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Characteristics, sources and regional inter-transport of ambient volatile organic compounds in a city located downwind of several large coke production bases in China

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HIGHLIGHTS

- Benzene levels and B/T ratios were higher in Taiyuan than other cities.
- Coke production contributed about 1/3 to the atmospheric VOCs in Taiyuan.
- Different potential source regions were identified for each source.
- Over 70% air masses flowed out from Taiyuan to BTH region in spring and winter.

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ABSTRACT

Volatile organic compounds (VOCs) are important precursors of atmospheric ozone (O_3) and particulate matter (PM). Taiyuan, located downwind of several large coke production bases, is a heavily polluted city in China, with high concentrations of PM and increasing concentrations of ground-level O_3. In this study, 116 air samples were collected in four seasons of 2015 and analyzed for non-methane hydrocarbon and halocarbon species. The annual average concentration of the total VOCs (TVOCs) in Taiyuan was observed to be higher and slightly lower than that in Beijing and Shenzhen, respectively. High concentrations of benzene and a high benzene to toluene (B/T) ratio were the most evident features. TVOCs levels showed significant seasonal variations, increasing from spring (31.08 ppbv) to winter (67.33 ppbv). Although the concentrations of many air pollutants declined to a minimum, TVOCs continued to show high levels during the summer. Six sources were resolved using positive matrix factorization (PMF), and results indicated that coking processes was the largest contributor (32.56%) to ambient VOCs in Taiyuan, followed by coal and biomass combustion (23.25%).

In winter, the contributions of combustion sources and liquefied petroleum gas/natural gas/coalbed methane (LPG/NG/CBM) usage significantly increased compared with those in other seasons. The coking bases located upwind of Taiyuan in the southwestern and western directions were the major potential source regions of coking related VOCs, as indicated using the potential source contribution function (PSCF) analysis. More than 70%, 40% and 80% of the air masses were transported from Taiyuan to the Beijing-Tianjin-Hebei (BTH) region during spring, autumn and winter, respectively. This study indicated that the coke production bases in Shanxi should be listed as the key regions to address the air pollution problems throughout north China. In addition, the combustion source in Taiyuan was associated with high local emissions, while Hebei province located in the northeastern direction, Shaanxi and Inner Mongolia located in the northwestern direction were the potential sources of solvent and LPG/NG/CBM usage, respectively.

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1. Introduction

With rapid urbanization and industrialization, air pollution, characterized by high levels of fine particulate matter ($PM_{2.5}$) and O_3, has become a serious concern for environmental pollution in many cities and regions of China. The most evident phenomenon is the frequent occurrence of haze in winter and photochemical smog in summer (An et al., 2019; Wu and Xie, 2017). Volatile organic compounds (VOCs) in the atmosphere are important precursors to ground-level ozone and secondary organic aerosols (SOA). Therefore, they play an important role in the formation of regional haze and photochemical smog (Liu et al., 2016b; Jia et al., 2016). Recent studies have revealed that VOCs contributed ~25–30% of the $PM_{2.5}$ mass (via SOA production) in China (Yuan et al., 2013a; Huang et al., 2014). In addition, some VOCs, such as benzene, toluene, ethylbenzene, and 1,3-butadiene have been found to adversely affect human health, causing nose and throat irritation, asthma, leukemia, cancer, and even death (Liu et al., 2017; Li et al., 2017a; Yan et al., 2017). Globally, China is among the largest emitters of VOCs. The concentration of VOCs in China has increased at a rate of 2.3% per year from 1990 to 2010 (Xing et al., 2014). Thus, it has become critical to control the VOCs, and obtain clarity on the present pollution situation. To formulate efficient abatement strategies, sources and transport pathways need to be examined first.

Atmospheric VOCs have been globally measured in many urban areas (Salameh et al., 2016; Gaimoz et al., 2011; Waked et al., 2016). Furthermore, it has been observed that VOC emission, especially in areas with a low greening rate, is mainly caused by anthropogenic activities, such as exhaust gases from vehicles using gasoline, diesel or liquefied petroleum gas (LPG) as fuel, fuel evaporation and refueling emissions during fuel transfer and leakage, solvent evaporation during painting, printing and cleaning processes, coal and biomass burning, cooking, industrial emissions during coal coking, shoe making, and medicine and plastic producing (Lyu et al., 2016; He et al., 2015).

As the sources mostly depend on energy consumption levels, urban development, and industrial structures, they vary between different cities and regions. For example, in Chinese cities, vehicle emission was found to be the largest source of VOCs in Lanzhou (58.34%) (Jia et al., 2016), Hongkong (48%) (Guo et al., 2011) and Wuhan (28%) (Lyu et al., 2016), whereas, industry was found as the largest contributor in Ningbo (35.64%) (Mo et al., 2017) and Shanghai (36%) (Cai et al., 2010), gasoline exhaust contributed the most in Beijing (32–46%) (Wu et al., 2016c), solvent use was the major source in the pearl river delta (PRD) region (46%) (Guo et al., 2011), and coal combustion and vehicle emissions were found as the two largest contributors in Shuozhou (29.98% and 21.25%, respectively) (Yan et al., 2017). In addition, the source characteristics exhibited significant seasonal variations. For example, in Beijing, transportation-related sources (32–46%), paint and solvent use and industry (18–30%) were found to be the major sources of atmospheric VOCs in summer (Wang et al., 2015; Li et al., 2016a), while vehicle exhaust (26–39%) and coal combustion (35–41%) were found to be the dominant sources in winter (Wang et al., 2013). In Ningbo, liquefied petroleum gas and fuel and tank evaporation contributed more in summer and autumn, while chemical and paint industries were found as the main contributors in spring and winter (Mo et al., 2017).

Although few studies reported the contribution of coke production, it has been found as the main source of VOCs emissions in China, constituting more than 10% of the total industrial VOCs emissions (Wu et al., 2016b). China is known as the largest coke producer globally, accounting for more than 70% of the global production (NSBC, 2017), while Shanxi Province is known as the largest coke producing province of China, accounting for 40% of the total coke production and 60% of total coke export in China (He et al., 2015). Coke producing industries in Shanxi are mainly located in the middle basin areas, which include Taiyuan, Linfen, and Yuncheng basins (Fig. 1). These areas are not only the VOCs emission hotspots in the emission inventory of China (Wu et al., 2016b; Wu and Xie, 2017), but also the high-incidence areas for haze as coking is a polluting industry (Zhang et al., 2012). As the northernmost city of Taiyuan Basin and the capital city of Shanxi province, Taiyuan has had poor air quality for a considerable period due to rapid urbanization, economic growth, and inflow of air pollutants from the coking industry gathered regions. Based on the results of on-line monitoring, the annual above standard days of 24-h averaged $PM_{2.5}$ concentration in Taiyuan exceeded 100 days in 2014, with the maximum value being approximately 220 μg/m^3. High concentrations of polycyclic aromatic hydrocarbons (PAHs) and water-soluble ions have also been frequently reported in Taiyuan (Xia et al., 2013; Li et al., 2016b; He et al., 2017).

