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Characteristics of atmospheric volatile organic compounds in urban area of Beijing: Variations, photochemical reactivity and source apportionment

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ABSTRACT

Atmospheric volatile organic compounds (VOCs) were observed by an on-line gas chromatography-flame ionization detector monitoring system from November 2016 to August 2017 in Beijing. The average concentrations were winter ($40.27 \pm 25.25 \mu\text{g}/\text{m}^3$) > autumn ($34.25 \pm 19.90 \mu\text{g}/\text{m}^3$) > summer ($32.53 \pm 17.39 \mu\text{g}/\text{m}^3$) > spring ($24.72 \pm 17.22 \mu\text{g}/\text{m}^3$). Although benzene (15.70%), propane (11.02%), ethane (9.32%) and *n*-butane (6.77%) were the most abundant species, ethylene (14.07%) and propene (11.20%) were the key reactive species to ozone formation potential (OFP), and benzene, toluene, ethylbenzene, *m*-xylene + *p*-xylene and *o*-xylene (54.13%) were the most reactive species to secondary organic aerosol formation potential (SOAFP). The diurnal and seasonal variations indicated that diesel vehicle emission during early morning, gasoline vehicle emission at the traffic rush hours and coal burning during the heating period might be important sources. Five major sources were further identified by positive matrix factorization (PMF). The vehicle exhaust (gasoline exhaust and diesel exhaust) was found to be contributed most to atmospheric VOCs, with 43.59%, 41.91%, 50.45% and 43.91%, respectively in spring, summer, autumn and winter; while solvent usage contributed least, with 11.10%, 7.13%, 14.00% and 19.87%, respectively. Biogenic emission sources (13.11%) were only identified in summer. However, both vehicle exhaust and solvent usage were identified to be the key sources considering contributions to the OFP and SOAFP. Besides, the contributions of combustion during heating period and gasoline evaporation source during warm seasons to OFP and SOAFP should not be overlooked.

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Introduction

Volatile organic compounds (VOCs), which include hydrocarbons, halogenated hydrocarbons, benzene and its derivatives, phenols and its derivatives, alcohols, aldehydes, ketones and fatty acids, etc., exist widely in the atmosphere. The main sources of atmospheric VOCs include primary emission sources and secondary generation of hydrocarbons discharged into the atmosphere. Primary emission sources of VOCs can be divided into anthropogenic emission sources and natural emission sources. It is believed that the contribution value of anthropogenic emission sources in the urban atmosphere is far greater than that of natural emission sources. Research showed that China's total emissions of anthropogenic VOCs were 25.03 million tons in 2015 (Zhang et al., 2017b) and total natural emission sources of VOCs were 12.83 million tons in 2013 (Chi et al., 2014). VOCs are involved in regional photochemical reactions, which affect the concentration of the hydroxyl radicals (OH radicals) (Wang et al., 2016; Wu et al., 2016a, 2016b), as well as the formation of near-ground-ozone and secondary organic aerosols (Li et al., 2018). Many VOCs are toxic, such as benzene, ethylbenzene, oxygenated-VOCs and halogenated-VOCs (e.g., acetaldehyde, 1,2-dichloroethane) (ATSDR Agency for Toxic Substances and Disease Registry, 2011). And their secondary products in the ambient air, such as aldehydes and ketones and peroxyacetyl nitrate (PAN) (Wu et al., 2017), also have direct poisoning effect on human health. As a result, VOCs have been extensively studied due to their high emissions, high reactivity and impact on human health.

Researches of VOCs mainly focused on the pollution levels' variations, sources and reaction mechanisms of VOCs in ambient air (Bari and Kindzierski, 2018; Kumar et al., 2011, 2018; McCarthy et al., 2013). These study showed that levels of VOCs have obvious seasonal and diurnal variation characteristics, such as anthropogenic VOCs generally higher in the morning and evening, while natural emission VOCs generally reach their maximum concentrations at noon or in the afternoon under high temperature (T) and high solar radiation (SR) (Lee and Wang, 2006); and that anthropogenic emission sources of atmospheric VOCs are mostly motor vehicle exhaust, petrochemical related industrial production and product consumption process. Natural emission sources mainly come from plant volatiles. The photochemical reactions of VOCs mainly include reactions with OH radicals, NO₃ radicals, as well as the oxidation reaction of peroxide radicals (RO₂) and NO (Cheng et al., 2013; Lyu et al., 2016). The chemical reactivity of VOC components is related to the concentration of free radicals. OH radical loss rate (L^{OH}) and ozone formation potential (OFP) are widely used to evaluate the chemical reactivity and the contribution to O₃ production (Carter, 1994; Niu et al., 2012; Wu et al., 2016a).

In recent years, the rapid development of China's economy has triggered many pollution problems. In 2016, among 338 prefecture-level and-above cities, 254 cities (75.1%) didn't meet the China Air Quality Standard (MEE of China, 2016). Thirteen cities in the Beijing-Tianjin-Hebei (BTH), 25 cities in the Yangtze River Delta (YRD) and 9 cities in the Pearl River Delta (PRD) exceeded the standard on an average of 43.2%, 23.9% and 10.5%, respectively (MEE of China, 2016). Thus, domestic researchers have conducted in-depth studies on the pollution characterizations of VOCs centered in the BTH, the YRD and the PRD regions. For example non-methane hydrocarbons (NMHCs) in ambient air in Beijing, Gucheng and Quzhou (BTH) in summer of 2014 were monitored by gas chromatography-mass spectrometer/flame ionization detector (GC-MS/FID). Alkanes were the largest group of NMHCs

(>50%). The L^{OH} of VOCs were calculated to estimate their chemical reactivities. Alkenes played a predominant role in VOC reactivity. Alkenes and aromatics were the largest contributors (47.65%–61.53% totally) to the total OFP. And vehicles emissions was main source of ambient VOCs in the BTH region (Li et al., 2015). Emission from vegetation was a major source of isoprene in summer (Li et al., 2015). Han et al. (2018) monitored VOCs emission of a petrochemical industry in YRD by an online GC-FID system. The results showed that the total VOCs concentration was 155.6 ppbV. Alkenes and alkanes were the major constituents, which accounted for 83.4% of the total VOCs. The diagnostic ratios of toluene / benzene (T/B) and *m*-xylene + *p*-xylene and *o*-xylene / ethylbenzene (X/E) indicated the measured air mass was affected by fresh emissions from this petrochemical industry. The fractional aerosol coefficient (FAC) method was used to estimate the yield of secondary organic aerosol formation potential (SOAFP), which accounted for 2.42%–75.60% of the corresponding PM_{2.5} concentration (Han et al., 2018). Ou et al. (2015) developed the PRD regional speciated oxygenated volatile organic compound (OVOC) emission inventories by using of the latest bulk VOC emission inventory and local source profiles. Results showed that methyl alcohol, acetone and ethyl acetate were the major constituents in the OVOC emissions from industrial solvents, household solvents, architectural paints and biogenic sources.

