Characteristics and Source Apportionment of VOCs in a City with Complex Pollution in China

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ABSTRACT

Volatile organic compounds (VOCs) are important precursors in the formation of ozone (O₃) and secondary organic aerosol (SOA). Hence, using an online monitor, we measured the concentrations of 56 VOC species in Handan, one of the most polluted cities in China, from Sep. 2017 till Aug. 2018. We also characterized the VOC pollution by measuring the O₃ and NO_x and determining the chemical reactivity of the VOCs at different levels of O₃ pollution, analyzing the regional O₃ formation mechanisms, and apportioning the VOC sources. The daily VOC concentrations displayed a wide range, from 37.7 to 288.9 µg m⁻³, with an average of 112.0 ± 45.5 µg m⁻³, during the observation period, and the contribution of alkenes and other aromatics to the O₃ formation potential (OFP) of the VOCs was higher on medium pollution days than clean days. Furthermore, the majority of the O₃ during spring and winter was formed in VOC-sensitive regimes, whereas the high diurnal concentrations during summer and autumn were produced in NO_x-sensitive regimes. Based on the *i*-butane/*n*-butane and *i*-propane/*n*-propane ratios, the main sources of butane and propane were vehicular exhaust and liquid gasoline, respectively. Source apportionment by principal component analysis (PCA) revealed that the VOCs in Handan originated from vehicular emission, industrial production, solvent use, gasoline evaporation, and combustion.

Keywords: Volatile organic compounds; Chemical reactivity; Ozone formation; Source apportionment; Handan city.

INTRODUCTION

VOCs are ubiquitous in the atmosphere. With the rapid economic growth, increasing energy consumption and vehicle population, VOCs and O₃ pollution gradually appears in Chinese cities (Wei *et al.*, 2018). VOCs are important precursors for initiating the formation of ground-level O₃, SOA and photochemical smog in atmospheric chemistry (Wei *et al.*, 2016; Wang *et al.*, 2017). The photochemical reaction mechanism of O₃ and its precursors (i.e., VOCs and NO_x) has been widely studied at home and abroad (Kasparoglu *et al.*, 2018; Tan *et al.*, 2018). In particular, regional O₃ pollution has become a major environmental problem in megacities of China, such as Beijing, Zhengzhou, and Shanghai (Gao *et al.*, 2017; Li *et al.*, 2017; Wei *et al.*, 2018). Some VOCs such as benzene and 1,3-butadiene are human toxic which have been listed as carcinogens by the U.S. EPA (U.S. EPA, 1990). VOC pollution characteristics, chemical components and source apportionment are one of the research hotspots in China in

recent years. Many VOCs studies are focused on Yangtze River Delta (YRD), Pearl River Delta (PRD) and Beijing-Tianjin-Hebei (BTH) region (Li *et al.*, 2013; Zhang *et al.*, 2013; Xu *et al.*, 2017). Zheng *et al.* (2013) found that paint manufacturing, wood furniture coating, and metal surface coating are main sources of aromatics and oxygenated VOCs in PRD (Zheng *et al.*, 2013). Wei *et al.* (2018) simulated the impact of VOCs emission of petrochemical industrial zone on the summertime O₃ in Beijing using the WRF-Chem model system (Wei *et al.*, 2018). Gong *et al.* (2017) found VOCs concentrations were higher in the underground subway compared to the above-ground track, and the life carcinogen risk of commuters in subway was above the acceptable level in Shanghai.

Handan locates in the southern margin of Hebei and is the intersectional city of Shanxi, Shandong, Henan and Hebei Province. Its major industries include coal production, iron and steel industry, cement, and chemical industry, which are all dense energy-consumption and emission industries (Meng *et al.*, 2016; Zhao Le and Tan, 2019). Handan was listed in the ten top polluted cities in China since 2013 (Ministry of Ecology and Environment of the People's Republic of China; <http://www.mee.gov.cn/hjzl/>). PM_{2.5} is the major air pollutant in Handan, but the O₃ concentrations showed a rapid increase in recent years. Since 2016, O₃ has replaced PM_{2.5}

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to be the major primary pollutant in summer in Handan. On November 7, 2018, Handan government promulgated the Volatile Organic Compound Prevention and Control Action Plan and set a target of 18 VOCs species reduction from 2018 till 2020 (The People's Government of Heibei Province; <http://info.hebei.gov.cn/eportal/ui?pageId=1981538&articleKey=14459367aa&columnId=6910479>). The limit of VOCs emission will be reduced to 250,000 tons in 2020, > 23% lower than the guideline established in 2015. Many previous studies on air pollution in Handan focused on PM pollution (Wei *et al.*, 2015; Ma *et al.*, 2016; Zhang *et al.*, 2018; Zhe *et al.*, 2019); however, very few studies focused on the increasing VOCs pollution. The objective of this paper to understand the pollution characteristics, chemical reactivity of VOCs in different level of O₃ pollution, formation process of O₃ pollution episode, and source apportionment of VOCs in Handan, to provide policy-making support for future VOCs and O₃ pollution control.

