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Temporal variations and source apportionment of volatile organic compounds at an urban site in Shijiazhuang, China

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ABSTRACT

Shijiazhuang, the city with the worst air quality in China, is suffering from severe ozone pollution in summer. As the key precursors of ozone generation, it is necessary to control the Volatile Organic Compounds (VOCs) pollution. To have a better understanding of the pollution status and source contribution, the concentrations of 117 ambient VOCs were analyzed from April to August 2018 in an urban site in Shijiazhuang. Results showed that the monthly average concentration of total VOCs was 66.27 ppbv, in which, the oxygenated VOCs (37.89%), alkanes (33.89%), and halogenated hydrocarbons (13.31%) were the main composite on. Eight major sources were identified using Positive Matrix Factorization modeling with an accurate VOCs emission inventory as inter-complementary methods revealed that the petrochemical industry (26.24%), other industrial sources (15.19%), and traffic source (12.24%) were the major sources for ambient VOCs in Shijiazhuang. The spatial distributions of major industrial activities emissions were identified by using geographic information statistics system, which illustrated the VOCs was mainly from the north and southeast of Shijiazhuang. The inverse trajectory analysis using Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) and Potential Source Contribution Function (PSCF) clearly demonstrated the features of pollutant transport to Shijiazhuang. These findings can provide references for local governments regarding control strategies to reduce VOCs emissions.

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Introduction

Volatile Organic Compounds (VOCs), the toxic air pollutants in regional ambient air, has gradually received widespread attention in China. Studies have found that exposure to high VOCs concentrations can increase the risk of cancer. In addition, VOCs can photooxidize with oxidants in atmosphere to form the secondary pollutants as Ozone (O_3), Secondary Organic Aerosols (SOAs), aldehydes, ketones, esters, alcohols, carboxylic acids and so on (Carrillo-Torres et al., 2017), which can lead to the occurrence of urban haze. The presence of atmospheric VOCs are complex in composition and diverse in source (Jeričević et al., 2019). Research had shown that the anthropogenic activities are the main contributors to VOCs concentrations in urban areas (Araya et al., 2019; Norris et al., 2019) which includes the coal burning, solvent usage, the petrochemical industry, vehicles exhaust emissions, biomass burning and cooking. In addition, the composition and source of VOCs emissions vary with the different industrial structures in different regions (Hui et al., 2018), which has significantly challenged the source analysis of VOCs.

Currently, source analysis is mainly conducted by using receptor models method. Receptor models can use the VOCs levels of the receptor site to quantify the source contribution to the receptor, such as Positive Matrix Factorization (PMF), Chemical Mass Balance (CMB) and Principal Component Analysis (PCA). Since CMB modeling approach require pre-measured source profiles, PCA and PMF are commonly applied to understand the impact of potential sources. However, PCA is frequently to identify a small number of factors, resulting in incomplete analysis of complex regions sources. Therefore, the PMF model is more desired to identify contributing factors (Leuchner and Rappenglück, 2010; Wang et al, 2018; Hsu et al, 2018). However, PMF analysis is affected by the uncertainty of monitoring data (Brown et al., 2015). In order to improve the accuracy and rationality of PMF result, a high resolution emission inventory was introduced to verify the PMF results.

Shijiazhuang, the capital of Hebei province, is one of the most important city in Beijing-Tianjin-Hebei (BTH) region. Shijiazhuang is suffering from serious air pollution problems with O_3. Based on the data of China National Environmental Monitoring Center, the comprehensive index of urban ambient air quality of Shijiazhuang ranked 169th in the 169 cities in China from 2016 to 2018. As the key precursors of O_3 formation, effective control of VOCs pollution is important for alleviating O_3 pollution in Shijiazhuang.

In this study, a comprehensive and continuous analysis of the concentration, composition, and variation of atmospheric VOCs was analyzed from April to August 2018, and determined source and VOCs emission spatial distribution by combining the results of emission inventory and PMF model. HYSPLIT combined with PSCF model to confirm the long-distance sources. This study's finding will assist in evaluating the impact of anthropogenic VOCs emission to support robust air pollution control policy formulation in Shijiazhuang.

1. Material and methods

1.1. Study area and sampling site

This study was conducted in Shijiazhuang City, North China, which contains eighteen districts or counties. An ambient air VOCs sampling site (38°03′N, 114°55′E) was set in Century Park with an altitude of 20 m on the television tower, which represents the urban area of Shijiazhuang with no apparent industrial sources present in the vicinity of the sampling site. Meanwhile, wind direction (WD) and wind speed (WS) were monitored nearby the sampling site.

1.2. Sampling

VOCs samplings were conducted using 6 L summa canisters from April to August each five days, and with eight 3 hr sampling periods (0:00-3:00, 3:00-6:00, 6:00-9:00,9:00-12:00, 12:00-15:00, 15:00-18:00, 18:00-21:00, and 21:00-0:00). In total, 240 VOCs samples were collected during this sampling period. In addition, during O_3 pollution period (July 6, 2018 to July 15, 2018), samples were collected with 10 consecutive days and each day with 3 hr sampling time for about 24 hr per day (total 80 samples). Then, totally 320 VOCs samples were obtained during the two sampling periods and analyzed within 24 hr after collection.

1.3. Analytical method

Through the atmospheric pre-concentration system (Model 7100, Entech Instruments Inc, USA), 117 VOCs species (including 57 Photochemical Assessment Monitoring Stations (PAMS), 13 aldehydes and ketones, and 47 component VOCs in TO-15) were qualitatively and quantitatively analyzed with Gas Chromatograph/Mass Selective Detector (GC/MS7890B-5977B, Agilent Technologies, USA) in accordance with the United States Environmental Protection Agency (US EPA) Method Toxic Organics (TO-15) (US Environmental Protection, 1999) and Ambient air-determination of volatile organic compounds - collected by specially-prepared canisters and analyzed by gas chromatography/mass spectrometry standard (Ministry of Ecology and Environment of the People's Republic of China, 2015; Zhou and Feng, 2018).