From 2015 to 2016, many emission control measures were put forward, such as upgrading low-efficiency coal-fired industrial boilers and furnaces, desulphurization of flue gas emitted by coal-fired power plants and adjusting the industrial structure of Beijing. Various regions have implemented a series of air pollution control policies, especially implementing the “2+26” urban (including Beijing) joint prevention and control measures. All these stringent air-quality control measures provide an opportunity to evaluate the effective, so it is necessary to carry out long-term observation on the atmospheric VOCs. In this study, VOCs in ambient air were continuously observed from 1 November 2016 to 4 August 2017, yielding information on concentration levels of atmospheric VOCs and temporal variations. In addition, their photochemical reactivities and key species contributed to the formation of O₃ and SOA were identified. Finally, sources were identified by positive matrix factorization (PMF) and the key sources were also studied. Based on these analyses, this study might provide scientific support for the government to take measures to effectively control O₃ and PM_{2.5} pollution.

1. Materials and methods

1.1. Sampling site and period

The sampling site is located on the roof of the Atmospheric Photochemical Smog Simulation Laboratory in the Chinese Research Academy of Environmental Sciences (CRAES) (40.04°N, 116.42°E) in the Chaoyang District of Beijing (Fig. 1). The sampling port is 8 m above-ground. The site is 2 km from the North Fifth Ring Road and about 3.6 km from the Beijing Olympic park. About 200 m to the west is the north to south Beijing Subway Line 5 and Beiyuan Road. About 100 m to the south is the east to west Chunhua Road. About 700 m to the north-east is the Beijing Subway Line 13. There are residential areas and shopping malls around, and the density of surrounding residents and traffic flow are large. There is no obvious air pollution source in the surrounding area, which meets the research requirements. The observing data basically rep-

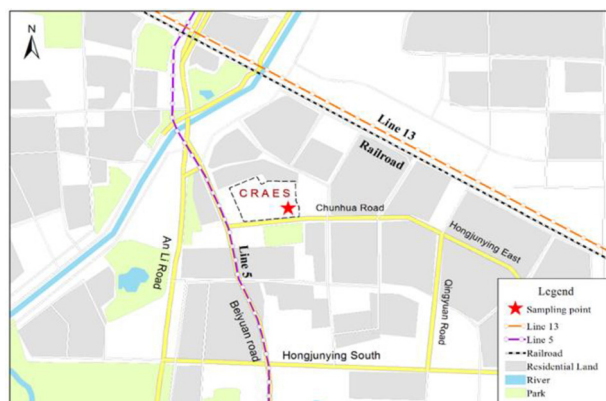


Fig. 1 – Observing site of VOCs.

representative of the pollution situation of Beijing urban area to a certain extent.

We selected 120 days to evaluate characterizations of VOCs in this study. The 120 days include 30 days in each season, which are 16 April to 15 May 2017, 6 July to 4 August 2017, 1 to 30 November 2016, and 20 December 2016 to 19 January 2017, respectively.

1.2. Observing instruments

VOCs were continuously observed and analyzed by an Air-moVOC online analyzer (GC-866, Chromato-sud, France). The instrument consists of two independent sampling and analysis systems. Their detector is flame ionization detector (FID). The detail information about the observing instruments was described detail in our previous studies (Cheng et al., 2018; Zhang et al., 2017a).

In order to ensure the accuracy and effectiveness of the Air-moVOC online observation data, strict quality assurance and control measures must be implemented. Table 1 lists standard curves of part of species and its relative standard deviations (RSD). External calibration result had strong correlations ($R^2 > 0.9$) and the RSD was less than 10% in each season. Meanwhile, the instrument was internally calibrated once per 24 hr, using *n*-butane, *n*-hexane and benzene and the deviation should not more than 10%. Sample tubes were wrapped with a heating jacket and a thermal insulation to ensure their T remained stable at 22 to 27°C.

2. Results and discussion

2.1. Ambient levels of VOCs

The annual mean value of the total concentration of 59 VOCs in ambient air was $32.94 \pm 20.46 \mu\text{g}/\text{m}^3$, with a range from 7.97 to $131.59 \mu\text{g}/\text{m}^3$ during the observation period. As shown in Table 2, the total VOCs mean values followed the order of winter ($40.27 \pm 25.25 \mu\text{g}/\text{m}^3$) > autumn ($34.25 \pm 19.90 \mu\text{g}/\text{m}^3$) > summer ($32.53 \pm 17.39 \mu\text{g}/\text{m}^3$) > spring ($24.72 \pm 17.22 \mu\text{g}/\text{m}^3$). The seasonal variation of VOCs concentration was affected by many factors: (1) The change of VOCs source (combustion sources) strength (Lin et al., 2015), coal burning in late autumn and winter in northern China led to the change of VOCs source strength. The concentration of SO_2 was found to be 0.73 times higher that before heating period during November 2016 was a proof of the strengthen emission of coal burning; (2) The T was low in autumn and

winter, and the atmospheric photochemical reaction was not active, which was not conducive to the removal of VOCs; (3) Changes in the mixed state of the atmosphere and different meteorological conditions (Lin et al., 2015). The atmospheric structure was relatively stable in autumn and winter, and inversion layer often occurred at night, which was not conducive to the diffusion and dilution of pollutants. Therefore, the concentration of VOCs in autumn and winter was relatively high; (4) There were many windy days in spring in Beijing, which was conducive to the diffusion of pollutants, so the concentration of VOCs in spring was lowest.

The major components in the four seasons were alkanes, followed by aromatics, alkenes and alkynes (Table 2), which was consistent with the studies of other area (Cai et al., 2010; Cheng et al., 2018; Hui et al., 2018). The seasonal variations of alkanes, alkenes and aromatics were the same as total VOCs, which was winter > autumn > summer > spring. The seasonal variation of alkynes was a little different, which was summer > autumn > spring > winter. In contrast to other VOCs species, the concentrations of alkynes were not high all through the year.

To evaluate atmospheric pollution levels of VOCs in urban area of Beijing, measured concentrations of alkanes, alkenes (alkynes), and aromatics were compared with those of other cities at home and abroad (Fig. 2). Comparison with data from the same observation site in 2014–2015 (Zhang et al., 2017a) showed that the VOCs concentrations in this study were dramatically decreased by 60.87%, 68.19%, 39.97% and 54.22% in winter, autumn, summer and spring respectively. This might mainly be ascribed to the implementation of air pollution control measures in the BTH region, such as replacement of coal-fired boilers, treatment of scattered coal, elimination of high-emission vehicles and treatment of industrial pollution. Besides, the higher average T in 2017 than that in the past years (China Meteorological Administration, 2017) which led to the enhancement of the removal of VOCs might be another reason. Compared with the previous studies of Beijing, the concentrations of alkanes, alkenes (alkynes) and aromatics in each season of this study were all lower than the seasonal corresponding concentrations of various compounds in the suburban sampling site in 2015 (Yang et al., 2018). And the concentrations of alkanes in the summer of 2017 decreased significantly compared with that in 2014 (Li et al., 2015). The concentrations of various compounds in each season in Beijing in 2017 were much lower than those in Wuhan in 2017 (the total VOCs of spring, summer, autumn and winter were 93.22, 60.88, 103.85 and $136.03 \mu\text{g}/\text{m}^3$, respectively) (Yang et al., 2019) and Tianjin in 2015 (the total VOCs of spring, summer, autumn and winter were 88.34, 142.38, 114.40 and $126.09 \mu\text{g}/\text{m}^3$, respectively) (Liu et al., 2016). Compared with international cities, the concentrations of benzene, toluene, ethylbenzene, *m*-xylene + *p*-xylene and *o*-xylene (BTEX) and alkenes (alkynes) with high photochemical activity during the observation period were higher than those of Canada in 2011–2015, but the concentrations of alkanes were lower than the average concentrations of Canada in 2011–2015 (Bari and Kindzierski, 2018). The concentrations of various compounds in this study were far lower than those in Mexico in spring of 2011 (the concentrations of alkanes, alkenes, alkynes and aromatics were 50.39, 7.65, 2.33 and $19.77 \mu\text{g}/\text{m}^3$, respectively) (Menchaca-Torre et al., 2015) and 2012 spring and autumn (the total VOCs of spring and autumn were 86.08 and $174.70 \mu\text{g}/\text{m}^3$, respectively) (Menchaca-Torre et al., 2015). The concentrations of alkanes and alkenes in each season in Beijing in 2017 were lower than those in Rome in 2011 (Fanizza et al., 2014). Except for the concentrations of BTEX in summer of 2017 in Beijing, the concentrations of BTEX in the atmosphere in Beijing in other seasons were higher than that in Rome of 2011 (Fanizza et al., 2014). This difference may be caused by many