METHODS

Sampling Site and Data Collection

VOCs concentrations were online monitored from Sep. 2017 to Aug. 2018 in Handan (114.5–143.9°E, 36.6–40.8°N). The observation site located on the roof of the Energy and Environment Laboratory, a four-floor building in the campus of Hebei University of Engineering (HEBEU) (36.57°N, 114.51°E), and it is about 10 m above the ground. This site, as show in Fig. 1, is located in the southern urban part of Handan, a typical mixed educational and residential area. There are no obvious emission sources and tall obstacles within 2 km around the site. NO_x and meteorological parameters were measured at the same site. NO_x was measured by 17i chemiluminescent NO-NO₂-NO_x analyzer (Thermo Scientific Co.). The O₃ concentration was obtained from another site in the campus of HEBEU, which was a national observation site. This site was about 650 m southwest from the above observation site.

VOCs concentrations were observed using the instrument of

GC 5000 volatile organic compound online chromatographic monitor manufactured by AMA Instruments (Germany). The monitoring system has been described in detail in other studies (An *et al.*, 2014; Zou *et al.*, 2015). It includes five parts, i.e., GC 5000 VOC (two-stage enrichment), GC 5000 BTX (single-stage enrichment), DIM 200 dynamic calibrator, HG 300, and ZAG 300. GC 5000 VOC (AMA, Germany) online analyzer and GC 5000 BTX (AMA, Germany) online analyzer continuously measured C₂–C₆ hydrocarbons and C₆–C₁₂ hydrocarbons, respectively, with gas chromatography-flame ionization detector (GC-FID) systems. High-purity nitrogen was used as the carrier gas, and the Photochemical Assessment Monitoring Stations (PAMS) standard gas was diluted to 10⁻⁹ volume by DIM 200 for the following analysis. HG 300 is used to obtain H₂ from electrolysis distilled water. ZAG 300 can remove organic impurities by catalytic decomposition of hydrocarbons. At first, sample gas was filtered by particulate filter and dehumidified by dehumidifier tube, then enriched by GC 5000 VOC and GC 5000 BTX, respectively. After that, it went through the focusing tube to the chromatographic column for separation. Finally, FID detector was used for detection. The instrument continuously sampled and analyzed VOCs with a temporal frequency of 1 h. The instruments detect 56 VOCs species, including 29 alkanes, 10 alkenes, 16 aromatics and 1 alkyne.

Quality Control

QC was executed to ensure the accuracy of observation data in the study. In order to avoid the peak shift of the chromatogram, we adjusted the peak of the spectrum on the previous day according to the standard spectrum and export the results to ensure the accuracy of the data. PAMS standard gases were used to calibrate the instrument by multi-point every month. The MDLs (method detection limits) of all VOCs species measured ranged from 0.01–0.16 ppb. If the baseline is not stable, zero gas (nitrogen) is required to remove organic impurity. The mass concentration (μg m⁻³) of each compound was calculated from the mixing ratios in ppbv, using the following Eq. (1) (Wang *et al.*, 2016):

Fig. 1. Location of the observation site in Handan (the red dot is the location of monitoring station).

$$C_i = \frac{M_i \times C'_i}{22.4} \times \frac{273.15}{273.15 + T} \times \frac{B_a}{101.325} \quad (1)$$

where C_i is the concentration of VOCs species in $\mu\text{g m}^{-3}$. The C'_i represents the volume concentration of corresponding VOCs species in ppb. M_i is molecular weight. T and B_a represent the temperature ($^{\circ}\text{C}$) and atmospheric pressure (kPa) during sampling period, respectively.