1.4. Quality control

To ensure all target compounds were not detected or under the method detection limits (MDL), sampling canisters were cleaned by repeated evacuating and filling of humid ultrapure nitrogen (N_2) (99.999%), and the concentration of VOCs in each blank was less than 1% of the sample values. A calibration curve was built for each of the compounds (bromochloromethane, 1, 2-difluorobenzene, chlorobenzene-d5 and 4-bromofluorobenzene) with seven different concentrations (0.5, 1.25, 2.5, 5, 10, 15 and 20 ppbv), and the R^2 values of established calibration curves were all larger than 0.999. MDLs ranged from 0.10 to 0.41 ppbv for all compounds. For each batch of samples, reproducibility check was performed using duplicated sample analysis. The relative average deviation of two runs in all cases (except OVOCs) were within ±10%. Due to the carbonyl compounds with strong polarity, which are liable to absorption on the sampling canisters, the relative average deviation of OVOCs was between 20%-55%. To ensure the authenticity and accuracy of the experimental data, the experimental instruments were checked and calibrated regularly.

1.5. Local source apportionment methodology

1.5.1. PMF model

In order to differentiate between local emissions and transport, PMF receptor model and backward trajectories were introduced. The fundamental principle of PMF is mass conservation, and mass balance analysis is used to identify and apportion source contributions of observed concentrations (Assan et al., 2018). The matrix X_{ij} decomposed into two matrices (including the matrix g_{ik} of source contribution and the matrix f_{kj} of pollutant source composition spectrum), and the

e_{ij} is the residual matrix. The specific calculation formula is shown as follows:

$$X_{ij} = \sum_{k=1}^{P} g_{ik} f_{kj} + e_{ij} \quad (1)$$

where, X_{ij} represents the concentration of component j in sample i; g_{ik} represents the contribution of the k_{th} source in the sample i; f_{kj} represents the concentration of component j in the k_{th} emission source; and P represents the number of pollution sources.

The PMF model is mainly used to calculate the minimum value Q based on the objective function of uncertainty u_{ij}. m and n are sample and species amounts, respectively, and $g_{ik} \geq 0, f_{kj} \geq 0$, and $u_{ij} > 0$. The calculation formula is as follows:

$$Q = \sum_{i=1}^{m} \sum_{k=1}^{n} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right] \quad (2)$$

The calculation formula of sample data uncertainty u_{ij} is shown as follows:

$$u_{ij} = \frac{5}{6} \times \mathrm{MDL} \quad (c \leq \mathrm{MDL}) \quad (3)$$

$$u_{ij} = \sqrt{(\mathrm{EF} \times c)^2 + (0.5 + \mathrm{MDL})^2} \quad (c > \mathrm{MDL}) \quad (4)$$

where, c represents the concentration data, EF (Error Fraction) represents the error score, and MDL is the method detection limit. Since VOCs are easily affected by photo-chemistry and temperature, some limitations has been introduced in this article. Firstly, this study determined EF value by considering the instrumental measurement precision, VOCs chemical activity, and VOCs concentration. The relevant research set the EF value to 10% - 50%%Nayebare et al., 2018), and this study set to 20% by experience. MDL values were obtained by repeatedly injecting standard samples close to the expected detection limit concentration seven times, and calculating the mean standard deviation of the analysis results and multiplying by the statistical coefficient t (3.14) at the 99% confidence interval. Secondly, the appropriate VOCs species for the PMF model were determined following some basic principles since VOCs are easily affected by photo-chemistry and temperature: ((1) excluding VOCs with their data loss is more than 25% or their concentration values fell below MDLs. (2) Eliminating VOCs with short atmospheric lifetimes (< 3 hr) (Zhang et al., 2019). Thereafter, 35 VOCs were selected to input the PMF model, because they were either the most abundant species, higher atmospheric lifetimes (VOCs lifetime with 5.9 hr to 53 day in atmosphere) or a source identification species. Based on the scaled residuals distributions and the interpretability of the resulting profiles, the eight factor solution was determined to be the optimal solution in PMF analysis (Li et al., 2019).

1.5.2. *VOCs emission inventory*

The emission characteristics calculated by the emission inventory were basically consistent with the monitoring period, since spring and summer are the main VOCs emission periods of industrial enterprises production in Shijiazhuang. Then, it was reasonable to determine VOCs source by combining the results of emission inventory and PMF model. The VOCs emission inventory was calculated by using the "Emission Factor (EF) method", which was recommended by "technical guidelines for compiling emission inventory of ambient air volatile organic compounds (trial)" (Ministry of Ecology and Environment of the People's Republic of China, 2014). VOCs emission inventory in Shijiazhuang from 2018, including fossil fuel combustion, biomass burning, solvent usage, industrial processes source, transportation, solid waste disposal, storage and transportation, and catering. Eq. (5) was formulated to calculate the total emissions.

$$E_{i,j} = \sum_{j,k} EF_{i,j,k} \times A_{i,j,k} \quad (5)$$

where, $E_{i,j}$ (Tg) is the emissions of source j in region i; $EF_{i,j}$ is source j in region i under the technological condition of k (g); and $A_{i,j,k}$ is the activity data of source j in region i under the technological condition of k. The data sources and VOCs emissions were shown as **Supporting Information (SI, Table S1 to S8)**.

In this study, Monte Carlo simulation was also adopted to calculate the uncertainty of emission inventory. First, input EFs and activity data into the data table and selected the best-fitting Probability Density Function (PDF). Second, determined the mean and standard deviation of each PDF. Third, repeated the simulation process 100,000 repetitions and set confidence intervals to 95%. Then, the dataset of VOCs total emissions and the uncertainty of the emissions were obtained. The uncertainties of standards or empirical parameters derived from TRACE-P observations, the uncertainty range was defined within ±80%, indicating that the object can represent the average level of source category in this region (Streets et al., 2003).