With a severe atmospheric pollution problem, Taiyuan is considered to be one of the important regional sources of air pollutants in the Beijing-Tianjin-Hebei (BTH) region, the political center of China with the most serious haze pollution. Most previous studies have focused on the effects of other cities or areas on the VOCs in the studied city, based on backward trajectories and potential source contribution function (PSCF) models (Liu et al., 2016a; Yuan et al., 2013a). However, outflow pathways and the influence of VOCs in the studied area on surrounding areas have scarcely been discussed. Improved knowledge about these aspects helps to assess the effects of VOCs in the targeted areas. Furthermore, very few studies have been conducted on ambient VOCs in Taiyuan. Additionally, their source structure and seasonal variation characteristics, as well as air mass transport pathways have not been examined.

To address these gaps and provide scientific knowledge for policy making, a campaign was carried out in Taiyuan to measure 49 VOC species. Pollution levels and seasonal variation characteristics of the VOCs were analyzed. Subsequently, positive matrix factorization (PMF) and PSCF models were prepared to identify the main sources of VOCs and potential source areas. Finally, HYSPLIT model was used to study the outflow pathways from Taiyuan to surrounding regions in different seasons. The PMF model is one of the most favorable methods to study the contributions of the sources of VOCs in urban areas, as only ambient data is required, and the factor profiles extracted by it were found to most closely represent the main sources used to generate the simulated data compared with other receptor models (Miller et al., 2002). As no prior knowledge regarding the number and exact sources is available, the factor profiles extracted by PMF need to be interpreted by the user based on the measured source profile information and general knowledge about the local sources (Baudic et al., 2016). Considering that the reported source profiles of the coking process are significantly limited

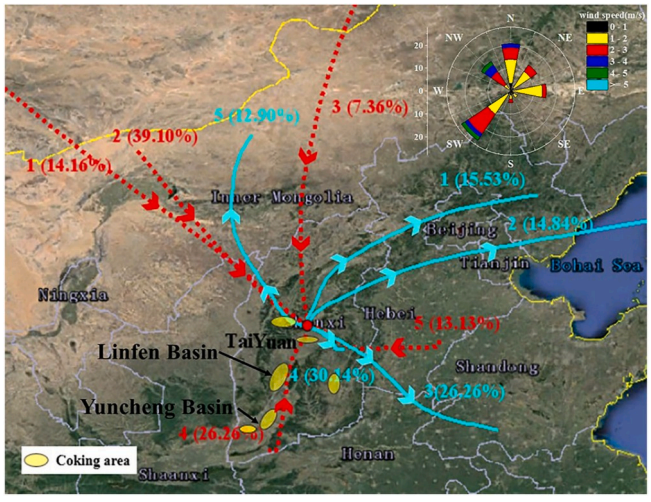

Fig. 1. Location of (a) the sampling site, coking area distribution (yellow area), 48-h backward (red), forward trajectories (cyan) and (b) wind condition in Taiyuan, China. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

with large differences, additional measurements from a coking plant were collected in this study to strengthen the identification of VOC profiles derived from PMF simulations.

2. Measurement and method

2.1. Sampling site

Taiyuan is the capital of Shanxi province in China, with a population of 4.2 million, 1.57 million motor vehicles, and a land area of approximately 1500 km^2. The terrain and climate are described by Li et al. (2016b). Briefly, Taiyuan is located in a valley-basin surrounded by mountain ridges on three sides, with a broad opening in the south. Semi-closed topography of the region makes the wind circulation difficult, causing frequent thermal inversions and pollutant stagnation. More than 60.34% of the winds flowing through the region have been noted to have a speed of less than 2 m/s. Most frequently, winds flow from west and southwest (Fig. 1), accounting for 34.48% of the total winds flowing through the region. Along the wind trajectories in these two directions, many large coking bases are also located, as shown in Fig. 1, which directly threaten the air quality of Taiyuan. In our previous study, we found that the wind speed from south to west exhibited positive correlation with coking sourced $PM_{2.5}$-PAHs level in Taiyuan (Li et al., 2016b). As an old industrialized city, several large factories continue to function here, including two thermal power plants, which generate electricity and heating supply, and two large heavy industrial plants, which produce stainless steel and heavy machinery with a continuous highest production in China and globally, despite many industries having been moved out in recent years. Furthermore, Taiyuan has a low greening rate, with approximately 30% vegetation cover due to low precipitation (approximately 527.89 mm yr^{-1} in 2018).

The sampling site was located on the roof of a 16-floor building of Taiyuan University of Science and Technology (37.88°N,112.50°E), approximately 50 m above ground (Fig. 1). Samples were collected from April 13 to 26 (spring), July 22 to 28, August 04 to 10 (summer), October 10 to 23 (autumn), and December 14 to 31 (winter) in 2015. Two samples were collected each day. The daytime and nighttime sampling times were 12:00–14:00 and 22:00–24:00, respectively. As a result, 28, 28, 24 and 36 samples were collected during spring, summer, autumn and winter, respectively.

2.2. Sampling, analysis, and quality assurance/quality control

The sampling canisters were cleaned and checked following the procedures mentioned in our previous studies (Li et al., 2017b). In brief, after the cleaning procedure, all vacuumed canisters were refilled with humidified zero air and afterwards stored in a laboratory for at least 24 h. Subsequently, they were analyzed using the same methods as the field samples. A canister was labeled clean, if all the target VOCs were found to be absent. During sampling, a restrictor valve (39-RS-x; Entech Instruments; 2207 Agate CT. Simi Valley, CA) was used to block the entry of dust and fine particles in the canister and to slowly fill the canister within approximately 2 h. Meteorological data (ambient temperature, pressure, relative humidity, wind speed and direction) and concentrations of SO_2, CO, NO_2, O_3, and PM were recorded during sampling from the meteorological information network of Shanxi province (http://www.sxqx.gov.cn/). The data for planetary boundary layer (PBL) height was obtained from Air Resources Laboratory of National Oceanic and Atmospheric Administration (NOAA) website (http://ready.arl.noaa. gov/READYamet.php).

After sampling, 300 mL of the sample was concentrated in a Entech 7100A preconcentrator (Entech Inc.,USA), where a three-stage preconcentration was carried out to remove water, carbon dioxide, nitrogen and oxygen. Afterwards, the sample was injected into the GC-FID/MS system (Agilent 7890A/5975C, USA), having dual capillary columns connected to different detectors. Subsequently, the C2-C4 VOCs were separated on a PLOT-Q column (30 m × 0.32 mm × 2.0 mm, Agilent Technology, USA) and quantified using FID, while the C4-C12 compounds (including hydrocarbons, oxygenated VOCs), halocarbons and other species) were separated on a nonpolar column (50 cm × 0.15 mm (I.D)) and detected using quadrupole MSD.

C2-C4 and C4-C12 compounds were quantified using external standard methods. Standard gases (Photochemical Assessment Monitoring Stations (PAMS) and TO-15) were used for calibration and verification of the equipment using the five-point method every two weeks (0.5, 1, 5, 15 and 30 ppbv), and linearity (R^2) of the calibration curves for all VOCs was kept higher than 0.99 to assure the quality of the analyzed data. In our study, the concentration response (peak area) correlation coefficients were 0.991–0.999. Routine calibration was operated every day using a calibration gas, with a mixing ratio of 10 ppbv. If the response was observed to be higher than ±10% of the initial calibration curve, recalibration was performed. The measurement precision was determined through seven repeated analysis of a standard mixture (1 ppbv), and controlled within 5%. The method detection limits (MDLs) of the analytical system ranged from 0.01 ppbv (tetrachloroethylene) to 0.69 ppbv (ethylene).