RESULTS AND DISCUSSION

VOCs Concentrations

Fig. 2 shows the mass concentrations of 56 VOCs species during observation period in Handan. The daily VOCs concentrations had a wide range in a year ($37.7\text{--}288.9 \mu\text{g m}^{-3}$), with the average of $112.0 \pm 45.5 \mu\text{g m}^{-3}$. The concentration

of 2-methylpentane ($11.3 \mu\text{g m}^{-3}$) was the highest among the 29 alkane species, due to the high concentration of 2-methylpentane in summer (the average reached $35.8 \mu\text{g m}^{-3}$), followed by *i*-pentane ($9.9 \mu\text{g m}^{-3}$) and ethane ($8.7 \mu\text{g m}^{-3}$). The BTEX had the highest concentration in aromatics ($16.2 \mu\text{g m}^{-3}$), accounting for 61.8% in total aromatics. Toluene had the highest concentration ($5.6 \mu\text{g m}^{-3}$) in all aromatics. In the observation period, the concentrations of the VOCs groups were listed as alkanes > aromatics > alkenes > alkynes, of the concentrations of $63.1 \mu\text{g m}^{-3}$, $26.2 \mu\text{g m}^{-3}$, $18.2 \mu\text{g m}^{-3}$, $4.6 \mu\text{g m}^{-3}$, respectively.

Fig. 3(a) presents the seasonal variations of the 4 major VOCs. The concentrations of alkanes reached highest in summer and lowest in spring, and the concentrations in summer was 43.3% higher than in spring. Aromatic concentrations in autumn and winter were higher than that in the other two seasons. The concentrations of alkenes in winter was 2.5 times

Fig. 2. Box plots of VOCs in Sep. 2017–Aug. 2018 in Handan ($\mu\text{g m}^{-3}$) (the yellow, blue, green and red box chart represent alkanes, alkenes, aromatics, and alkynes, respectively).

Fig. 3. (a) Seasonal variations of VOCs and their component concentrations. (b) VOCs and their component concentrations in winter: long-chain alkanes have a $C > 4$; other aromatics refers to aromatics except BTEX in this study.

higher than that in summer. The total VOCs concentrations during observation as following trend: winter > autumn > summer > spring. This was likely due to the variations of the ambient temperature, sunlight, the meteorological factors and the different emission strength of atmospheric pollutants during different seasons (Liu *et al.*, 2016). The concentrations of VOCs in winter was highest, in which the short-chain alkanes ($C \leq 4$) accounted for 57.3% in total alkanes, and short-chain alkenes ($C \leq 4$) accounted for 88.4% of total alkenes. The long-chain alkene ($C > 4$) concentrations were very low ($3.9 \mu\text{g m}^{-3}$) in winter (Fig. 3(b)). BTEX was the abundant group in aromatics, which accounted for 70.5% in aromatics with the average concentration of $24.2 \mu\text{g m}^{-3}$. Light alkanes and short-chain alkenes contributed most of VOCs in winter.

Table 1 presents the comparison of VOCs concentrations and the other reported cities (Liu *et al.*, 2014; Chang *et al.*, 2015; Wang *et al.*, 2016; Hu *et al.*, 2018; Bozkurt *et al.*, 2018; Bari and Kindzierski, 2018; Yurdakul *et al.*, 2018). VOCs concentrations in Handan were higher than Chinese cities such as Beijing, Jinan, and Hefei. However, the major VOCs species in the four seasons in Handan were similar to those in other Chinese cities, e.g., both alkanes and aromatics were the major species (except Shijiazhuang). The VOCs concentrations in winter of Shijiazhuang was 1.3 times higher than that in Handan. Solvent use for pharmaceutical and chemical were major VOCs sources in Shijiazhuang (Chang *et al.*, 2015). Düzce and Calgary had lower VOCs concentrations than that in Handan. Major VOCs species in

Table 1. Comparison of VOCs concentrations in Handan and in other cities.