Table 1 – Standard curves of part species and its relative standard deviations (RSD).

Variety	Species	Standard curve	R ²	RSD (%)
Alkanes	Ethane	y=2.1409x-0.0551	0.9814	2.02
	Propane	y=1.2887x-0.1208	0.9475	0.64
	Isobutane	y=1.2280x-0.0586	0.9998	1.07
	n-Butane	y=1.2222x-0.0601	0.9999	0.46
	Cyclopentane	y=1.3465x-0.0247	0.9979	0.36
	Isopentane	y=1.1822x-0.0009	0.9996	0.36
	2,3-Dimethylbutane	y=1.2393x-0.0425	0.9842	1.15
	n-Hexane	y=0.8718x-0.0563	0.9987	0.37
	Cyclohexane	y=0.8976x-0.0591	0.9976	0.29
	2,3-Dimethylpentane	y=0.8268x+0.0401	0.9995	0.36
	Alkenes	Ethylene	y=2.0773x-0.1442	0.9266
Propene		y=1.2718x-0.0106	0.9998	1.20
trans-2-Butene		y=1.4549x-0.0431	0.9998	0.49
1-Butene		y=1.2149x-0.0656	0.9993	2.23
cis-2-Butene		y=1.2268x-0.6600	0.9809	0.91
1,3-Butadiene		y=1.5927x+3.3221	0.9963	2.99
trans-2-Pentene		y=1.1681x+0.0035	0.9999	0.33
1-Pentene		y=1.0865x-0.0042	0.9995	1.10
cis-2-Pentene		y=1.0549x+0.0091	0.9992	0.43
2-Methyl-1-pentene		y=0.9877x+0.0092	0.9507	41.04
Alkynes		Acetylene	y=2.6406x-0.3198	0.9563
Aromatics	Benzene	y=0.8308x-0.1294	0.9993	0.43
	Toluene	y=0.6884x+0.1293	0.9965	0.64
	Ethylbenzene	y=0.7102x-0.0875	0.9988	1.44
	m-Xylenes + p-Xylenes	y=1.3465x-0.1881	0.9987	1.80
	Styrene	y=0.9062x-0.2081	0.9972	2.16
	o-Xylene	y=0.8291x-0.0804	0.9964	2.22
	m-Ethyltoluene	y=0.8985x-0.0741	0.9769	3.03
	1,3,5-Trimethylbenzene	y=0.8327x-0.0571	0.9959	4.25
	1,2,4-Trimethylbenzene	y=0.9154x-0.0319	0.9963	3.35
	o-Ethyltoluene	y=0.8434x-0.0793	0.9939	3.90

x and y refer to the response concentration of the instrument and the calibration standard value of each target species, respectively.

factors, such as the differences of major city activities as well as energy structure (An et al., 2012), observing method, different topographical, wind directions and wind speeds in different areas.

2.2. Diurnal variations

Fig. 3 shows the diurnal variations of total VOCs, alkanes, alkenes, alkynes and aromatics during four seasonal periods, together with meteorological conditions. The average diurnal variations of the total VOCs showed a general similar shape in the four seasons with the first concentration peak in the morning and the second one in the evening, both corresponding to traffic rush hours in Beijing, which indicated that the emissions of vehicle exhaust had a certain impact on atmospheric VOCs. The first peak occurred at 08:00, 08:00, 09:00 and 08:00 in spring, summer, autumn, and winter, respectively. Their concentrations were 27.30 ± 10.96 , 34.44 ± 13.52 , 36.32 ± 13.65 and $54.60 \pm 21.11 \mu\text{g}/\text{m}^3$, respectively. Later, high T and strong SR leads to the enhancement of photochemical reactions. As the main participant of photochemical reaction, VOCs react with NO_x to form O_3 . The rapid consumption of photochemical reaction and the diffusion of pollutants reduce the concentration of VOCs in the ambient air, making the concentration of total VOCs reached the lowest value in a day at 15:00 or 16:00. And lower relative humidity (RH) is also conducive to photochemical reactions. The lowest concentrations in spring, summer, autumn and win-

ter were $21.11 \mu\text{g}/\text{m}^3$ (15:00), $25.48 \mu\text{g}/\text{m}^3$ (16:00), $29.21 \mu\text{g}/\text{m}^3$ (15:00) and $31.11 \mu\text{g}/\text{m}^3$ (15:00), respectively. From 17:00 to 18:00, total VOCs concentrations kept increasing and reached another peak at 22:00 or 23:00. Their concentrations were $27.16 \mu\text{g}/\text{m}^3$ (23:00), $35.82 \mu\text{g}/\text{m}^3$ (23:00), $42.71 \mu\text{g}/\text{m}^3$ (23:00) and $45.27 \mu\text{g}/\text{m}^3$ (23:00), respectively. This may be caused by the reduced photochemical reactions due to the decrease of T and OH radicals, and lower height of mixed boundary layer, the increase in vehicle exhaust emissions and the discharges of other pollution sources that were not conducive to the diffusion of pollutants, resulting in the continuous increase of total VOCs concentrations in the ambient air (Garzón et al., 2015; Kumar et al., 2018). According to the regulation of Beijing heavy diesel vehicle driving limit, from 00:00 to 06:00 every day, the 5th Ring-Road allows diesel vehicles to pass, resulting in the continuous increase of the total VOCs concentration at 02:00 to 09:00 (except autumn).

In addition, the concentration of total VOCs was significantly higher at night than that during daytime. The reactions with OH radicals and O_3 are the main sedimentation reactions for VOCs during daytime, and the reactions with NO_3 radicals and O_3 are the most important chemical reactions occurring at night (Carter, 2007; Nakashima et al., 2010; Xu et al., 2017). However, the reaction rate of the NO_3 radical is much lower than that of the OH radical, and thus, the concentration of total VOCs was generally higher at night (Nakashima et al., 2010; Xu et al., 2017). The lower mixed boundary layer and the appearance of heavy-duty diesel vehicles at night were also im-

Table 2 – Average mass concentrations ± standard deviation (SD) of VOCs during four seasonal observation periods.