2.3. Source apportionment

PMF 5.0 software provided by the U.S. EPA was used for source apportionment in this study. Its detailed principles and applications were described in the user guide (U.S. EPA, 2014) as well as in other studies (Wu et al., 2016a; Shao et al., 2016; Dumanoglu et al., 2014). Receptor concentrations (C), with values below the MDL remained unchanged, and uncertainty (Unc) was calculated as follows: Unc = 5/6 × MDL. Uncertainties for other data were calculated using the following equation: $Unc = [(Error\ Fraction \times concentration)^2 + (MDL)^2]^{1/2}$. Furthermore, the error fraction was suggested as 20% by Hailin et al. (2018).

To determine the optimal number of sources, three to seven factors were examined. Eventually, six factors were identified in this study. The optimal number of factors (p) was achieved based on the closeness of Q (robust) and Q (true) to Q (theoretical). Q (theoretical) = n × m – p × (n + m), where n = number of samples, m = number of species, and p = number of factors. In the selected base run solutions, Q (theoretical), Q (robust), and Q (true) were 2604, 2637.8, and 2638.2, respectively. An optimum solution was determined based on both a good fit to the data and the most reasonable result. Most scaled residuals were observed to be mostly normally distributed in the range of +3 and - 3. The correlation between the model fitting and actual sample concentrations was observed to be 0.90 with the slope as 1.08 (see Fig. S1), indicating a good model fit.

2.4. Air mass transport trajectory analysis

In this study, 48 h of backward and forward trajectories were calculated four times a day at starting times of 00:00, 06:00, 12:00 and 18:00 LT, for each sampling day using reanalysis data from National Centers for Environmental Prediction. The calculation was performed using MeteoInfo-TrajStat. The starting location was the sampling site at an elevation of 100 m above ground level. Then, the trajectories in one season or the whole year were clustered into groups with similar geographic origins and histories. Each group, hereafter, was represented by its mean trajectory. The detailed principles and methods were similar to those reported by Squizzato and Masiol (2015).

2.5. Estimation of potential source locations of VOCs

PSCF, a conditional probability function, was used to calculate and describe possible source locations using back trajectories and composition-values (Liu et al., 2016a). Backward trajectories were calculated using the same method as that described in section 2.4, with

the time interval as 1h. The composition-value referred to the source contributions resolved by the PMF model. The computation of PSCF value also performed using MeteoInfo-TrajStat.

To calculate the PSCF, geographic region covered by the trajectories was divided into an array of 0.5° × 0.5° grid cells. The location function is denoted by cell indices i and j. Number of trajectories passing through the ijth cell is denoted by n_{ij}. Number of trajectories resulting in a source contribution, exceeding the 75th percentile is denoted by m_{ij}. The probability that any given cell can be related to the enhanced source contribution is expressed as $PSCF_{ij} = m_{ij}/n_{ij}$ (Zhu et al., 2017). Cells with high values of PSCF were considered as the potential source areas. To reduce the effect of small values of n_{ij}, the PSCF values were multiplied by an arbitrary weight function W(ij) to better reflect the uncertainty in the values for these cells. Here, W(ij) was defined as follows (Liu et al., 2016a):

$$WPSCF_{ij} = \frac{m_{ij}}{n_{ij}} \times W(ij)$$

$$W(ij) = W(ij) = \begin{cases} 1.00 & 80 < n_{ij} \\ 0.70 & 20 < n_{ij} \leq 80 \\ 0.40 & 10 < n_{ij} \leq 20 \\ 0.20 & n_{ij} < 10 \end{cases}$$

3. Results and discussions

3.1. General levels of VOCs

The annual average mixing ratio of the ambient VOCs in Taiyuan during the observation period was found to be 38.43 ppbv (Table S1). Among the measured VOCs, alkanes, alkenes, aromatics, halocarbons and acetylene accounted for 47.20% (18.14 ppbv), 15.06% (5.79 ppbv), 22.14% (8.51 ppbv), 4.63% (1.78 ppbv) and 10.40% (4.00 ppbv) of the total VOCs (TVOCs), respectively. Table S1 also provided the concentration of methyl tertiary butyl ethe (MTBE) (0.21 ppbv), an important source marker of traffic exhaust, contributed only 0.56% to the TVOCs.

Total concentration of 15 species listed in Table 1, which represented those having common concerns for the atmosphere, was observed to be significantly higher than that reported for Jinan (20.69 ppbv) (Liu et al., 2016b), Wuhan (19.90 ppbv) (Lyu et al., 2016), Shanghai (23.88 ppbv) (Cai et al., 2010), Nagoya (23.14 ppbv) (Saito et al., 2009) and London (22.17 ppbv) (Schneidemesser et al., 2010), similar to that reported for the urban areas of Beijing (Zhang et al., 2017), and slightly lower than that reported for Shenzhen (42.39 ppbv) (Zhu et al., 2012). Concentrations of benzene and acetylene in Taiyuan were found to be higher than those reported for other cities, which may have resulted from large quantity of coal-burning and coking production activities in local and surrounding regions. Furthermore, N-butane, isobutane and 1-butene, considered to be good tracers for LPG (Song et al., 2007), were also observed to have higher values among the compared cities, except Shenzhen, where LPG has a large contribution. Moreover, the concentration of isopentane, a typical indicator of vehicle exhaust and gasoline evaporation (Cai et al., 2010; Yuan et al., 2013b), was observed to be lower than that reported for other cities at home and abroad, due to relatively low traffic flow density in Taiyuan. Compared with the cities of PRD and Yangtze river delta (YRD) regions of China, such as Shenzhen and Shanghai, where many plastic and coating industries are located, the industrial emission-related compounds (such as toluene, ethylbenzene, and xylene) in Taiyuan were observed to be relatively lower due to different industrial structures.

3.2. Seasonal variations

Fig. 2 shows an overview of the temporal variations of VOCs, SO_2, CO, and PM concentrations as well as meteorological conditions present during the observation period. TVOCs were observed to demonstrate significant seasonal variation, increasing from spring to winter (spring, 31.08 ppbv; summer, 32.44 ppbv; autumn, 44.89 ppbv; and winter, 67.33 ppbv). This result was found to be similar to that of many other cities of China, such as Guangzhou, Wuhan and Lanzhou, where the mixing ratios of most VOCs were found to be higher in winter than in spring and summer (Yang et al., 2018; Zou et al., 2015; Jia et al., 2016). However, the result were observed to be different from Liu et al. (2016a, b) and Zhang et al. (2017), who reported VOCs concentrations were higher in autumn and lower in spring for Tianjin and Beijing. This was likely due to variations in ambient temperature, sunlight, meteorological factors, and different emission-strength of atmospheric pollutants.

Table 1
Comparison of selected VOCs concentration (ppbv) in different urban areas, ppbv.