City	Period	VOCs concentrations ($\mu\text{g m}^{-3}$)	Major pollutants	Instrument/detector	Reference
Handan, China	Spring	88.8	<i>i</i> -Pentane (13.8%), ethene (7.8%), ethane (7.7%), propane (7.6%)	GC 5000	This work
	Summer	105.2	2-Methylpentane (34%), <i>i</i> -pentane (15.3%), isoprene (3.7%), ethane (3.2%)		
	Autumn	123.04	Ethene (11.3%), ethane (7.7%), <i>n</i> -dodecane (7.7%), toluene (5.7%)		
	Winter	136.6	Ethene (17.8%), ethane (12.1%), propane (8.2%), benzene (6.7%)		
Beijing, China	Nov. 2014	27.6	Aromatics (44.2%), alkanes (40.9%)	GC-MS	(Wang <i>et al.</i> , 2016)
Shijiazhuang, China	Jan. 2014–Apr. 2014	309.9	Aromatics (31%), halohydrocarbons (30.7%)	Agilent 6890N/5975B	(Chang <i>et al.</i> , 2015)
Jinan, China	Jun. 2010–May 2012	53.1	Cyclopentane (14.3%), <i>i</i> -pentane (9.7%), toluene (9.5%), propane (8.1%)	airmo VOC	(Liu <i>et al.</i> , 2014)
Hefei, China	Sep. 2016–Jan. 2017	57.31	Toluene (19.2%), chloroethene (14.2%), benzene (14.0%), dichloromethane (13.4%), 1,2,4-trimethylbenzene (13.3%)	GC-MS	(Hu <i>et al.</i> , 2018)
Düzce, Turkey	Spring	13.5	BTEX (31.1%)	Thermal desorber GC-FID GC-MS	(Bozkurt <i>et al.</i> , 2018)
	Summer	11.6	BTEX (29.1%)		
	Autumn	20.9	BTEX (39%)		
	Winter	29.8	BTEX (50.4%)		
Bursa, Turkey	Mar. 17, 2006–May 10, 2006	86.0	Toluene (30%), <i>m,p</i> -xylene (7.4%), benzene (4.3%)	Agilent Model 6890	(Yurdakul <i>et al.</i> , 2018)
Calgary, Canada	2010–2015	38.6	Ethane (15.1%), propane (12.3%), <i>n</i> -butane (9.7%)	GC-MS	(Bari and Kindzierski, 2018)

Düzce were BTEX, but it still lower than BTEX concentrations in Handan. In the spring, the VOCs concentrations in Bursa was similar to that in Handan, while major VOCs pollutants were different (Table 1).

Chemical Reactivity of VOC in Different Levels of O₃ Pollution

VOCs are important precursor of O₃ formation in atmospheric environment. It report that the O₃ concentration and exceeding-standard days in 2018 obviously increased compared to those in 2017 (Ministry of Ecology and Environment of the People's Republic of China; <http://www.mee.gov.cn/hjzl/>). The O₃ pollution levels in four seasons in Handan were shown in Fig. 4. 160 µg m⁻³ and 215 µg m⁻³ are limits of Grade II and III standard of National Ambient Air Quality Standard (NAAQS). We separate the days into *clean period* (defined as the maximum 8-h O₃ concentration being less than 160 µg m⁻³), *mild pollution* (defined as the maximum 8-h O₃ concentration being between 160–215 µg m⁻³), *medium pollution* (defined as the maximum 8-h O₃ concentration exceeding 215 µg m⁻³). It can be seen there was no excessive O₃ in winter and a few days exceeded the standard in autumn. The mild pollution days account for 37% total days in spring. More than half of days were under O₃ pollution in summer, with medium O₃ pollution account for 20.7% in total days. Therefore, this study only discussed O₃ pollution in summer.

O₃ is an important product of photochemical reaction of VOCs and NO_x in atmosphere. In order to determine the role of VOCs in O₃ photochemistry, we evaluated OFP for 55 VOCs (except acetylene). MIR (maximum incremental reactivity) considers the maximum number of O₃ molecules generated by given VOCs species, as well as the interaction between kinetic reactivity and mixtures. The calculation Eq. (2) is given as below:

$$\text{OFP}(A) = \text{MIR}(A) \times C(A) \quad (2)$$

where $C(A)$ represents the mass concentration (µg m⁻³) for species A. The MIR (g-O₃ g-VOCs⁻¹) value for each species can be found by Carter (1994).

Prop-Equiv method put all VOCs species on a baseline to

compare their reaction activity. In order to estimate the VOCs reaction activity according to their kinetic reactivity, Prop-Equiv concentration for each VOC species were calculated by following Eq. (3) (Lawrimore et al., 1995):

$$\text{Prop-Equiv}(A) = \frac{C(A) \times \text{KOH}(A)}{\text{KOH}(C_3H_6)} \quad (3)$$

where $\text{KOH}(A)$ is the rate constant for the reaction of VOC species A with OH radical; and $\text{KOH}(C_3H_6)$ is the rate constant for C₃H₆ with OH radical. The specific values of rate constant for VOCs can be seen in references (Atkinson and Arey, 2003).