Variety	Species	Spring ($\mu\text{g}/\text{m}^3$)		Summer ($\mu\text{g}/\text{m}^3$)		Autumn ($\mu\text{g}/\text{m}^3$)		Winter ($\mu\text{g}/\text{m}^3$)	
		Range	Average±SD	Range	Average±SD	Range	Average±SD	Range	Average±SD
Alkanes	Ethane	0.23-5.89	1.93±1.10	0.12-8.36	2.33±1.03	0.13-12.10	3.42±2.22	0.39-20.53	4.60±4.19
	Propane	0.30-10.14	2.33±2.20	0.41-13.47	2.65±1.63	0.04-16.39	2.85±2.03	0.64-23.20	6.70±5.09
	Isobutane	0.00-4.83	1.07±0.67	0.00-3.71	0.75±0.60	0.00-11.35	1.37±1.28	0.00-2.56	0.95±0.40
	<i>n</i> -Butane	0.52-5.76	1.88±0.97	0.65-7.80	2.58±1.24	0.03-7.04	1.19±1.06	0.75-16.37	3.26±2.68
	Cyclopentane	0.00-3.69	0.96±0.61	0.00-5.47	1.25±1.23	0.00-4.84	0.68±0.62	0.00-2.55	0.12±0.10
	Isopentane	0.00-3.25	0.68±0.52	0.00-5.70	0.86±0.67	0.00-2.51	0.09±0.09	0.00-4.22	0.74±0.71
	2,3-Dimethylbutane	0.00-5.12	1.02±0.93	0.00-6.89	1.60±1.16	0.00-11.46	1.21±1.01	0.00-9.68	0.86±0.56
	<i>n</i> -Hexane	0.00-4.93	0.72±0.65	0.00-1.85	0.29±0.24	0.00-1.37	0.33±0.33	0.00-10.68	0.96±1.02
	Cyclohexane	0.00-5.05	0.69±0.42	0.00-3.31	0.30±0.27	0.00-4.25	0.23±0.25	0.00-5.31	0.23±0.26
	2,3-Dimethylpentane	0.00-2.15	0.25±0.20	0.00-2.28	0.14±0.09	0.00-1.05	0.29±0.21	0.00-1.12	0.28±0.19
	Other alkanes	–	2.03±1.97	–	3.25±2.10	–	3.51±2.35	–	2.11±1.92
	Total alkanes	–	13.56±8.96	–	16.00±7.43	–	15.17±9.31	–	20.81±14.26
Alkenes	Ethylene	0.15-2.42	0.59±0.51	0.16-6.04	0.57±0.49	0.42-6.28	2.13±1.02	0.49-7.19	2.43±1.45
	Propene	0.10-1.99	0.46±0.42	0.03-5.94	1.11±1.01	0.01-3.95	0.99±0.83	0.49-5.33	0.89±0.91
	<i>trans</i> -2-Butene	0.00-0.70	0.06±0.05	0.00-0.48	0.07±0.07	0.00-0.45	0.05±0.06	0.00-0.53	0.06±0.06
	1-Butene	0.00-0.65	0.08±0.08	0.00-1.13	0.14±0.13	0.00-1.10	0.14±0.10	0.00-0.90	0.22±0.19
	<i>cis</i> -2-Butene	0.00-0.85	0.32±0.19	0.00-0.43	0.23±0.65	0.00-4.93	0.44±0.58	0.00-0.84	0.69±0.53
	1,3-Butadiene	0.00-1.16	0.03±0.05	0.00-1.45	0.03±0.08	0.00-1.23	0.01±0.04	0.00-0.56	0.01±0.05
	<i>trans</i> -2-Pentene	0.00-1.06	0.08±0.10	0.00-1.84	0.47±0.62	0.00-0.34	0.10±0.14	0.00-2.03	0.10±0.21
	1-Pentene	0.00-0.91	0.01±0.02	0.00-2.24	0.07±0.10	0.00-4.81	0.44±0.64	0.00-2.96	0.19±0.22
	<i>cis</i> -2-Pentene	0.00-0.28	0.01±0.03	0.00-5.20	0.14±0.14	0.00-4.10	0.60±0.55	0.00-7.53	0.55±0.48
	2-Methyl-1-pentene	0.00-0.26	0.06±0.05	0.00-3.64	0.10±0.13	0.00-2.16	0.20±0.23	0.00-5.07	0.50±0.53
	Other alkenes	–	0.15±0.12	–	0.25±0.15	–	0.37±0.34	–	0.24±0.22
	Total alkenes	–	1.85±1.16	–	3.18±2.55	–	5.47±3.64	–	5.88±5.08
	Alkynes	Acetylene	0.14-3.71	0.51±0.49	0.26-6.00	0.90±0.55	0.05-3.52	0.68±0.62	0.05-3.80
Aromatics	Benzene	1.28-10.88	5.41±1.28	0.04-12.90	6.99±1.27	0.95-10.29	4.74±1.95	1.03-7.78	6.04±2.79
	Toluene	0.08-5.22	1.17±0.85	0.04-8.88	1.34±1.03	0.14-12.90	2.00±1.43	0.04-11.17	1.82±1.41
	Ethylbenzene	0.00-1.90	0.40±0.31	0.00-2.28	0.68±0.40	0.00-3.18	0.91±0.74	0.00-3.72	0.76±0.48
	<i>m</i> -Xylenes + <i>p</i> -Xylenes	0.09-4.12	0.80±0.66	0.00-5.31	1.41±0.79	0.00-6.28	1.96±1.53	0.00-7.16	1.28±1.07
	Styrene	0.00-0.37	0.05±0.07	0.00-0.70	0.15±0.15	0.00-0.70	0.05±0.09	0.00-1.23	0.12±0.09
	<i>o</i> -Xylene	0.00-1.18	0.22±0.22	0.00-1.99	0.51±0.39	0.00-3.03	0.63±0.61	0.00-3.39	0.68±0.42
	<i>m</i> -Ethyltoluene	0.00-0.75	0.11±0.09	0.00-1.50	0.16±0.16	0.00-2.50	0.32±0.32	0.00-3.09	0.19±0.14
	1,3,5-Trimethylbenzene	0.05-0.48	0.16±0.05	0.00-0.43	0.13±0.06	0.00-0.91	0.21±0.16	0.00-0.92	0.29±0.16
	1,2,4-Trimethylbenzene	0.00-0.91	0.23±0.13	0.00-1.34	0.38±0.18	0.00-9.07	0.76±0.32	0.00-8.08	0.34±0.23
	<i>o</i> -Ethyltoluene	0.00-0.27	0.06±0.05	0.00-0.38	0.07±0.08	0.00-1.82	0.13±0.25	0.00-3.39	0.23±0.16
	Other aromatics	–	0.19±0.12	–	0.63±0.53	–	1.22±1.19	–	1.57±1.34
	Total aromatics	–	8.80±3.11	–	12.45±7.69	–	12.93±7.55	–	13.32±6.69
	Total VOCs	–	24.72±17.22	–	32.53±17.39	–	34.25±19.90	–	40.27±25.25
Alkanes	–	54.85%	–	49.19%	–	44.29%	–	51.68%	
Alkenes	–	7.48%	–	9.78%	–	15.97%	–	14.60%	
Alkynes	–	2.06%	–	2.77%	–	1.99%	–	0.65%	
Aromatics	–	35.60%	–	38.27%	–	37.75%	–	33.08%	

portant reasons for the higher concentration of total VOCs at night than that during daytime.

