrocarbons (PAHs) in Taiyuan, China. Environ. Pollut. 173, 150–156.

Zhang, Y., Tao, S., Cao, J., Coveney, R.M., 2007. Emission of polycyclic aromatic hydrocarbons in China by county. Environ. Sci. Technol. 41, 683–687.

Zhang, M., Xie, J., Wang, Z., Zhao, L., Zhang, H., Li, M., 2016. Determination and source identification of priority polycyclic aromatic hydrocarbons in $PM_{2.5}$ in Taiyuan, China. Atmos. Res. 178-179, 401–414.