Fig. 5 shows the OFP and Prop-Equiv concentration of six VOCs groups during clean period, mild pollution and medium pollution days in summer in Handan. It can be seen that the rank of OFP and Prop-Equiv percentages of the six VOCs groups have different change under three pollution level. OFP followed the order of long-chain alkenes > long-chain alkenes > short-chain alkenes > other aromatics > BTEX > short-chain alkenes. Prop-Equiv concentrations were long-chain alkenes > long-chain alkenes > BTEX > short-chain alkenes > other aromatics > short-chain alkenes. It should be noted that the OFP of long alkenes were the highest among the six VOCs groups, partially due to that 2-methylpentane concentration was quite high, with 28.3–37.5% of total VOCs concentrations (Fig. 6). Therefore, long alkenes and alkenes play an important role in O₃ formation in summer in Handan.

The OFP of long-chain alkenes and short-chain alkenes in medium pollution were 7.3 µg m⁻³ and 6.3 µg m⁻³ higher than that in clean period, respectively. The OFP of short-chain alkenes and other aromatics were higher in medium pollution than in other two conditions. In especially, the OFP of short-chain alkenes were 45.3 µg m⁻³. But OFP of long-chain alkenes in O₃ pollution days were lower than the other two pollution levels. The proportion of Prop-Equiv concentration of long-chain alkenes and BTEX in medium pollution was higher than that in clean period. The results of Prop-Equiv method are basically consistent with OFP. Thus it can be seen alkenes and other aromatics were more important in O₃ medium days.

Fig. 4. The percentages of O₃ pollution days in the four seasons in Handan.

Fig. 5. Chemical reactivity of major VOC components in different O_3 pollution level in Handan: (a) clean period, (b) mild pollution, and (c) medium pollution.

Prop-Equiv concentrations and OFP of major VOCs as well as their concentrations under different O_3 pollution levels in summer in Handan were presented in Fig. 6. Isoprene, 2-methylpentane and *o*-xylene have high Prop-Equiv

concentrations with strong chemical reaction activity in summer. 2-Methylpentane, isoprene, ethene and *i*-pentane are major contributors to form O_3 . In particular, the concentration of isoprene accounted for 3.4–4.1% of VOCs, while its OFP

Fig. 6. Percentages of the concentrations, OFP and Prop-Equiv concentrations of major VOCs under different levels of O_3 pollution in Handan: (a) clean period, (b) mild pollution, and (c) medium pollution.

accounted for 30–35% in total OFP. Toluene and xylene were the top contributors of O_3 formation among aromatic, which was consistent with previous work (Tan *et al.*, 2012; Kumar *et al.*, 2017). It can be seen that the OFP of *i*-pentane, ethene and *o*-xylene were lower in clean period than that in mild pollution days and medium pollution days, while 2-methylpentane was the opposite. The OFP for VOCs in medium pollution ($250.4 \mu\text{g m}^{-3}$) was not significantly higher than that in mild pollution ($249.2 \mu\text{g m}^{-3}$). It implies that VOCs were not the main factor of medium O_3 formation in summer. NO_x also had important effect on O_3 concentration, which verifies the assumption in the following sections.

Regional O_3 Formation Mechanism

The concentration variations and hourly change rates of O_3 can better illustrate diurnal variations and formation processes of O_3 . The value of change rate can be calculated using following Eq. (4):

$$\frac{d[X]}{Dt} = [X]_t - [X]_{t-1} \quad (4)$$

where $[X]_t$ is the concentration of O_3 at time t , $[X]_{t-1}$ represents the concentrations for the last hour before time t .

The ratio of VOCs and NO_x can be used to qualitatively evaluate the relationship between O_3 and its precursors (VOCs and NO_x). Assessing whether the city is VOC-sensitive or NO_x -sensitive is necessary to effectively control O_3 pollution. Under typical atmospheric conditions, the reaction rate constants between NO_x and OH (1.7×10^{10}) is 5.5 times that of VOC and OH (3.1×10^9) (Tang *et al.*, 2006). When the emission ratio of VOC/ NO_x is 5.5, photochemical reactions of O_3 are in equilibrium (Chen *et al.*, 2019). For the ratio to be valid, the VOCs concentration must be expressed on per-carbon-atom basis (Sinha *et al.*, 2012). Fig. 7 shows the diurnal variation of O_3 concentration, VOC/ NO_x and VOC(OFP)/ NO_x ratios, change rate of O_3 in four seasons

Fig. 7. The diurnal variation of O_3 concentration, VOC/ NO_x and VOC(OFP)/ NO_x ratios, change rate of O_3 in different seasons in Handan (the blue line is the VOC (ppbc)/ NO_x (ppb) ratio of 5.5:1).