VOCs	Taiyuan (This study)	Beijing[a]	Jinan[b]	Shenzhen[c]	Shanghai[d]	Wuhan[e]	Nagoya Japan[f]	London UK[g]
	201504-201512	201404-201501	201006-201205	201002-201102	200701-201003	201302-201410	201312-201411	the year 2008
ethane	4.13 ± 2.94	4.90	1.54	NA	NA	5.20	3.86	7.10
propane	3.87 ± 2.67	5.21	2.28	4.38	4.81	1.90	3.34	2.70
Isobutane	3.04 ± 5.18	1.46	2.08	4.08	1.43	1.10	1.40	1.20
n-Butane	2.43 ± 3.08	2.19	1.24	2.84	2.03	1.30	2.64	2.00
Isopentane	1.10 ± 0.88	0.07	1.30	2.05	2.29	1.00	1.33	1.60
n-pentane	0.74 ± 0.64	0.55	0.37	4.55	NA	0.50	0.68	0.54
Ethylene	3.02 ± 2.70	5.98	0.32	NA	NA	3.30	2.79	2.40
propene	1.00 ± 1.22	2.06	0.20	1.8	0.84	0.50	0.65	0.71
1-Butene	0.88 ± 1.28	0.21	0.15	0.68	0.26	0.30	0.21	0.17
Benzene	2.20 ± 2.65	1.43	2.04	2.23	1.81	1.70	0.47	0.32
Toluene	1.26 ± 1.51	1.83	2.24	10.4	4.70	2.00	2.46	1.00
ethyl-benzene	1.01 ± 0.78	0.69	0.44	2.76	1.23	0.50	0.51	0.14
m/p-Xylene	2.23 ± 2.30	1.43	2.08	3.41	1.40	0.40	0.65	0.79
o-Xylene	0.76 ± 0.65	0.32	0.84	3.21	0.38	0.20	0.24	0.20
acetylene	4.00 ± 3.41	4.02	1.30	NA	2.70	NA	1.91	1.30
∑VOCs	31.67	32.34	20.69	42.39	23.88	19.90	23.14	22.17

NA, no data.
[a] Zhang et al. (2017).
[b] Liu et al. (2016b).
[c] Zhu et al. (2012).
[d] Cai et al. (2010).
[e] Lyu et al. (2016).
[f] Saito et al. (2009).
[g] Schneidemesser et al. (2010).

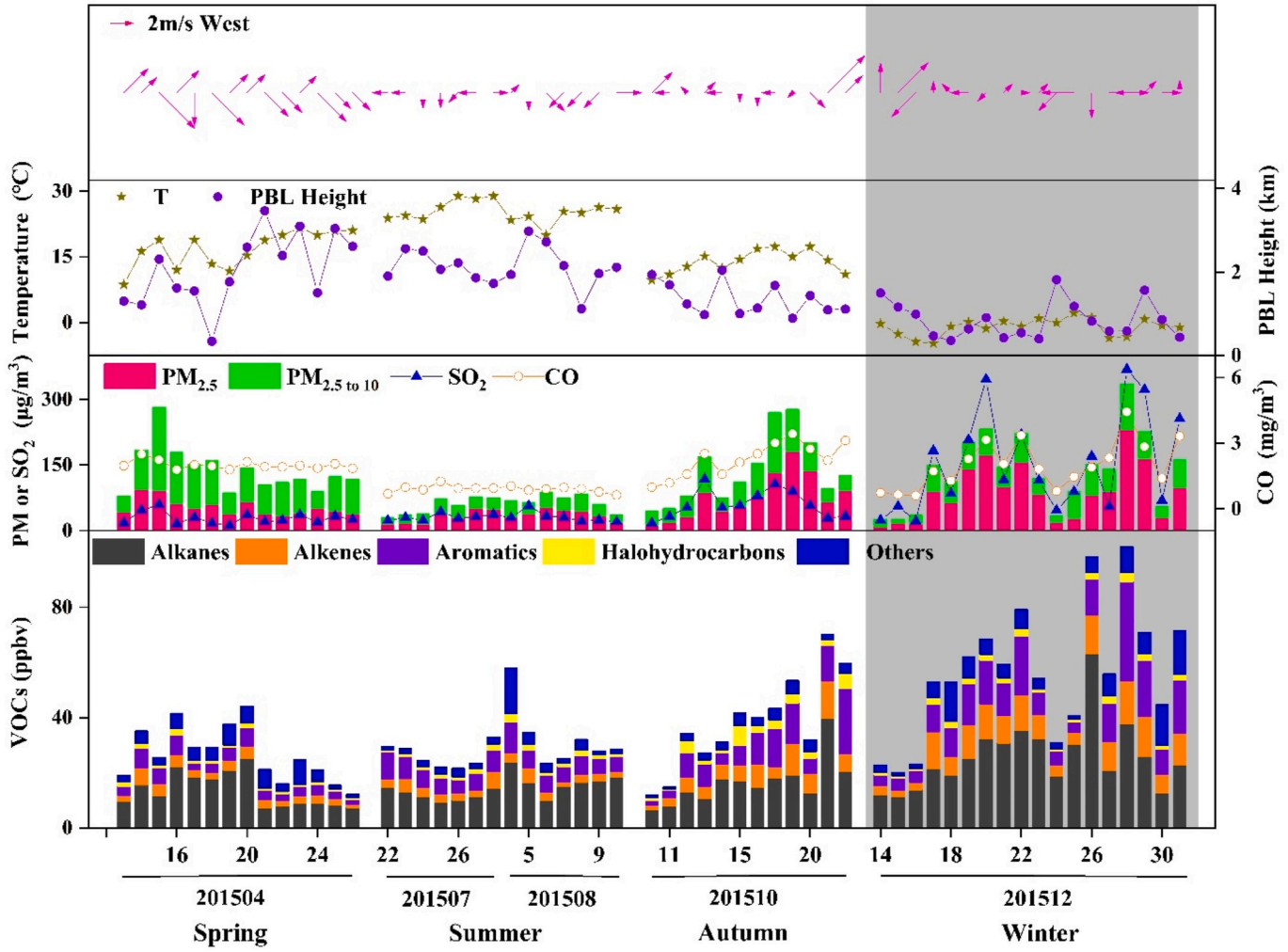

Fig. 2. Time series of the daily average mixing ratios of VOCs, inorganic gases (SO_2, CO, NO_2, O_3), PM and average levels of meteorological parameters (wind speed and direction, temperature and planetary boundary layer height (PBL)) during the sampling period in Taiyuan.

Further, variation trend of TVOCs was observed to be similar to that of the criteria pollutants SO_2, CO, and $PM_{2.5}$, with strong correlations (correlation coefficients r = 0.76, 0.67, 0.72, respectively) (Fig. S2). SO_2 mainly emitted from coal combustion, which was also an important source of CO and $PM_{2.5}$ emissions in North China. Our results indicated that coal combustion was a significant source of VOCs in Taiyuan.

During spring, the low concentration of VOCs could be attributed to a relatively low energy demand to some extent. Furthermore, wind played an important role in diffusing and diluting the VOCs. The average wind speed in spring was significantly higher than that in other seasons (2.62 m/s) (Fig. S3), with the dry and clean air flowing in from Mongolia and Siberia, along with the northwest wind.

During summer, the wind speed during the sampling period was observed to be relatively lower than that in other seasons (Fig. S3). However, the concentration of TVOCs was found to be significantly lower than that during autumn and winter. The first reason for this was the low coal-combustion related emissions, as indicated by the lowest levels of SO_2, CO, and PM during the summer. The second reason was the depth and instability of PBL during this season, which promoted the vertical diffusion of air pollutants. The third reason was the high temperature and strong UV irradiation in summer, which favored the oxidation of the VOCs (Zhang et al., 2016). Unexpectedly, no evident decrease was observed in the concentration of TVOCs in summer compared with that in spring, although significant declines were observed for SO_2, CO, and PM.