1.5.3. *VOCs source classification*

In order to precisely determine the source contribution, the results of the same period emission inventory was applied to validate PMF model result. The sources categorization in the emission inventory were matched with the PMF, including biomass burning (including industrial biomass boiler and biomass stove), petrochemical industry, other industrial sources (containing metallurgy, building materials, chemical fiber and pharmaceutical manufacturing), solvent usage (including surface coating, printing and dyeing, pesticide application and other solvent usage), coal burning (containing industrial boilers, civil combustion and rural household coal combustion sources), traffic (including on-road vehicles and off-road transportation) and others sources (including solid waste disposal, storage and transportation, catering and others). While, fuel evaporation and LPG leakage were classified unorganized emission source, which was no calculated within the emission inventory. Consequently, the results of fuel evaporation and LPG leakage emission were incomparable between the two methods. A detailed source classification is shown in Table 2.

1.6. *Long-range transport apportionment*

In this study, trajectory calculating, clustering and changing of VOCs concentrations in the clusters were conducted using K-means method in TrajStat software (Cheng and Kabela, 2016). This study set hourly 24 hr back trajectory starting from the sampling site since VOCs with transportation may decay and the long simulation time of the back trajectory will decrease the accuracy of simulation result (Li, 2017). The appropriate VOCs species for this model were determined following some basic principles since VOCs are easily affected by photo-chemistry and temperature: ((1) excluding VOCs with their data loss is more than 25% or their concentration values fell below MDLs. (2) Eliminating VOCs with short atmospheric lifetimes (< 24 hr) (Salmabadi and Saeedi, 2019). Thereafter, the selected VOCs input the model, because they were the most abundant species, and higher atmospheric lifetimes (VOCs lifetime with 24 hr to 53 day in atmosphere). Then, this result can reflect the transport characteristics of pollutants (Sun et al., 2018; Cui et al., 2019).

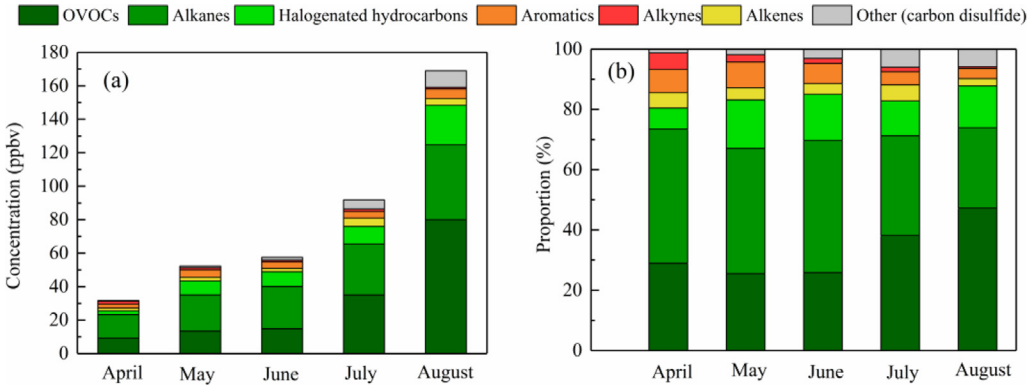

Fig. 1 – Concentration (a) and proportion (b) of VOCs species during study period.

The PSCF was applied to locate the regional sources contributing to elevated VOCs levels. The higher PSCF indicated a higher contribution to VOCs concentration. The region corresponding to the high PSCF value grid represents a potential source area for VOCs species. As shown in Eq. (6):

$$\mathrm{PSCF} = m_{ij}/n_{ij} \tag{6}$$

where, n_{ij} represents the number of all trajectories in the air flow through the ij_{th} cell grid in the study area and m_{ij} is the number of pollution trajectories through the ij_{th} cell grid. The criterion values were determined as 75^{th} percentile values (sufficiently elevated critical value) for the whole period in each parameter to better perceive the external influences to VOCs (Nicolás et al., 2011). To minimize the uncertainties due to few endpoints that result in high PSCF values, by multiplying the arbitrary weight function (W_i) into the PSCF value, the potential contribution algorithm combined with weight factors (WPSCF) is obtained as follows (Lee et al., 2016):

$$\mathrm{WPSCF}_i = \mathrm{PSCF}_i \times \mathrm{W}_i \tag{7}$$

$$\mathrm{W}\left(n_{ij}\right) = \begin{cases} 1.00 & n \geq 160 \\ 0.75 & 160 > n \geq 80 \\ 0.50 & 80 > n \geq 40 \\ 0.20 & 40 > n \end{cases} \tag{8}$$

2. Results and discussion

2.1. *VOC pollution characteristics of explosive growth in Shijiazhuang*

The monthly average concentration and contribution of VOCs are shown in Fig. 1. The monthly VOC concentrations gradually increased from 29.13 ppbv in April to 135.51 ppbv in August (Fig. 1a). The VOCs concentration growth processes with at least sextuple can be identified as explosive growth processes, as it generally keep rising consistently with vary sensitively and rapidly in response to the wind shifting from northwest to south and southwest (Fig. 2). The industrial complex are mainly located in south and southwest of the urban area and the explosive growth processes for local wind convergence occurs with weak wind velocity (Zhong et al., 2018). In order to further understand the influence of wind speed on VOC concentrations, we conducted Pearson correlation coefficient test with SPSS 19.0. With slower wind speeds (typically less than 3.0 m/s) occurring in July and August, and the peak VOC concentration was correlated with wind speed in July (R^2 = -0.649) and August (R^2 = -0.781). VOCs and wind speed were not correlated from April to June, indicating that wind speed had little influence on VOC concentrations from April to June. The prevailing winds being southeasterly (from July to August), transport of pollutants is also at its highest since industrial enterprise are mainly distributed at the southeast of the city. Low wind speed mainly influences the dilution and diffusion of pollutants, which became one of the important factors affecting the concentration level of pollutants. Consequently, this increase in VOC concentrations was most likely caused by the combined effects of intra-city area transmission and local accumulation under unfavorable meteorological conditions.