Fig. 7. (continued).

for one year. In spring and winter, the VOC/NO_x ratios were more than 5.5 from 10:00 to 16:00 LT, and the ratio of the other time of the day were less than 5.5. This illustrates that O_3 formation mainly occurred under the VOC-sensitive regime. At this time, the reaction rate of NO₂ with OH is higher than VOCs with OH, and the reaction can remove OH from VOC oxidation cycle. Under this condition, reducing NO_x emission will bring more O_3 . In summer, the ratio reached a relatively high level from 07:00 to 22:00 LT, with the average of 12:1. Except the period from 05:00 to 08:00 LT, the ratio was greater than 5.5 in autumn with average of 9. In those two seasons the O_3 formation was under the NO_x-sensitive regime, that is, reducing NO_x is beneficial to the reaction of peroxide radicals (HO₂ and RO₂) and hinders the formation of O_3 .

The maximum ratio of VOC/NO_x and VOC(OFP)/NO_x appeared around 13:00 LT in each season and their trends are similar. The VOC(OFP)/NO_x ratio is 1.5 times of VOC/NO_x in the four seasons. We also find that the ratio of VOC(OFP)/NO_x and VOC/NO_x will decrease with the increase of O_3 pollution frequency. The VOC(OFP)/NO_x

ratio is 1.3 times of VOC/NO_x in summer. Fig. 7 presents the change rate of O_3 began to increase at 07:00 LT, reaching a maximum three hours later. At about 15:00 LT, the O_3 concentrations reached the maximum in all the four seasons, which is a typical process of O_3 accumulation in atmosphere. The O_3 concentration is much higher in summer than that in other three seasons, especially from 12:00 to 18:00 LT. In the high- O_3 episode, the O_3 chemistry was under the NO_x-sensitive regime, which is similar to previous studies in Guangzhou (Zou *et al.*, 2015) and Pearl River Delta region (Li *et al.*, 2013).

Fig. 8 shows diurnal variation of VOC/NO_x ratio during clean period, mild pollution and medium pollution days in summer. The diurnal variation trend and value of VOC/NO_x ratio in mild pollution and medium pollution days were similar. The VOC/NO_x in clean period were highest in the three pollution levels, however, the O_3 concentration was much higher in medium pollution days than those in clean period and mild pollution days. Considering the conclusions with OFP of VOCs, the OFP in the three pollution levels have no significant difference. NO_x average concentration

Fig. 8. The diurnal variation of VOC (ppbc)/NO_x (ppb) ratio in different O₃ pollution levels in Handan (the black line is the VOC (ppbc)/NO_x (ppb) ratio of 5.5:1).

in medium pollution days were $14 \mu\text{g m}^{-3}$ higher than clean period. Therefore, it can be concluded that NO_x and VOCs dominated the O₃ formation, especially in medium pollution. Whether there is regional O₃ transmission remains to be proved.

Ambient Ratios: Photochemical Characteristics and Sources

The change in concentration ratio of special hydrocarbon can reflect their atmospheric photochemical processes, and effect of atmospheric physical transmission is eliminated by their ratio (Nelson and Quigley, 1983). The photochemical age of air masses can be described by the measured ratio between benzene and toluene. Using the observed ratio, the photochemical age of sampled air masses was estimated as following Eq. (5) (Roberts *et al.*, 1984):

$$t = \frac{1}{[\text{OH}](K_{\text{toluene}} - K_{\text{benzene}})} \times \left[\ln \left(\frac{[\text{toluene}]}{[\text{benzene}]} \right)_{t=0} \right] - \ln \left(\frac{[\text{toluene}]}{[\text{benzene}]} \right) \quad (5)$$

where [OH] is the 24-h average concentration of OH, i.e., $3 \times 10^6 \text{ molecules cm}^{-1} \text{ s}^{-1}$. K_{toluene} and K_{benzene} represent the coefficients for the reaction of OH with toluene and benzene, the values were $5.63 \times 10^{-12} \text{ molecules cm}^{-1} \text{ s}^{-1}$ and $1.22 \times 10^{-12} \text{ molecules cm}^{-1} \text{ s}^{-1}$, respectively (Atkinson and Arey, 2003). $[\text{toluene}]/[\text{benzene}]$ is ratio between toluene and benzene of observation. The ratio $([\text{toluene}]/[\text{benzene}])_{t=0}$ is the initial concentration ratio. The concentrations of toluene and benzene in ratio $[\text{toluene}]/[\text{benzene}]_{t=0}$ were estimated from the 5th percentile of the observation at 07:00 LT in this study (Li *et al.*, 2019).