During autumn, concentrations of SO_2 and CO were observed to be significantly higher compared with those during spring and summer, indicating larger combustion-related emissions (Fig. 2). As a result, VOCs concentrations were also observed to significantly increase. This increase was mainly observed for alkenes, aromatics, and halocarbons. Previous studies have reported that biomass burning could release large amounts of C6-C8 aromatics and halocarbons, such as chloromethane (Baudic et al., 2016; Ling et al., 2011; Cai et al., 2010), and the harvest season falls in autumn. It can be observed from Fig. S4 that the number of fire hotspots significantly increased in this season in Shanxi. Therefore, increase in biomass burning activities may have resulted in the higher concentration of VOCs in autumn.

During winter, the concentration of TVOCs was observed to be significantly higher than that during other seasons, with the average value being as high as 67.33 ppbv. Main reason for this was the increase in VOCs emissions from coal combustion. Coal-fired heating is carried out in winters in most places of northern China, from November 1 to March 31 of the following year, during which large quantities of air pollutants, including VOCs, SO_2, CO, and $PM_{2.5}$ are emitted. Combined with weaker photochemical reactions, low height of the PBL, as well as the deep inversion layer, especially at night, enables the pollutants to always accumulate in the local regions (Zhang et al., 2016; Wu et al., 2016c). During stable weather, the concentration is considered to rapidly increase. Furthermore, for cities located in a basin, the effect is considered to be more evident, similar to Taiyuan. As shown in Fig. 2,

the TVOC concentration remained in the range of 23.50–25.91 ppbv, when the wind speed was greater than 3 m/s, during December 14 to 16. From December 16 to 22, the air pollutants were observed to rapidly accumulate, with the concentration of TVOCs tripling under low wind speed conditions. Furthermore, after December 22, the TVOC concentration was observed to again sharply reduce (34.33 ppbv), along with the increase in wind speed. After December 24, the meteorological conditions stabilized, wind speed decreased, and the concentration of TVOCs exceeded 100 ppbv and reached a maximum of 122.59 ppbv on December 28. This was observed to be comparable to the levels of the most seriously polluted cities in China, such as Lanzhou (Jia et al., 2016) and Beijing (Wang et al., 2013).

3.3. Source apportionment

3.3.1. Benzene to toluene (B/T) ratio analysis

Several studies have shown that the composition characteristics of VOCs released by one source were relatively stable and different from those of other sources (Jobson et al., 1999; Barletta et al., 2005). According to correlations and the characteristic ratios between the representative pollutants, the source of ambient VOCs can be crudely deduced. The benzene to toluene (B/T) ratio is the most widely used ratio to distinguish vehicle exhaust from other combustion sources as well as industrial processes (Perry and Gee, 1995). A B/T ratio higher than 1 implies a considerable influence from the combustion of biomass, charcoal, and coal on the receptor environment (Liu et al., 2008; Andreae and Merlet, 2001). A ratio of 0.3–0.7 suggests that the type of pollution is dominated by vehicle exhaust, and a ratio less than 0.2 indicates the dominance of industrial pollution (Brocco et al., 1997; Perry and Gee, 1995). In this study, seasonal averages of the B/T ratios estimated using the slopes of linear regression lines for spring, autumn, and winter were found to be higher than 1 (Fig. 3), indicating that coal and biomass combustion was the primary source in Taiyuan. Benzene exhibited strong correlation with toluene in autumn ($R^2 = 0.84$) and winter ($R^2 = 0.77$), and weak correlation in spring ($R^2 = 0.37$), which implied that benzene and toluene had similar sources in autumn and winter, while the sources were complex in spring for these. During summer, the B/T slope was 0.59. Although the value was very close to that of vehicle exhaust, it may not be the main source. Rather, the slope could be the result of a combination of several sources, because the correlation between benzene and toluene was very weak ($R^2 = 0.37$).

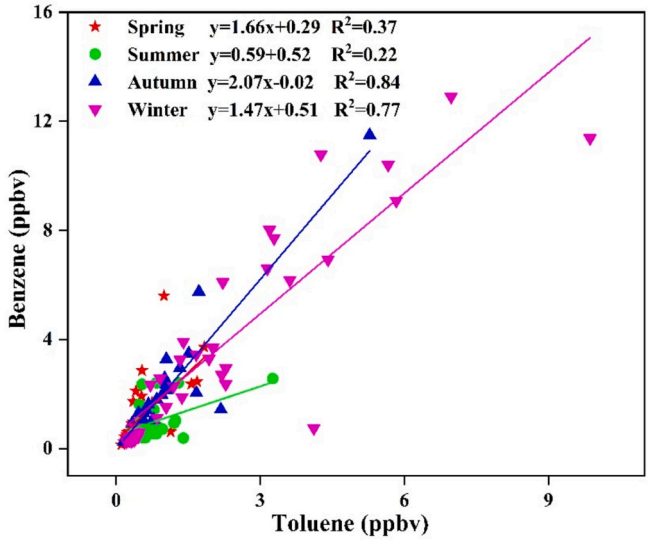

Fig. 3. Scatter plots of benzene to toluene at the sampling site with different colors representing different seasons. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.3.2. Source attribution by PMF and PSCF

To identify both pollution sources and their respective potential source areas in Taiyuan more accurately, the PMF5.0 model was used with PSCF model. In this study, six factors were resolved through PMF and were identified as coking process, liquefied petroleum gas/natural gas/coalbed methane (LPG/NG/CBM) usage, vehicle exhaust, combustion sources, industrial processes, and biogenic emissions (Fig. 4). The possible regions of their sources, explored through PSCF analysis, are shown in Fig. 5.

Factor 1 was labeled as the coking process, mainly because the factor profile, resolved using PMF (Fig. 4a), was found to be similar to the source profile of the coking process (Text S1 and Fig. S5) based on our local survey. Both profiles demonstrated high abundances of ethylene, ethane, propane, benzene, methyl chloride, and 1,2-dichloroethane, and very high B/T ratios. The PMF results showed that the coking process was the largest source of VOCs in Taiyuan, with a contribution of 32.56% to TVOCs (Fig. 4b). PSCF results showed that its main source areas were concentrated in the west and southwest direction of Taiyuan (Fig. 5a), which was found to be similar to the distribution of the coking areas shown in Fig. 1. Cluster analysis of backward trajectories indicated that 26.26% (Trajectory 4 in Fig. 1) of the air masses in Taiyuan were from the Yuncheng-Linfen-Jinzhong-Taiyuan pathway in the southwest direction, around which many coking industries were located. Therefore, this pathway was probably the major transport pathway of the coking process related pollutants to Taiyuan.

In factor 2, high percentages of low molecular weight compounds were found, especially n-butane, isobutane, butene and propane (Fig. 4a), which are common species in NG, CBG, and LPG (Cai et al., 2010; Tang et al., 2008). Therefore, this source was labeled as NG/CBG/LPG usage, with the contribution of 16.37% (Fig. 4b). PSCF analysis showed that the potential source region was in the northwest direction, which can be linked to LPG/NG processing activities carried out in western China, such as in Changqin and Yanchang oil fields. The exploration areas of Changqin and Yanchang oil field are mainly located in the Shaanxi-Gansu-Ningxia basin, including Yanan and Yulin in Shaanxi and Erdos in Inner Mongolia (Fig. 5b).