Combined with the contribution of six VOCs species, as shown in Fig. 1a, The highest VOCs species were measured encountered on the OVOCs, with an average contribution of by 37.89%, whose value increased from 9.20 ppbv in April to 79.96 ppbv in August as a result of its widespread sources and strong oxidation activity (Vichi et al., 2019). The second highest contributor was alkanes with an average contribution of 33.89%, which increased from 14.10 ppbv in April to 44.90 ppbv in August by its widespread sources and longevity (Gadi et al., 2019), and the third was halogenated hydrocarbons with an average contribution of 13.31%, increased from 2.21 ppbv in April to 23.54 ppbv in August due to the highly volatile and long atmospheric lifetimes (Zheng et al., 2019). Aromatics, other (carbon disulfide), alkenes, and alkynes were the four lowest contributors. The average contribution of aromatics was 5.09%, which increased from 2.34 ppbv in April to 5.72 ppbv in August. The average contribution of carbon disulfide was 4.59%, which increased from 0.40 ppbv in April to 9.85 ppbv in August. The average contribution of alkenes was 3.65%, which increased from 1.63 ppbv in April to 4.01 ppbv in August. Alkynes were the minimal contributor with an average contribution of 1.57% that decreased from 1.73 ppbv in April to 0.94 ppbv in August.

Table 1 shows the comparisons of the top 10 VOC species measured in Shijiazhuang, other cities in China, and around the world. The sampling and analysis method of most citations were consistent with this study, such as Chengdu, Taiwan and Sao Paulo, while have minor discrepancy with Beijing, Wuhan and Jiashan. By analyzing the discrepancy of sampling and analysis methods for these cities, we found that the discrepancy has little effect on the data, since their operating analytical principles were consistent with this article. The sampling site of selected cities were located at city center and were less affected by industrial sources. Therefore, it has a great significance to compare VOC concentration levels among these cities.

Among the top 10 VOC species, OVOCs were the most abundant species encompassing 28.55% of the total concentrations, including acetaldehyde (13.14%), acetone (8.77%), isopropyl alcohol (3.91%), and ethyl acetate (2.73%). Followed by

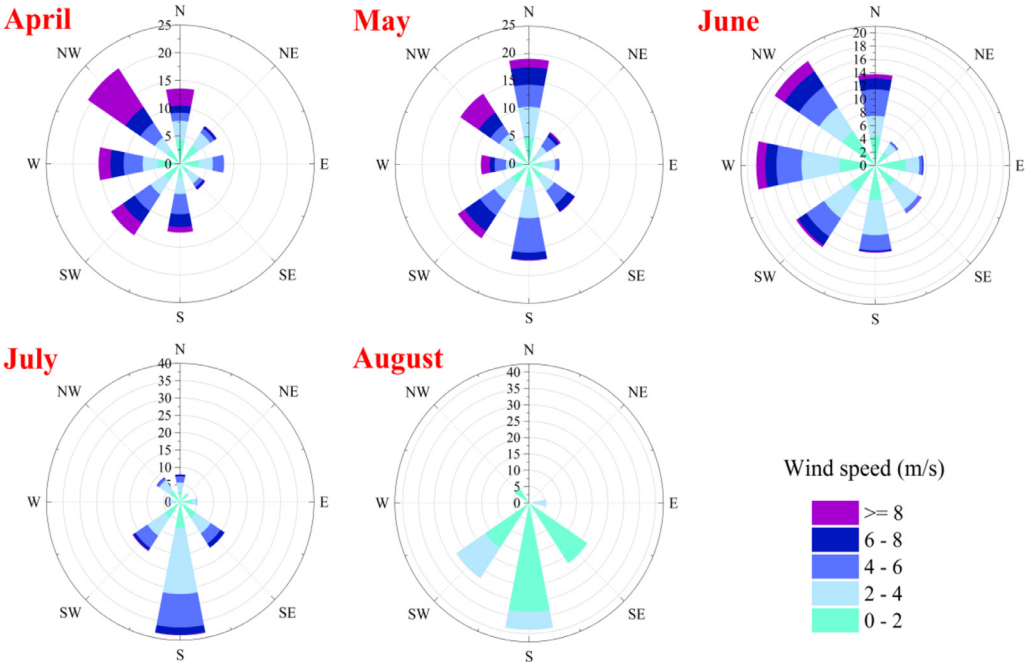

Fig. 2 – Wind direction frequency (%) and wind speed (m/sec) during study period.

Table 1 – Comparisons of the top 10 VOCs measured in Shijiazhuang and other cities in China and around the world (ppbv).

Species	Shijiazhuang (This study)	Beijing[a]	Chengdu[b]	Wuhan[c]	Jiashan[d]	Taiwan[e]	Sao Paulo[f]
Time	2018.4-2018.8	2015.11-2016.1	2016.2-2017.3	2016.7-2017.6	2016.8-2016.9	2014.8	2008.6-2008.9
Sampling duration	3 hr	1 hr	3 hr	5 min	5 min	3 hr	2 hr
Sampling and analyzed method	Summa canister-GC/MS	Adsorption tube - GC/ NMSD	Summa canister-GC/MS	On-Line VOCs Monitoring System	On-Line VOCs Monitoring System	Summa canister-GC/MS	Summa canister-GC/MS
Acetaldehyde	8.71	0.68	-	-	-	-	5.64
Acetone	5.81	3.00	-	5.93	4.07	1.74	-
1, 2-dichloroethane	4.33	-	0.01	-	-	0.43	-
Carbon disulfide	3.70	-	-	-	-	-	-
Ethane	3.24	1.86	10.29	4.56	1.28	-	5.76
Isopropyl alcohol	2.59	-	-	-	-	-	-
Iso-butane	2.45	0.48	1.38	2.16	1.09	1.48	2.26
Propane	2.42	2.00	3.98	7.25	2.11	0.02	2.99
Dichloromethane	2.35	-	2.64	1.58	1.42	0.73	-
Ethyl acetate	1.81	-	-	-	-	9.42	-
Total of top 10 VOCs species	37.41	8.02	18.3	21.48	9.97	13.82	7.51