The assumption that the source of anthropogenic VOCs removal is governed by reactions with OH implies that any two compounds with the similar OH rate coefficient must be well correlated (de Gouw *et al.*, 2005). As shown in Fig. 9(a), the scatter plot of benzene versus acetylene painted by photochemical age shows that a good correlation of benzene and acetylene with correlation coefficient of 0.7. The ethylbenzene and acetylene are positively correlated (Fig. 9(b)), however, the correlation coefficient ($r = 0.54$) is less than that of benzene and acetylene. We also found that the ethylbenzene/acetylene ratio decreased with increasing photochemical age (slope = -8.06), while the ratio of benzene and acetylene increased with photochemical age (slope = 2.1). The reason is that the removal efficiency of ethylbenzene in the atmosphere is faster than toluene, the removal rate of ethylbenzene is about 6 times larger than benzene. The scatter plot of propane versus *n*-butane and *i*-butane were also colored by photochemical age (Figs. 9(c) and 9(d)). The two figures show good correlation of both *n*-butane and *i*-butane with propane, especially correlation coefficient of *n*-butane with propane is 0.93, indicating *n*-butane and propane have similar source. Propane and butane are main components of liquefied petroleum gas (LPG)/nature gas (NG) (McCarthy *et al.*, 2013; Baudic *et al.*, 2016). The *n*-butane and *i*-butane have similar reaction rates with the OH radicals, the ratio of these pair species indicated different sources (Huang *et al.*, 2018). Previous studies have shown that *i*-butane/*n*-butane ratio varied according to sources: ~ 0.2 – 0.3 for urban vehicular exhaust, 0.46 for LPG, ~ 0.6 – 1 for NG (Barletta *et al.*, 2002; Russo *et al.*, 2010). Our result indicated the slope of *i*-butane/*n*-butane (0.23 – 0.47) within the range of emission mainly from vehicular exhaust and LPG (Fig. 10(a)), this is relative to the actual situation, LPG is the fuel for taxis and private cars in Handan. As shown in Fig. 10(b), the slope of the correlation

Fig. 9. Scatter plots of acetylene versus (a) benzene and (b) ethylbenzene, and propane versus (c) *n*-butane and (d) *i*-butane. The scatter points are painted by photochemical age.

Fig. 10. Correlations between compounds with similar atmospheric lifetimes: (a) *n*-butane versus *i*-butane, and (b) *n*-pentane versus *i*-pentane.

of *i*-pentane and *n*-pentane (−0.29) in summer was quite different other seasons (1.42–1.73), so we speculated that pentane were from liquid gasoline source in spring, autumn and winter in term of the ratio (~1.5–3) (Russo *et al.*, 2010).

Source Apportionment

PCA, as one of the receptor models, is applied for solving a bilinear model by analyzing multivariate dataset. PCA is based on correlation matrix analysis to find the independent factors in large number of components. The number of principal components depends on the retained variance. The calculation procedures of PCA can refer to Meng *et al.* (2016). In recent years, many researches applied this model to analyze VOCs sources (Chang *et al.*, 2009; An *et al.*, 2014; Franco *et al.*, 2015; Meng *et al.*, 2016).

The top 20 VOCs species account for more than 80% of total VOCs concentrations in this study; therefore, we select the top 20 kinds of VOCs to analyze source by statistical software SPSS 21 in four seasons. The Kaiser-Meyer-Olkin (KMO) index detected by input data was more than 0.8 and the sphericity test of Bartlett is 0. It indicates that the PCA model can be applied in this study. The factors were extracted with eigenvalue more than 1. Tables S1–S4 list the results of PCA model in four seasons. The cumulative variances of factors were 72.5% (spring), 76.4% (summer), 72% (autumn) and 81% (winter), which covered most of the information of data.