Factor 3 was identified as vehicle exhaust, because its main components were the typical tracers of vehicle exhaust, such as MTBE, cis/trans-butene, 3-methylpentane and n/i-pentane (Cai et al., 2010; Xia et al., 2014; Sauvage et al., 2009; Yuan et al., 2013b) (Fig. 4a). B/T ratio in this factor was 0.46, which was also consistent with the value of vehicle exhaust (0.3–0.7) (Brocco et al., 1997; Perry and Gee, 1995). This source contributed only 14.55% to the VOCs in Taiyuan (Fig. 4b), significantly smaller compared with other developed cities, such as Beijing (44.45%) (Zhang et al., 2017), Shanghai (25.00%) (Cai et al., 2010) and Wuhan (27.80%) (Lyu et al., 2016). PSCF results showed that traffic related pollutants were mainly from local emission sources (Fig. 5c).

Factor 4 featured the greatest contributions from the benzene series, 1,2-dichloroethane, and methyl-chloride. Ethylene, acetylene, and ethane also displayed high contributions (Fig. 4a). Previous studies have reported that 1,2-dichloroethane, methyl-chloride, and acetylene were typical indicators of the combustion source (Cai et al., 2010). The B/T ratio in this factor was found to be 1.85. As discussed in section 3.3.1, a value > 1 suggests the dominance of coal and biomass combustion. Therefore, factor 4 was considered to be the combustion source, and contributed 23.25% to TVOCs (Fig. 4b). PSCF results showed that the combustion source was characterized by a local high emission (Fig. 5d).

Factor 5 featured relatively higher contributions from the benzene series and high molecular weight alkanes (Fig. 4a). Studies have shown that in addition to the combustion of fossil fuels and vehicle exhaust, industrial solvent usage is another important source, such as paints, coatings, synthetic fragrances, adhesives, and ink cleaners (Leuchner and Rappenglück., 2010). For example, styrene is an important

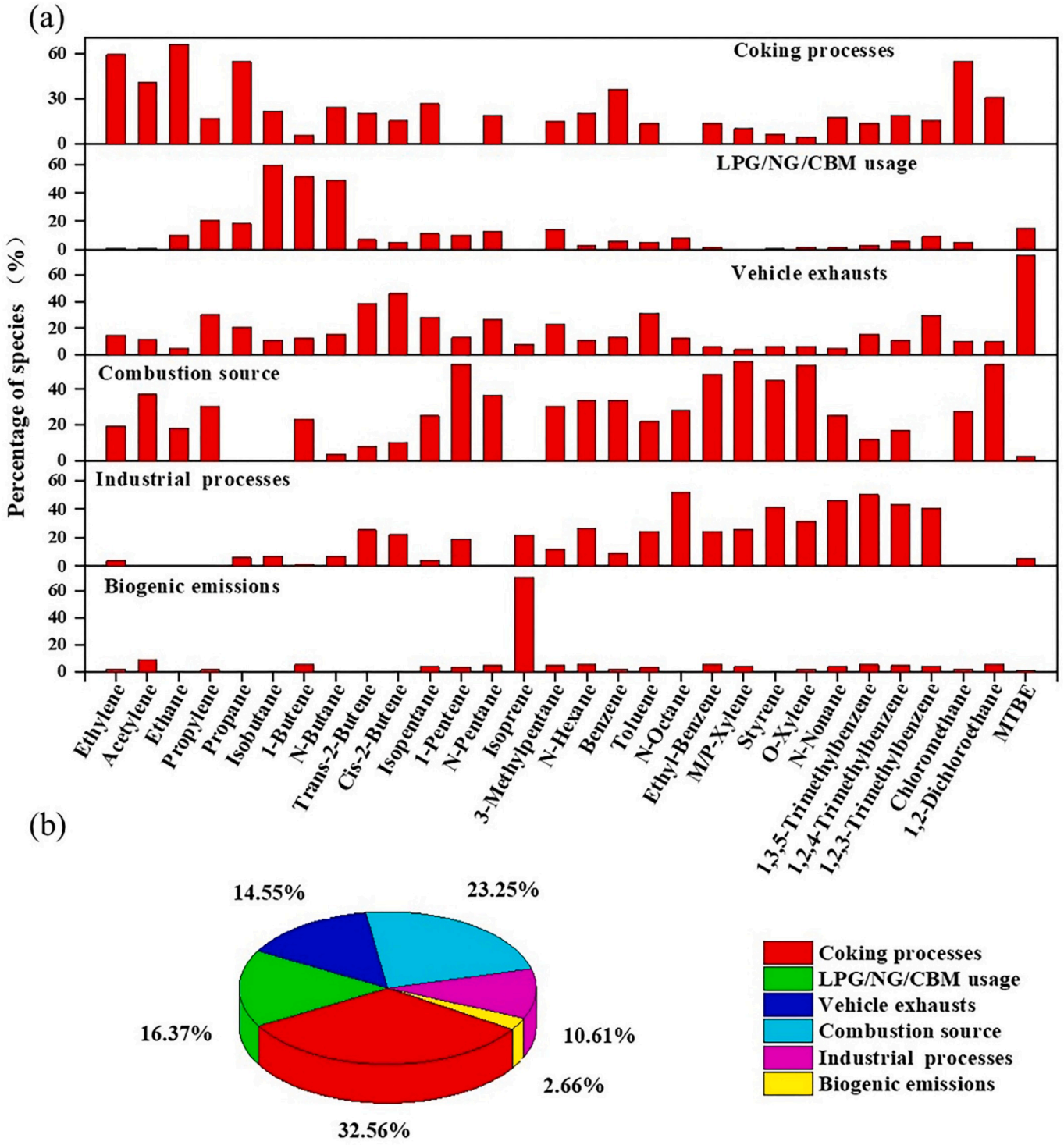

Fig. 4. Source profiles of VOCs (a) and contributions of each source (b) resolved by PMF model.

monomer of industrial synthetic resins, ion exchange resins, and synthetic rubbers (Civan et al., 2015). N-octane is the main component of printing inks (Buzcu and Fraser, 2006). Thus, factor 5 was labeled as industrial processes associated with solvent usage, contributing 10.61% of the TVOC (Fig. 4b). A significantly high PSCF value was observed in the northwest part of Inner Mongolia province and the southwest part of Hebei province, which was found to be consistent with the spatial distribution of VOC emissions associated with the solvent usage in China in 2005 (Fig. S6) (Bo et al., 2008). The air masses from the southwest part of Hebei province accounted for 13.13% of the total air masses inflowing into Taiyuan (Trajectory 5 in Fig. 1).