-: Not detected or not listed.
[a] Liu et al., 2016.
[b] Tan et al., 2018.
[c] Hui et al., 2018.
[d] Zou et al., 2017.
[e] Kuo et al., 2015.
[f] Alvim et al., 2017.

halogenated hydrocarbons (10.09%, including 1,2-dichloroethane (6.54%) and dichloromethane (3.55%)), alkanes (12.24%, including ethane (4.89%), iso-butane (3.69%), and propane (3.66%)) and carbon disulfide (5.58%). By comparison with other studies, the total concentration of the top 10 VOCs in Shijiazhuang was higher than other cities, which possibly attributed by the VOCs emission varied with city activities as well as development stage and energy structure (Wang et al., 2018).

Compared to Beijing and Sao Paulo, Shijiazhuang and Sao Paulo had higher concentrations of acetaldehyde. It may be attributed to the higher generation concentration of secondary organic aerosol in summer than in winter, where the aldehydes is the main component (Yang et al., 2018). Moreover, the acetaldehyde released from many industrial products are also the important contribution to the ambient air, for example, the treated wood resins, cosmetics, plastic adhesives, construction materials, cleaning agents, disinfectants, particleboard, medium-density fiberboard, plywood, carpeting, cigarette smoke, and fabrics (Kamal et al., 2016), which may be implied that Shijiazhuang had higher industrial activities than Sao Paulo.

The concentration of acetone was slightly lower than that of Wuhan and higher than Beijing, Jiashan, and Taiwan. Acetone is derived from solvent usage, varnishes, paint thinners, and photochemical reaction (Kamal et al., 2016). Wuhan and Shijiazhuang are important industrial bases and solvent usage and other industrial sources were the main sources to affect quality of ambient air. Therefore, it was concluded that the higher local industrial emissions and their photochemical products were likely a contributing factor to the episodes of high acetone levels in Shijiazhuang and Wuhan.

Compared to other cities around the world, Shijiazhuang presented a higher concentration of iso-butane, a comparable concentration of propane, and a lower concentration of ethane. Since iso-butane and propane are the main components of liquefied petroleum gas (LPG) (Lyu et al., 2016), and ethane is an important tracer for natural gas (Kayadelen, 2017). As a consequence, the usage of LPG and natural gas (e.g., LPG commercial buildings, household, and also directly under the influence of emissions from a busy road nearby) may effect on the ambient air in these cities, and the concentration of iso-butane may be greatly influenced by the usage of LPG in Shijiazhuang.

The concentration of 1, 2-dichloroethane (6.54%) in Shijiazhuang was significantly higher than Chengdu and Taiwan, whereas the concentration of dichloromethane was comparable to that of other cities around the world. Generally, halogenated hydrocarbons (such as 1, 2-dichloroethane and dichloromethane) are mainly originate from solvent usage (Huang et al., 2014). The large number of formulations and processing of chemical extractants, paints, and adhesives, drugs manufacturing, polymer syntheses, as solvents in chemical reactions, and as cleaning agents involving large amounts of solvent usage may be the main reason for the higher composition of 1, 2-dichloroethane and dichloromethane in Shijiazhuang. These results have illustrated differences of energy structure and anthropogenic perturbations in different cities have a significant impact on VOCs pollution characteristics.

2.2. *Source analysis*

In order to identify the major factors of the source characterization results, this study provided the characteristic pollutants of different factors and the source contributions respectively calculated by PMF model (Fig. 3a and b) and emission inventory (Table 2).

The VOC emissions inventory indicated that the highest contribution was industrial process sources. And, the Monte Carlo simulation results showed that the overall uncertainty of VOC emission inventory was [-40%, 58%] at 95% confidence intervals, which suggested that the result was within the reasonable uncertainty range and have high reliability to represent the average level of source category. Meanwhile, the source contributions of emission inventory is shown in the Fig. 3c. Also, the PMF model mass fraction indicated the mass concentration ratio of each VOC components of the same factor, and the contribution rate indicated the relative contribution of each factor to the same VOC component mass concentrations.

The characteristic pollutant in Factor 1 was chloromethane with the highest contribution of 57.6%. Chloromethane is normally considered to be a typical tracer for biomass burning (Wang et al., 2007). Therefore, factor 1 represented the biomass burning source with a contribution of 10.12% to VOCs concentration. This result in the PMF was significantly enhanced relative to that in the emission inventory (Fig. 3c). Biomass combustion, the important VOC sources in the urban area of Shijiazhuang, originating mainly from civil uses and industrial production emissions.

Factor 2 was characterized by high percentages of m/p-xylene (58.9%), o-xylene (68.7%), which belong to the Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) group. In the petrochemical industry, BTEX group are the tracers of petrochemical refining and storage (Tiwari et al., 2010). In addition, 1, 2-dichloroethane (83.7%) also provided higher percentage of the percentages, belonging to the petroleum hydrocarbons pollutants in the petrochemical industry (Zhang et al., 2017; Heibati et al., 2018). Hence, factor 2 can be identified as the petrochemical industry source with a contribution of 26.24%, which was also the largest source of VOCs pollution in Shijiazhuang as shown in Fig. 3b. This result was in good agreement with emission inventory (21.97%).

Factor 3 was characterized by high percentages of OVOCs, including vinyl acetate (52.1%), acetaldehyde (43.0%), propionaldehyde (40.2%), butyraldehyde (51.70%), and benzaldehyde (41.20%). In addition, the percentages of acetone and 2-butanone were relatively lower as 13.5% and 10.5%, but also higher than in other factors. Aldehyde is the main pollutant to textiles, paints, and the furniture manufacturing industry, and acetone and 2-butanone were used as solvent in the manufacturing industry (Legreid et al., 2007; Liang et al., 2017; Qi et al., 2019). Therefore, factor 3 can be regarded as other industrial sources with a contribution of 15.19%.