2.3. Identification of key species

Hydrocarbons are one of the precursors of the ground-level ozone and SOA formations. Table 3 lists the top 10 key species based on concentration, OFP and SOAFP and their contributions during the observation period. The result showed that there were some differences in the top 10 VOCs species based on concentration, OFP and SOAFP, and their contributions to the total were 65.66%, 71.18% and 81.39%, respectively. The top 10 species from the concentration, OFP and SOAFP both included benzene, toluene, *m*-xylene + *p*-xylene and *p*-ethyltoluene. They mainly came from the use of coatings/solvents and vehicle exhaust emissions (Chen et al., 2019; Huang et al., 2018; Liu et al., 2008). For the concentration, benzene was the largest species, accounting for 15.70%, followed

by propane (11.02%), ethane (9.32%) and *n*-butane (6.77%). Benzene is from fossil fuel combustion sources (Huang et al., 2018; Liu et al., 2008), solvent use sources (Huang et al., 2018; Ma et al., 2019), and vehicle exhaust emission (Huang et al., 2018; Liu et al., 2008). Propane, ethane and *n*-butane are markers of vehicle exhaust emission (Guo et al., 2011; Lai et al., 2009). The top 10 concentration species include 4 alkanes and 4 aromatics, which accounted for 30.66% and 28.08% of the total concentration, respectively. For OFP, ethylene and propene were the largest species, accounting for 14.07% and 11.20% of the total OFP, respectively. Ethylene and propene are the main fuel source tracers (Zhu et al., 2018). The top 10 OFP species include 4 alkenes and 6 aromatics, and their proportion were 35.53% and 35.65%, respectively. For SOAFP, aromatics had 7 species, and the proportion was as high as 65.51%, among which BTEX accounted for 54.13%. Toluene as a solvent is used in furniture, footwear, adhesives, printing and other industries (Liu et al., 2008). Ethylbenzene and

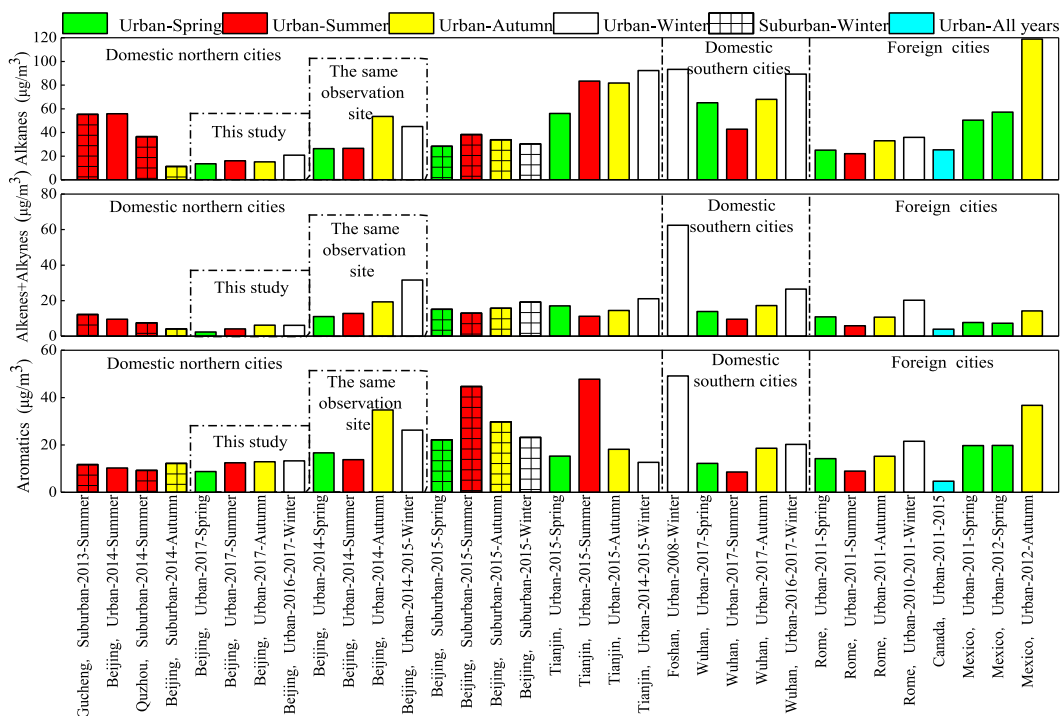


Fig. 2 – Comparison of ambient levels of alkanes, alkenes (alkynes) and aromatics in various cities and forest regions.

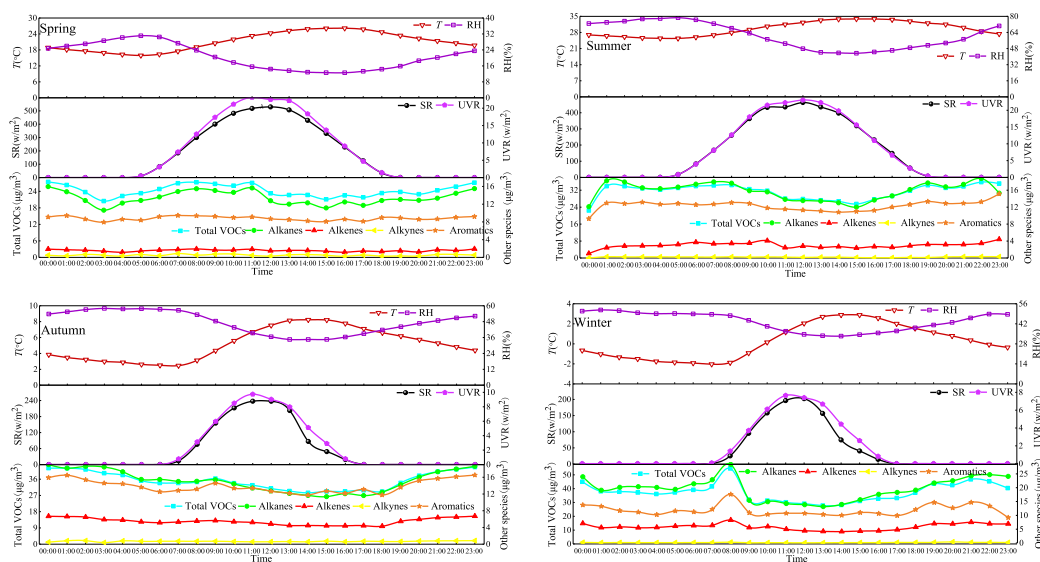


Fig. 3 – Diurnal variation of total VOCs, alkanes, alkenes, alkynes and aromatics and meteorological parameter during four seasonal observation period. SR: solar radiation; T: temperature; UVR: ultra violet radiation; RH: relative humidity.