The major contributor to factor 6 was isoprene, a typical tracer of biogenic emission (Sauvage et al., 2009) (Fig. 4a). It was proposed that isoprene is also a characteristic pollutant of industrial processes and is emitted with other industrial pollutants, such as styrene and n-octane (Buzcu and Fraser, 2006). It may also be emitted by heavy vehicles (Song et al., 2007). However, the contributions of these two sources to isoprene emissions in Taiyuan can be ignored because the correlations of isoprene with the main indicators of the traffic source were found to be significantly low, with correlation coefficients being only 1.1×10^{-3}

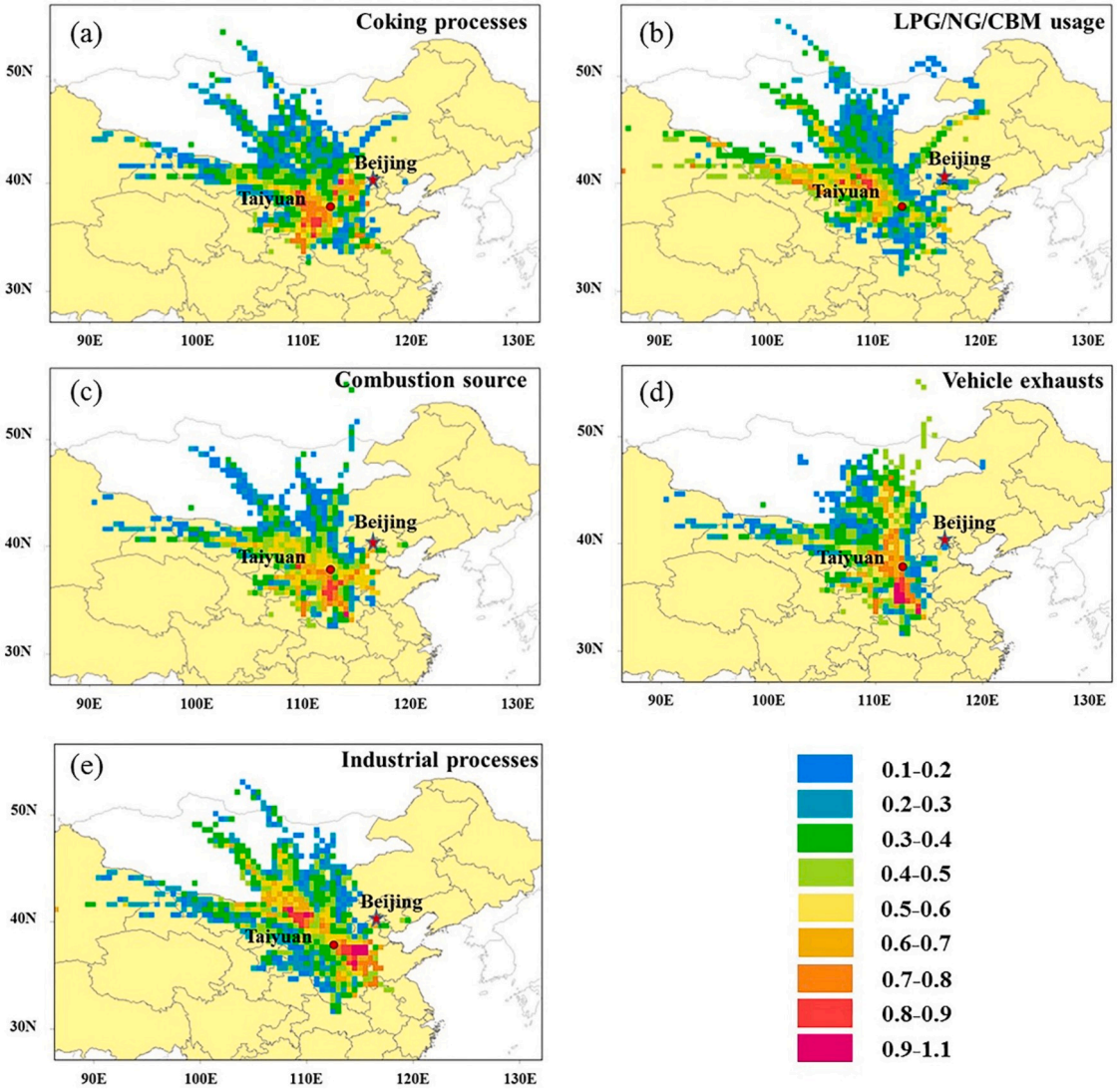

Fig. 5. Probable source regions of VOCs in Taiyuan during the observation period.

and 9.79 × 10^{-6} for isopentane and MTBE, respectively (Fig. S7a), similar to its correlation with the industrial indicators (styrene, 0.37; n-octane, 0.29) (Fig. S7b). Thus, factor 6 was considered to be biogenic emissions, contributing 2.66% to the TVOCs (Fig. 4b). The contribution of biogenic emission was too small to carry out PSCF analysis.

Fig. 6 shows the concentration composition of the source factors during the four seasons. During spring, VOCs associated with the coking process accounted for a large proportion. This could be attributed to the high frequency of the southwest wind in spring (Fig. S3). The southwest wind passed through the coking area (Fig. 1), and carried the air pollutants emitted during coke production into Taiyuan. During summer, the concentrations of VOCs from industrial and biogenic emissions, which exhibited a positive relationship with temperature, were observed to significantly increase (Dumanoglu et al., 2014), but that from the coking process was observed to reduce by almost half due to very low frequency of the southwest wind (Fig. S3). During autumn and winter, the concentrations of VOCs from the coking process recovered and again reached the level observed in spring, as the frequency of the southwest wind increased. The concentrations of VOCs from combustion emissions gradually increased from summer to winter due to biomass burning in autumn and heating supply in winter. A significant increase was also observed for LPG/NG/CBM related VOCs in winter, similar to that observed for Nanjing in China (An et al., 2017). Surprisingly, the

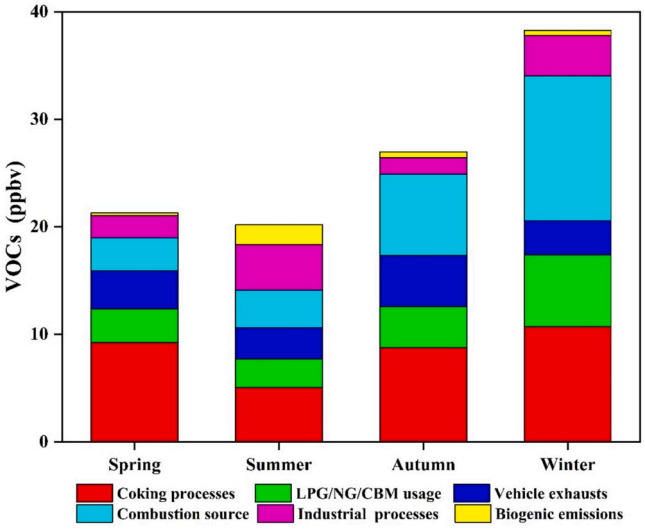

Fig. 6. Contribution composition of the source factors resolved by PMF in different seasons.

concentration of VOCs from vehicle exhausts was much higher in autumn than other seasons.

3.4. Outward transport pathways of VOCs from Taiyuan to surrounding areas

Taiyuan was listed as one of the "2 + 26" air pollution transmission channel cities ("2 + 26 cities" hereafter) where special action plan for air pollution prevention and control is to be implemented, as there is a possibility that atmospheric pollutants can get transferred from Taiyuan to the BTH region, the national political center and the most polluted area in China. This plan is the most stringent air pollution plan implemented in China, which requires the "2 + 26 cities" to rapidly and thoroughly reduce major air pollutant emissions than other regions (Chen and Chen, 2019). Therefore, the 48h-outward transport pathways of VOCs from Taiyuan to surrounding areas were analyzed to provide valuable references for regional joint control in North China.