Factor 4 identified characteristic pollutants including 2-methyl-1,3-butadiene, trichloromethane, dichloromethane, and n-hexane with contributions of 43.60%, 56.40%, 42.30%, and 50.3%, respectively. The halogenated hydrocarbons, such as trichloromethane, and dichloromethane, are mainly used in industrial processes, and n-hexane accounts for a large proportion of industrial solvents (Shao et al., 2016; Sun et al., 2016). Therefore, factor 4 was identified as a solvent usage source. The contribution of solvent usage source to VOCs concentration was 11.60%, which was the third source of VOC pollution in Shijiazhuang. This phenomenon mainly ascribed to the usage of architectural coatings, industrial painting and auto repair industries. Factor 5 was characterized by high percentages of C_3-C_6 alkanes, especially isopentane (48.6%) and n-pentane (40.9%). Isopentane and n-pentane are typical tracers for volatile gasoline (Li et al., 2018). Therefore, factor 5 identified as the fuel evaporation source with a contribution of 6.76%. Hence, high temperatures are most likely the primary driver of high fuel evaporation in Shijiazhuang in summer.

Factor 6 was portrayed by high percentages of propane (45.5%), ethylene (34.9%), toluene (31.2 %), acetylene (39.5%), ethane (39.1%), and propylene (48.1%). In addition, the percentage of benzene was relatively lower as 26.8% but also higher than in other factors. The acetylene, C_2-C_3 alkanes, C_2-C_3 alkenes, and aromatics mainly originated from coal burning (Li et al., 2018). Therefore, factor 6 was identified as the coal burning source with a contribution of 11.36%. Factor 7 was characterized by high percentages of propane (41.2%), isobutene (35%), n-butane (41.0%) and ethane (45.3%) are typical tracer of emission from LPG. In addition, ethylene (34.7%) and propylene (28.7%) also occupied considerable proportions, which are released from the use of LPG (Ma et al., 2019). Therefore, factor 7 was identified as an LPG usage source with a contribution of 6.49%.

Factor 8 was characterized by high percentages of C_2-C_5 alkanes such as ethane (52.5%), propane (58.7%), n-butane (67.9%), and iso-pentane (54.9%). In addition, acetylene (42.3%) also occupied considerable proportions. C_2-C_5 components derived from traffic source are mainly emitted from light-duty gasoline vehicles (Chen et al., 2019), acetylene have been used extensively as a tracer for combustion emissions (Zhu et al., 2018). Therefore, factor 8 was identified as the traffic source with a contribution of 12.24%, representing the fourth highest source of VOC pollution in Shijiazhuang.

Simultaneously, by comparing Fig. 3b and c. Result demonstrated that a significant consistency between the two methods with respect to contributions from biomass burning, the petrochemical industry, other industrial sources, solvent us-

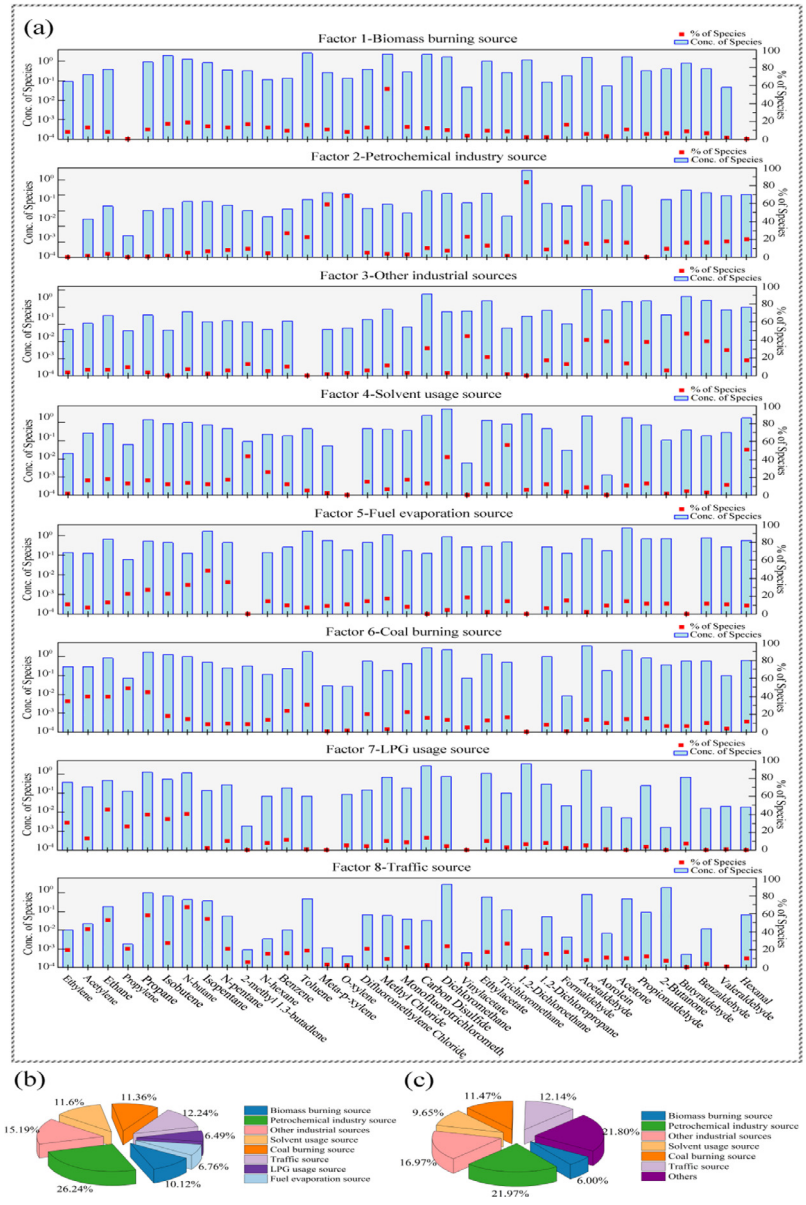

Fig. 3 – Source contributions to VOCs concentration analyzed by the PMF model (a and b), and emission inventory (c).

age, fuel evaporation, coal burning, and traffic sources to VOCs in the PMF were comparable to those in emission inventory. It illustrated that the PMF model effectively analyzed the sources of VOCs in Shijiazhuang.