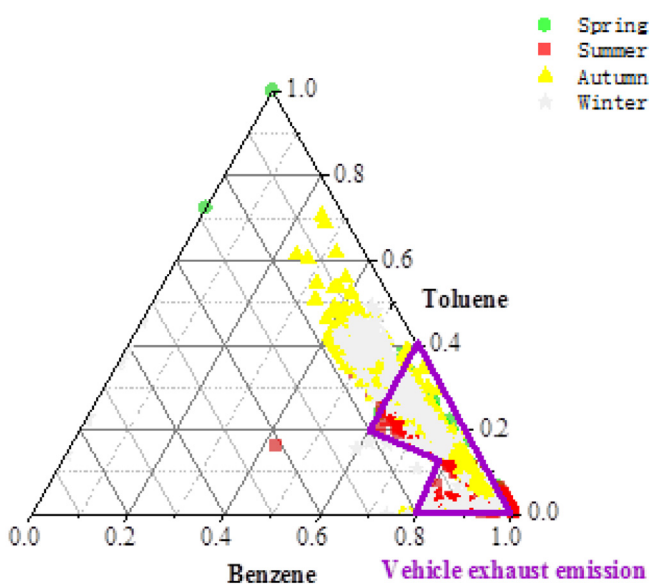
xylenes are mainly used in paints, synthetic fragrances, adhesives and cleaning agents (Huang et al., 2018; Hui et al., 2018; Liu et al., 2008). Therefore, although alkanes and aromatics, especially benzene, propane, ethane and n-butane, were the most abundant species, alkenes and aromatics, especially ethylene and propene, were the key reactive species to OFP, and aromatics especially BTEX were the key reactive species to SOAFP. The vehicle exhaust and paint/solvent use volatiles might be important sources for atmospheric VOCs in Beijing.

2.4. Source identification by PMF

The ratio of toluene and benzene (T/B) has been widely used as a simple method to evaluate the VOCs sources. When T/B value is close to 2, VOCs in ambient air mainly come from vehicle exhaust emissions (Barletta et al., 2008; Na, 2006; Niu et al., 2012). When T/B value is < 2, VOCs from other sources are emitted into the atmosphere in addition to vehicle exhaust emissions (Barletta et al., 2008; Niu et al., 2012). When T/B is > 2, VOCs mainly come from solvent evaporation and combustion sources (Barletta et al., 2008; Niu et al., 2012). This

Table 3 – Top 10 VOCs species based on concentration, ozone formation potential (OFP) and secondary organic aerosol formation potential (SOAFP) and their contributions during the observation period.

Species	Concentration (%)	Species	OFP (%)	Species	SOAFP (%)
Benzene	15.70	Ethylene	14.07	Benzene	18.32
Propane	11.02	Propene	11.20	Toluene	14.86
Ethane	9.32	<i>m</i> -Xylenes + <i>p</i> -Xylenes	10.91	<i>m</i> -Xylenes + <i>p</i> -Xylenes	10.04
<i>n</i> -Butane	6.77	Toluene	7.17	α -Pinene	7.07
Toluene	4.61	<i>cis</i> -2-Butene	6.83	Ethylbenzene	6.43
Ethylene	4.31	<i>p</i> -Ethyltoluene	4.62	<i>p</i> -Ethyltoluene	6.29
<i>m</i> -Xylenes + <i>p</i> -Xylenes	4.01	Benzene	4.78	β -Pinene	5.27
<i>p</i> -Ethyltoluene	3.76	1,2,4-Trimethylbenzene	4.65	<i>o</i> -Xylenes	4.88
2,3-Dimethylbutane	3.55	<i>o</i> -Xylenes	3.52	<i>m</i> -Diethylbenzene	4.69
Propene	2.61	<i>cis</i> -2-Pentene	3.43	<i>n</i> -Dodecane	3.54
Sum of the top 10	65.66	Sum of the top 10	71.18	Sum of the top 10	81.39

**Fig. 4 – Ratio of toluene to benzene (T/B) during four seasonal observation periods.**

method has been adopted by many researchers (Barletta et al., 2005; Na, 2006; Niu et al., 2012; Wang et al., 2012). Fig. 4 shows the ratio of toluene to benzene (T/B) during four seasonal observation periods. The average T/B value in spring, summer, autumn and winter were 0.21 ± 0.13 , 0.19 ± 0.12 , 0.55 ± 0.34 and 0.36 ± 0.24 , respectively in this study. This indicated that there were other sources of VOCs in addition to vehicle exhaust emissions.

In order to provide scientific support, PMF model was applied to identify the VOCs contribution sources during four seasons. Details about the concept, principle and parameters of PMF model can be found in relevant references (Buzcu and Fraser, 2006; Chen et al., 2019; Hui et al., 2018; Lyu et al., 2016; Paatero and Tapper, 1994; Shao et al., 2016). PMF5.0 was used in this study. And 30 species with higher ambient air concentration, strong source indicator and relatively complete monitoring data selected from 59 VOCs species were input into the model for calculation.

Five factors were identified in spring (Fig. 5). Factor 1 explained 15.29% of the contribution and had high loadings of isopentane (95.45%), acetylene (92.90%), propene (86.40%). Methylcyclopentane, 2,3-dimethylpentane, ethylene and *n*-butane occupied certain proportions. Isopentane is typical

tracers of volatile gasoline (Hui et al., 2018; Lau et al., 2010). 2,3-Dimethylpentane is a tracer emitted by the oil industry (Civan et al., 2015; Liu et al., 2008) and *n*-butane is a vehicle exhaust emission marker (Guo et al., 2011; Lai et al., 2009). Therefore, Factor 1 was responsible for the source of gasoline evaporation. Factor 2 explained 11.10% of the contribution and had high loadings of *o*-xylene (86.41%), *m*-ethyltoluene (77.76%), toluene (19.34%), ethylbenzene (17.17%) and *m*-xylene + *p*-xylene (18.35%). Ethylbenzene, *m*-xylene + *p*-xylene and *o*-xylene mainly come from the use of paints, synthetic spices, adhesives and cleaning agents (Huang et al., 2018; Hui et al., 2018; Liu et al., 2008). *m*-Ethyltoluene comes from the coating process in the metal surface treatment industry (Ma et al., 2019). Toluene as a solvent is used in furniture, footwear, adhesives, printing and other industries (Liu et al., 2008). Therefore, Factor 2 was responsible for the source of solvent usage. Factor 3 explained 30.03% of the contribution and had high loadings of ethane (39.46%), ethylene (35.05%), and benzene (26.81%). Propene and propane were lower, but they should not be neglected. Acetylene, 1-butene and ethylene are tracers of combustion source (Brown et al., 2007; Hsu et al., 2018; Liu et al., 2008; Zhu et al., 2018). Propane and ethane are markers of natural gas emissions (Brown et al., 2007; Liu et al., 2008; Zhu et al., 2018). Therefore, Factor 3 was responsible for the combustion source. Factor 4 explained 26.41% of the contribution and had high loadings of propane (64.85%), cyclopentane (50.39%) and *n*-butane (31.26%) (vehicle exhaust emissions marker). C2-C7 linear alkanes, ethylene and BTEX were found. Therefore, Factor 4 was responsible for the gasoline exhaust emission. Factor 5 explained 17.18% of the contribution and had high loadings of *n*-hexane (85.68%), *n*-undecane (45.53%) and *n*-butane (30.60%). BTEX also appeared. Heavy hydrocarbons above C8 are considered as the exhaust gas emission mark of diesel engines (Buzcu and Fraser, 2006; Cai et al., 2010; Liu et al., 2008). Therefore, Factor 5 was responsible for the diesel exhaust emission.