Throughout the year (Fig. 1), the outward transport pathways of VOCs in Taiyuan were observed to be dominated by the forth pathway due to the influence of northern westerly wind belt system (30.14%). The speed of the air mass in this pathway was so low that the pollutants remained in Shanxi. However, the first, second, and third air masses (>50%) demonstrated the potential to transport the atmospheric VOCs to the BTH region. The first air mass (15.53%) could bring the VOCs from Taiyuan to Shijiazhuang and Beijing after passing through Xinzhou and Datong prefectures. The second air mass (14.84%) could transport the VOCs of Taiyuan to Baoding and Tianjin through Xinzhou.

Focusing on the situation of each season, nearly 70% of the air masses in Taiyuan were transported to the BTH region in spring following the first, second, and third pathways. However, their influence on VOC pollution in the BTH region may be weak because VOC levels were low in Taiyuan in this season. In summer, only 15.15% of the total air masses were transported from Taiyuan to the BTH region (Fig. 7b). In autumn, over 40% of the total air mass was evidently transported to Beijing following the first and second transport pathways, with a relatively high concentration of VOCs. These two pathways mainly passed through Xinzhou and Datong, and then arrived at Zhangjiakou, Baoding, and Beijing. The third pathway transported 25% of the total air masses to Shijiazhuang through Yangquan. In winter, the concentration of TVOCs in Taiyuan was observed to be as high as 67.33 ppbv, while more than 80% of the air masses were transported to the west and reached Shijiazhuang, Xingtai, and Handan following the first pathway. The fifth pathway (35.09%), with a short route, exhibited slow movement and thus, many air pollutants were expected to be carried to Shijiazhuang.

Around 70%, 65%, and 80% of the air masses were transported from Taiyuan to the BTH region during spring, autumn, and winter, respectively, which may be related to the high frequency of the southwest wind in these three seasons (Fig. S3). The southwest wind carried the air pollutants emitted during coke production to the BTH region. Therefore, it is necessary to control the air pollutant emissions of coke production bases in Shanxi to improve the regional air quality in the "2 + 26 cities", especially during autumn and winter.

4. Conclusions

In this study, pollution characteristics of ambient VOCs in Taiyuan was investigated. Results indicated that Taiyuan exhibited high levels of VOCs, dominated by alkanes and aromatics. Concentration of TVOCs exhibited significant seasonal variation, increasing from spring to winter. Concentration of TVOCs in winter was 2.16 times that in spring. Significant emissions of air pollutants from coal combustion was the dominant factor causing heavy VOC pollution during winter, followed by adverse atmospheric diffusion and degradation conditions. Main species in different cities were similar, with different relative abundances from each other (Fig. S8). Total concentration of the 15 main species in urban regions was significantly higher in Taiyuan than many other cities in China and globally, except Beijing and Shenzhen in China. Located in a single basin or connected basins with several large coke production bases, species associated with coal combustion and coking activities exhibited high concentrations in Taiyuan. The most distinctive feature was the higher level of benzene than that of toluene. Although the value of B/T in summer was close to that of the vehicle exhaust, it might not be the main source but due to several sources.

Performance of the PMF model resolved six main pollution sources of

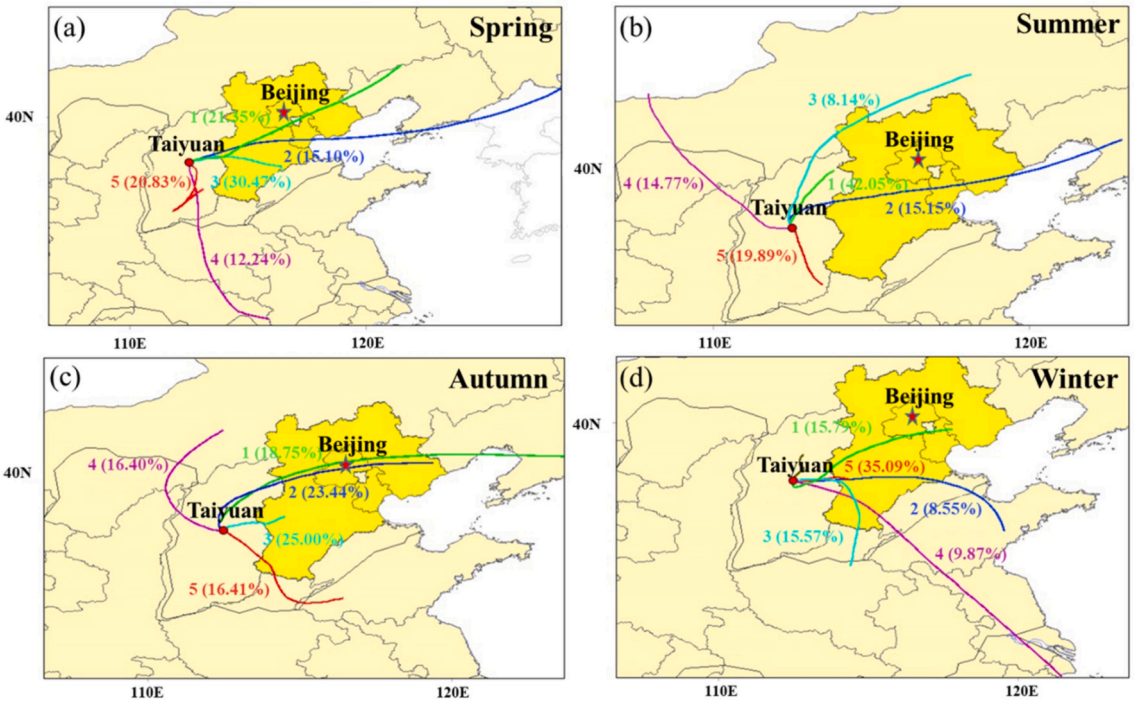

Fig. 7. Forward trajectory clusters for Taiyuan in different seasons. The numbers in brackets indicate the percentage allocated to each cluster.

VOCs in Taiyuan: coking processes (32.56%), combustion sources (23.25%), LPG/NG/CBM usage (16.37%), vehicle exhaust (14.55%), industrial processes (10.61%), and biogenic emissions (2.66%). The potential source regions were further explored using PSCF model, and it was found that atmospheric transportation of VOCs from the coke production bases significantly influenced the VOC concentrations in Taiyuan during all seasons. Analysis of forward trajectories indicated that more than 70%, 40%, and 80% of the air masses were transported from Taiyuan to the BTH region during spring, autumn, and winter, respectively. Therefore, it is necessary to control air pollutant emissions from coke production bases in Shanxi to improve regional air quality in the "2 + 26 cities". Additionally, local combustion emission of the air pollutants also needs stringent control, especially in autumn and winter.

In this study, we also found that emissions associated with motor vehicles mainly came from local sources. However, LPG/NG/CBM related VOCs might be related, to some extent, to LPG/NG processing activities carried out in northwestern China. VOCs associated with the use of solvent in the industrial processes could be attributed to the input from the southwestern part of Hebei. To provide more convincing evidences for joint control of ambient VOC pollution in Taiyuan and related regions, quantitative impact of regional inter-transport should be further analyzed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jie Li: Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Hongyan Li:** Conceptualization, Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Funding acquisition. **Qiusheng He:** Conceptualization, Data curation, Writing - review & editing, Supervision, Funding acquisition. **Lili Guo:** Investigation, Writing - review & editing, Visualization. **Hefeng Zhang:** Conceptualization, Data curation, Writing - review & editing, Supervision. **Guishi Yang:** Investigation, Writing - review & editing. **Yuhang Wang:** Writing - review & editing. **Fahe Chai:** Writing - review & editing.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2020.117573.

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