2.3. *Spatial distribution*

To identify the spatial variation characteristics of the anthropogenic VOC emissions in Shijiazhuang, the VOC emission inventory with a resolution of 3 km × 3 km were established under the geographic information statistics system (GIS), as depicted in Fig. 4. It shows the VOC emissions in the northeastern and southeastern were much higher than that in the west, which were related to the well-developed industry in these areas. The rest of Shijiazhuang produced less emissions, with no region exceeding 500 g/m^2. In the northeast, the high emission of industrial VOC was mainly concentrated in the high tech industrial development zone (Hengshan Industrial Zone, Tiexi Industrial Zone, and Zhengding New District), which includes electronics processing, pharmaceutical industries, building materials, and food processing industries. In the southeast, the high emission of industrial VOC values was mainly concentrated in the Circular Chemical Industrial Park, which is located with the petrochemical plants, chemical raw materials, chemical manufacturers, and chemical plants, etc.

The spatial variation characteristics of the VOC emissions in Shijiazhuang can verify the effects of industrial sources in the southeastern on VOC concentrations, since the southeast wind prevailing in summer facilitated the transportation of VOCs to urban area. Meanwhile, it illustrated the tremendous differences in VOCs emissions among different regions were consistent with the unbalanced economic development in Shijiazhuang. Therefore, VOCs concentrations can only be significantly reduced by optimizing the industrial structure properly, promoting rational distribution of regional economy, and enhancing the VOCs management based on the existing problems in Shijiazhuang.

Table 2 – Emission contributions of sources calculated by emission inventory in 2018.

Primary classification source	Secondary classification source	VOC emissions (ton)	Tertiary classification source	VOC emissions (ton)	VOC contributions (%)
Fossil fuel combustion source	Industrial boilers	6429.471	Coal burning	13837.35	11.47
	Civil boilers	32			
	Rural household coal combustion	7376			
Industrial process source	Petrochemical industry	26507	Petrochemical industry source	26507	21.97
	Metallurgy	3598	Other industrial sources	20470	16.97
	Building materials	14382			
	Chemical fiber	191			
	Pharmaceutical manufacturing	2298			
Transportation source	On-road vehicles	12078.51	Traffic source	14644	12.14
	Off-road transportation	2565.64			
Solvent usage source	Surface coating	8038	Solvent usage source	11646	9.65
	Printing and dyeing	1355			
	Pesticide application	765			
	Other solvent usage	1488			
Biomass combustion source	Industrial biomass boiler	180	Biomass combustion source	7234	6.00
	Biomass stove	7054			
Other sources	Solid waste disposal	891	Other sources	26321.65	21.80
	Storage and transportation	2645			
	Catering	259			
	Others	22527			

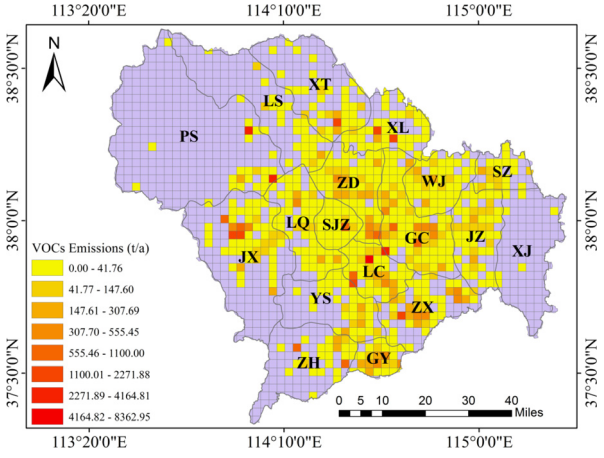

Fig. 4 – Spatial distribution of the total VOCs emissions in Shijiazhuang region.

2.4. *Air transport patterns*

VOCs pollution is also affected by air transport. Regional and long-range transport pathways were investigated by using the HYSPLIT model-derived air back-trajectories, the proportion of the top 10 VOC species in each air mass, and the top 10 VOC species contributions in each air mass to local ambient air, which were analyzed by cluster analysis, whereas the PSCF model was combined for the identification of non-local potential source regions (Fig. 5). Fig. 5a highlights the dominant transport pathways of air masses in Shijiazhuang, and the proportion of the top 10 VOC species of each air mass trajectory was also observed.

In cluster 1, air-masses predominantly originated from the southeastern region of the city. The category can be considered as short-distance air-masses as most of the trajectories originated from regional transport. This cluster were low in altitude, accounted for 36.74% of total trajectories. In cluster 2, it contributed 20.02% of total air-masses and predominantly originated from Bohai Sea and passing through highly polluted regions of Cangzhou and Hengshui, and which may be polluted. In cluster 3, this middle-distance air-masses accounted for the second highest frequency of 20.45%, and which originated from highly polluted regions of Anyang and passing through Handan and Xingtai. Cluster 4ss was identified as middle-distance air-masses and originated from the Jinan to the study site, with an accounted of 16.29% of total trajectories. Cluster 5, as the long-distance air-masses, originated from Zhengzhou via the study area, which accounted for 6.44% of total air-masses. It showed that the short-distance and middle-distance air masses from the south and southeast had the most pollution trajectories respectively, with a total contribution of 73.48% of total trajectories.