Six factors were identified in summer (Fig. 6). Factor 1 explained 21.84% of the contribution and had high loadings of isopentane (93.22%), propene (92.67%). C2-C5 alkanes such as ethane, *n*-butane (vehicle exhaust emissions marker), 2,3-dimethylpentane (tracer emitted by the oil industry) and acetylene. Benzene were found. Therefore, Factor 1 was responsible for the source of gasoline evaporation. Factor 2 explained 7.13% of the contribution and had high loadings of *m*-ethyltoluene (77.12%), *o*-xylene (64.76%), ethylbenzene (77.12%) and *m*-xylene + *p*-xylene (55.84%). Ethylbenzene, *m*-xylene + *p*-xylene and *o*-xylene mainly come from the use of paints, synthetic spices, adhesives and cleaning agents. *m*-Ethyltoluene comes from the coating process in the metal sur-

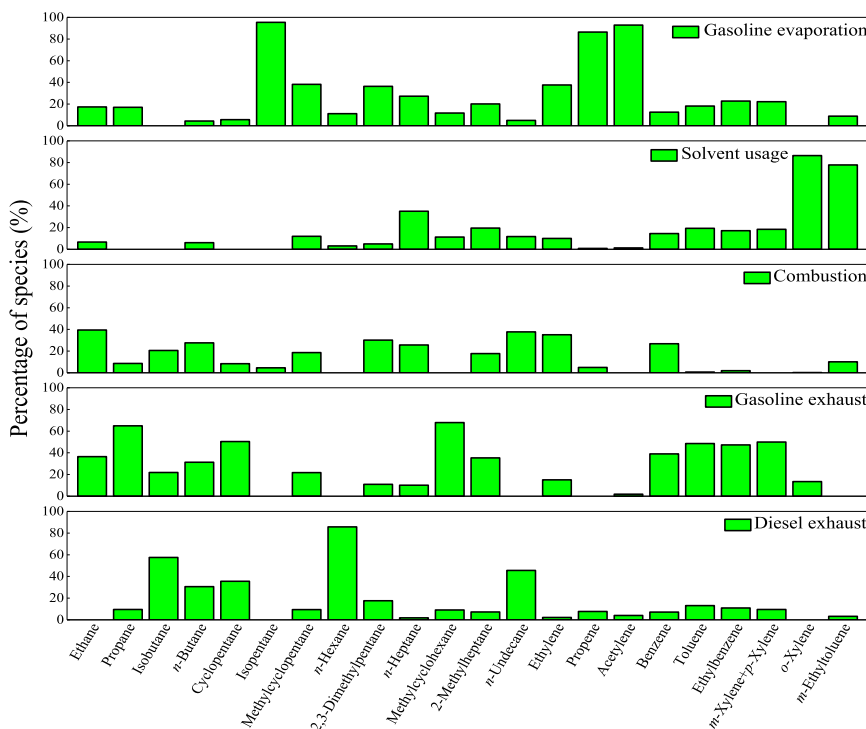


Fig. 5 – Factor profiles of each source in spring.

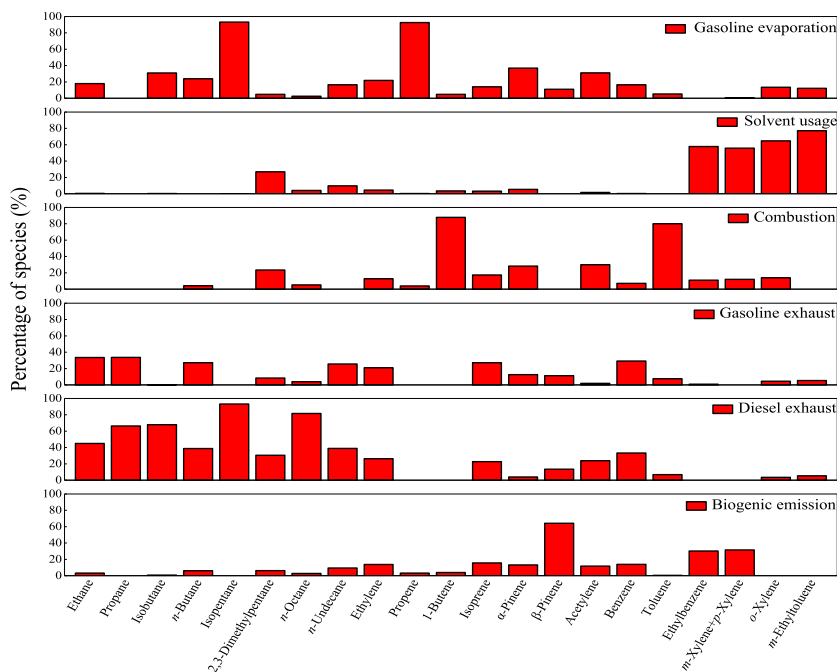


Fig. 6 – Factor profiles of each source in summer.

face treatment industry. Therefore, Factor 2 was responsible for the source of solvent usage. Factor 3 explained 16.00% of the contribution and had high loadings of 1-butene (87.81%) acetylene (29.94%) and ethylene (12.66%). Acetylene, 1-butene and ethylene are tracers of combustion sources. Therefore, Factor 3 was responsible for the combustion source. Factor 4 explained 17.93% of the contribution and had high loadings of alkanes and acetylene, especially C2-C5 linear alkanes such as

ethane (33.48%), acetylene (2.99%). BTEX were found. Therefore, Factor 4 was responsible for the gasoline exhaust emission. Factor 5 explained 23.98% of the contribution and had high loadings of n-octane (81.58%), n-undecane (38.89%), n-butane (38.73%) (vehicle exhaust emissions marker) and benzene (33.18%), propane (33.71%), n-butane (27.10%). And heavy hydrocarbons above C8 are considered as the exhaust gas emission mark of diesel engines. Therefore, Factor 5 was re-

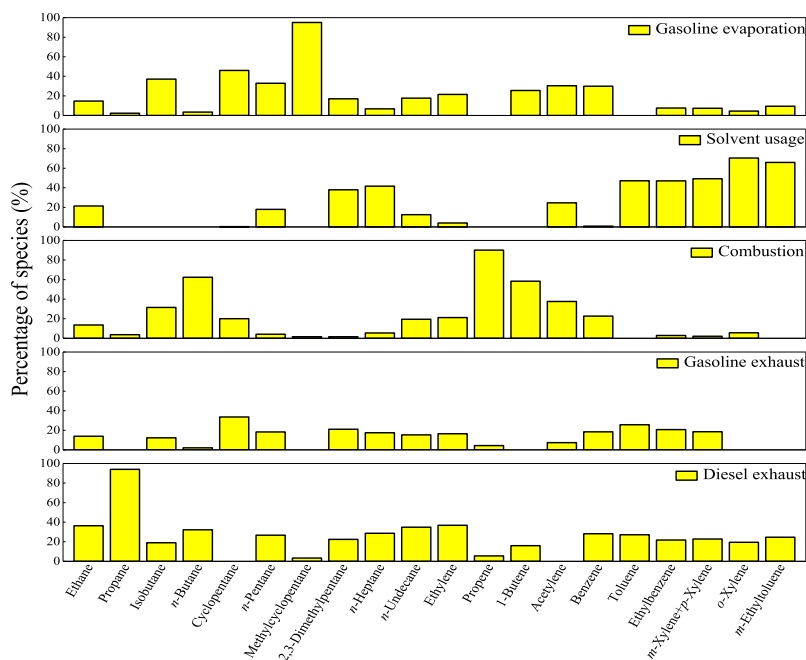


Fig. 7 – Factor profiles of each source in autumn.