Meanwhile, OVOCs (ethyl acetate, acetaldehyde, and acetone), alkanes (ethane, iso-butane, and propane), and halogenated hydrocarbons (1, 2-dichloroethane and dichloromethane) were the top three contributors in each air mass trajectory. The proportion of isopropyl alcohol was relatively lower in the top 10 VOCs of each air mass trajectory, and which only appeared in trajectory 1 and trajectory 2. It indicated that the isopropyl alcohol mainly came from local regions emissions. According to the contributions of the top 10 VOCs in the five air mass trajectories, the proportion of VOCs varied. Simultaneously, the differences of the top 10 VOC proportions in the dominant air mass trajectories (trajectory 1, trajectory 3 and trajectory 2) were relatively small, but they differed from the other two air mass trajectories. It is noted that the proportion of acetaldehyde, acetone, dichloromethane, carbon disulfide, and propane were relatively higher in trajectory 1, which may be due to the local industrial enterprise emissions in Shijiazhuang and transport to the urban through the air mass. In addition, owing to the longer transmission distances, VOCs proportion were lower in other trajectories, due to the aging and responding through the transmission process. In summary, the short-distance transport of air masses had a certain impact on the VOCs pollution in Shijiazhuang.

As shown in Fig. 5b, the regions with higher PSCF value implied the potential source areas at a distance, which may

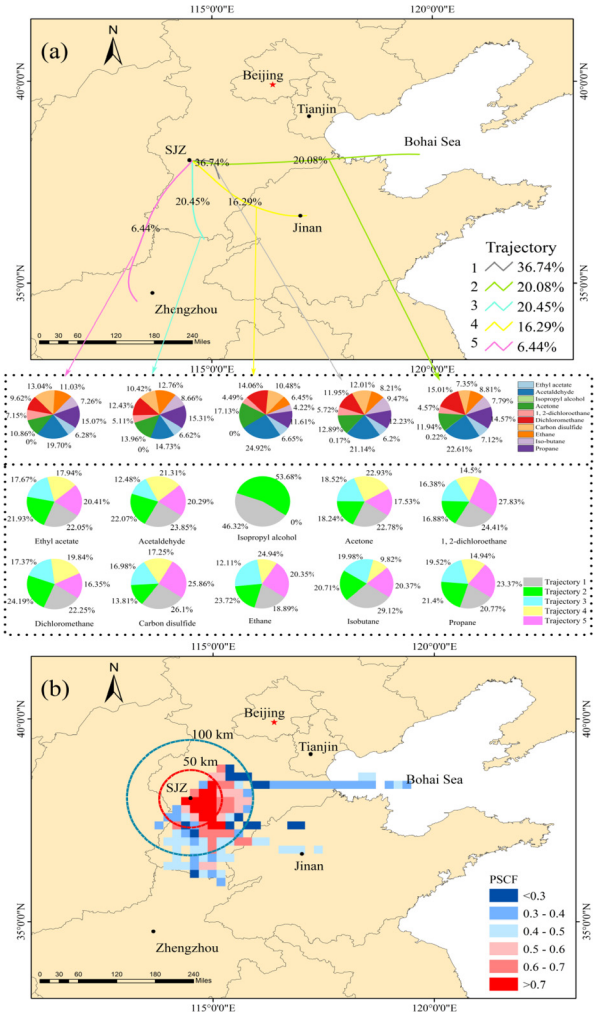

Fig. 5 – The 24-hr backward trajectories (a) and PSCF (b) during study period in Shijiazhuang.

have a larger impact on VOC concentrations. According to the radius of Shijiazhuang (50 km), the potential transmission sources were divided into three parts with a 50 km contour. Consequently, the area within a 50 km radius represent the contribution of local sources, and other areas corresponding to the regional areas (> 50 km). Combined with the spatial distribution as shown in Fig. 4, the regions with lower PSCF values (< 0.5, blue grids) can be regarded as the low potential VOC source area, which were mainly located at greater than 100 km. In addition, the area within 50–100 km with PSCF values (0.5–0.7, pink grids) represented the higher potential VOCs source area. The area within 50 km with PSCF values (> 0.7, red grids) represented the highest potential VOC source area centered in Shijiazhuang, which were in highly industrial districts. Moreover, the potential sources were located at the east, southeast, and south of Shijiazhuang. Therefore, this map suggests that most of the regional VOCs in Shijiazhuang is likely to be local emission in origin.

3. Conclusions

In this study, the pollution characteristics of 117 atmospheric VOCs were analyzed from April to August 2018. The monthly average concentration of total VOCs was 66.27 ppbv. OVOCs were the primary pollutants with an average contribution of 37.89%, followed by Alkanes (33.89%), halogenated hydrocarbons (13.31%), aromatics (5.09%), carbon disulfide (4.59%), alkenes (3.65%), and alkynes (1.56%). The source analysis results obtained by a PMF receptor model with VOCs emission inventory explained the reason of higher concentration VOC species, and illustrated that the petrochemical industry source is the primary pollution source with a contribution of 26.24%, followed by other industrial sources (15.19%), traffic (12.24%), solvent usage (11.60%), coal burning (11.36%), biomass burning (10.12%), fuel evaporation (6.76%), and LPG usage sources (6.49%). According to the spatial distribution of VOCs emissions at a regional scale, the VOC emissions in the northeastern and southeastern were much higher. The HYSPLIT model combined with the PSCF model illustrated that long-range transport had less impact on the observed VOCs concentrations than local emissions. This study verified the effects of industrial sources on VOC concentrations in the southeast region from different perspectives. Therefore, in order to reduce ambient air VOC concentrations in Shijiazhuang, the government should take effectively control policies for mainly local emission sources, such as petrochemical sources, other industrial sources, and transportation sources.

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “Temporal variations and source apportionment of volatile organic compounds at an urban site in Shijiazhuang, China”(JES-2019-3115).

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.04.022.

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