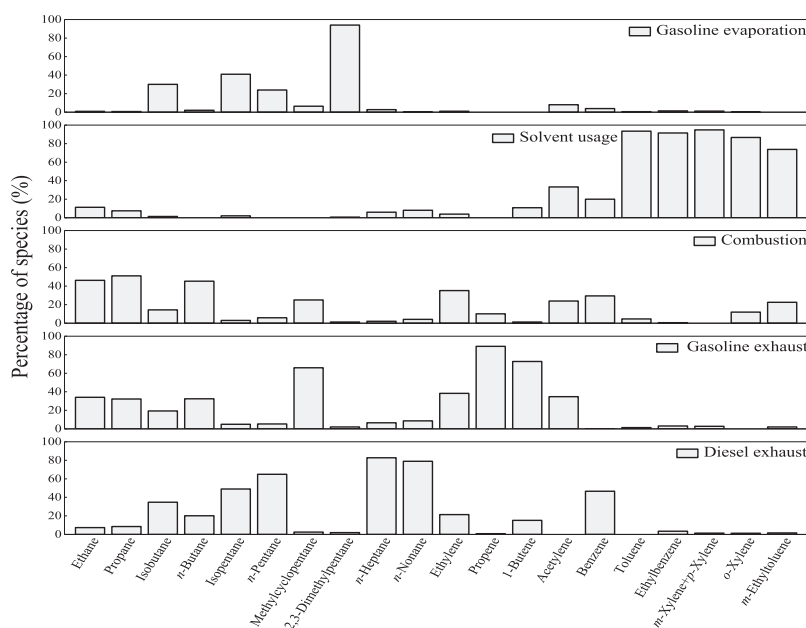


Fig. 8 – Factor profiles of each source in winter.

responsible for the diesel exhaust emission. Factor 6 explained 13.11% of the contribution and had high loadings of β -pinene (64.23%), isoprene (15.57%) and α -pinene (13.13%). Isoprene and monoterpenes (α -pinene and β -pinene) are a common tracer for plant emissions (Wu et al., 2016a; Yurdakul et al., 2013). Therefore, Factor 6 was responsible for the biogenic emission.

It could be found that five factors were also identified during the autumn and winter observations periods (Figs. 7 and 8). Similarly, Factors 1, 2, 3, 4 and 5 were responsible for the source of gasoline evaporation (20.46% and 5.08%, respectively), solvent usage (14.00% and 19.87%, respectively), com-

busation (15.10% and 31.13%, respectively), gasoline exhaust emission (22.52% and 23.43%, respectively) and diesel exhaust emission (27.93% and 20.48%, respectively).

2.5. Identification of key emission sources contributions based on OFP and SOAFP

Estimations of different sources contributions to OFP and SOAFP during four seasonal observation periods are shown in Table 4. Vehicle exhaust (gasoline exhaust and diesel exhaust) emission was found to be the main contributor to ambient VOCs concentrations in Beijing, which were 43.31%, 41.98%,

Table 4 – Estimations of different sources contributions based on OFP and SOAFP during four seasonal observation periods.

Sources	Spring			Summer			Autumn			Winter		
	CON (%)	OFP (%)	SOAFP (%)	CON (%)	OFP (%)	SOAFP (%)	CON (%)	OFP (%)	SOAFP (%)	CON (%)	OFP (%)	SOAFP (%)
Gasoline evaporation	15.20	32.15	16.16	21.82	33.75	11.66	20.46	13.35	9.98	4.98	3.84	1.80
Solvent usage	11.65	16.07	24.85	7.13	19.65	21.83	14.02	26.58	39.54	19.54	31.73	72.98
Combustion	29.83	13.60	36.34	15.97	16.17	21.76	15.04	21.92	6.11	30.66	24.25	11.16
Gasoline exhaust	26.24	27.17	17.06	18.01	7.92	13.27	22.53	14.93	19.12	23.05	24.59	1.29
Diesel exhaust	17.07	11.01	5.60	23.97	11.17	13.79	27.94	23.22	25.25	21.78	15.59	12.77
Biogenic emission	–	–	–	13.10	11.34	17.69	–	–	–	–	–	–
Total	100	100	100	100	100	100	100	100	100	100	100	100

CON: concentration.

50.47% and 44.83% respectively in spring, summer, autumn and winter; and this result was consistent with the result conducted previously in Beijing (Huang et al., 2018). Its contributions to OFP were 38.18%, 19.09%, 38.15% and 40.18% respectively, with the contributions to SOAFP were 22.66%, 27.06%, 44.37% and 14.06% respectively. Thus, vehicle exhaust also accounted for the largest proportions of OFP except summer and it was the biggest contributor to SOAFP except spring and winter. Gasoline evaporation was identified to be the largest source contributor to the OFP in summer, followed by solvent usage. For sources contributed to SOAFP in spring, the largest contributor was combustion and secondary contributor was solvent usage. For sources contributed to SOAFP in winter, solvent usage contributed 72.98%, followed by vehicle exhaust (14.06%). It could be seen that although solvent usage only accounted least proportions of concentration in different seasons (except winter), it was the first two biggest contributors to OFP and SOAFP (except spring). In addition, biogenic emission source was found to be 13.10%, 11.34% and 17.69% contributed to the total VOCs concentration, OFP and SOAFP, respectively.

Although the contribution of vehicle exhaust emissions contributed almost the same to ambient VOCs concentrations in Beijing among different seasons, its contribution to OFP was lower in summer due to the contribution of biogenic emission in summer and the contribution of biogenic emission in other seasons were almost neglectable. The contributions of combustion in spring and winter to ambient VOCs concentrations were found to be much higher than those of summer and autumn might mainly due to the coal burning for heating. The differences of its contributions to OFP and SOAFPs implied to the change of sources for combustions among different seasons. The contributions of gasoline evaporation to concentration, OFP and SOAFP were much lower than those of other seasons due to the lower temperature which has a negative effect on the evaporation.

Therefore, vehicle exhaust and solvent usage must be paid special attention to effectively reduce the O₃ and PM_{2.5} pollution in Beijing. Besides, the combustion during the heating period and gasoline evaporation source during warm seasons should not be overlook. More effective measures must be adopted to reduce the pollution caused by VOCs, such as improving the vehicle exhaust fuel emission standards, usage of oil and gas recovery device in gas station, spraying industry using water paint etc.

3. Conclusions

The distinct seasonal and diurnal variations of atmospheric VOCs in Beijing suggested that diesel vehicle emission dur-

ing the early morning, gasoline vehicle emission at the morning and evening traffic rush hours and coal burning during the heating period were important sources of atmospheric VOCs in Beijing. The significant decrease of the average seasonal concentrations in this study than those in 2014 and 2015 mainly be ascribed to the decrease in source strength due to the implementation of air pollution control measures in the BTH region since 2015. Although benzene, propane, ethane and *n*-butane were the most abundant species, ethylene and propene were the key reactive species to OFP and BTEX were the key reactive species to SOAFP. Vehicle exhaust and solvent usage were identified to be key sources of the O₃ and PM_{2.5} pollution in Beijing. Besides, the combustion during heating period and gasoline evaporation source during warm seasons should not be overlook. Biogenic emission sources can make a non-negligible contribution to the ambient VOCs in summer in Beijing.

Declaration of competing interest

No conflict of interest exists in the submission of this manuscript, and this manuscript is approved by all co-authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication elsewhere, in whole or in part. All the authors listed have approved the manuscript.

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