Table 2 show the source apportionment for VOCs in different seasons. Table S1 shows that there are five factors in spring. Factor 1 is identified as butane, propane, and *n*-pentane, 2-methylpentane and toluene, *m,p*-xylene with obvious loading of 0.6–0.9. The butane and propane are released from LPG/NG (McCarthy *et al.*, 2013; Lyu *et al.*, 2015), Handan implemented the project of replacing coal with gas from 2017. Therefore, the usage and emission of LPG/NG began to increase. While toluene, *m,p*-xylene and 2-methylpentane are likely to be from solvent use. Toluene and xylene are widely used as in printing, furniture and adhesives (Buzcu and Fraser, 2006; Ling *et al.*, 2011), and long-chain alkane may be from industrial production (Shao *et al.*, 2016). The variance of vehicle emission contributed 27%. For Factor 2, ethene, ethane and benzene were weighted relatively higher, the three compounds are important markers of combustion sources (Liu *et al.*, 2008; Hui *et al.*, 2019). While benzene

originate from automobile exhaust in urban area. Therefore, Factor 2 can be regard as automobile exhaust about combustion. Factor 3 only consists of *n*-dodecane and *p*-diethylbenzene, the compounds containing > 10 carbon atoms are from diesel vehicle (Liu *et al.*, 2008). Factor 4 includes *n*-hexane, styrene and *i*-pentane. *n*-Hexane and *i*-pentane could be attributed to temperature-related source or artefacts (Leuchner *et al.*, 2015; Baudic *et al.*, 2016), and styrene may originate from petrochemical plants and solvent usage (Chang *et al.*, 2009). Therefore, Factor 4 represents industrial source. For Factor 5, 2,2-dimethylbutane and *m*-diethylbenzene is identified as solvent in industrial manufacture (An *et al.*, 2014; Baudic *et al.*, 2016).

The main sources of factor analysis in summer, autumn and winter are listed in Tables S2–S4. There are six VOC sources and variance in summer: Factor 1 is gasoline evaporation (20.7%); Factor 2 is solvent use (18.7%); Factor 3 is automobile exhaust (14.5%); Factor 4 is industrial production (10.9%); Factor 5 is diesel vehicle (6.3%); Factor 6 is biogenic emission (5.5%). Five sources are found in winter: Factor 1 is solvent use and fuel volatilization (36.7%); Factor 2 is gasoline vehicle emission (15.5%); Factor 3 is industrial (8%); Factor 4 is diesel vehicle (6.6%); Factor 5 is biomass combustion (5.1%). In winter there are four primary sources: Factor 1 is LPG and solvent use (36.5%); Factor 2 is combustion (internal combustion engine emission and fossil fuel combustion) (30.5%); Factor 3 is industrial (8.1%); Factor 4 is diesel vehicle (5.9%).

CONCLUSIONS

In this study, we observed the concentrations of the VOCs, as well as the gaseous pollutants O₃ and NO_x, online in Handan, one of the most polluted cities in China, from Sep. 2017 till Aug. 2018. Furthermore, we characterized the VOC pollution by determining the chemical reactivity of the VOCs, the individual VOCs' contributions to the O₃ formation, and the associated source apportionment.

The annual VOC concentration in Handan was 112.0 ± 45.5 µg m^{−3} on average, which exceeded the values reported for other Chinese cities (Beijing, Jinan, and Hefei) and foreign cities (Düzce and Calgary). The composition of the VOCs consisted of alkanes > aromatics > alkenes > alkynes, and

Table 2. Source apportionment of VOCs in four seasons.

Source	PC1	PC2	PC3	PC4	PC5	PC6
Spring	LPG/NG and solvent use (27.0%)	Automobile exhaust (12.5%)	Diesel vehicle (11.8%)	Industrial (11.6%)	Solvent use (9.6%)	
Summer	Gasoline evaporation (20.7%)	Solvent use (18.7%)	Automobile exhaust (14.5%)	Industrial (10.9%)	Diesel vehicle (6.3%)	Biogenic (5.5%)
Autumn	Solvent use and fuel volatilization (36.7%)	Gasoline vehicle emissions (15.5%)	Industrial (8%)	Diesel vehicle (6.6%)	Biomass combustion (5.1%)	
Winter	LPG/NG and solvent use (36.5%)	Combustion (internal combustion engine emission and fossil fuel; 30.5%)	Industrial (8.1%)	Diesel vehicle (5.9%)		

the concentrations exhibited clear seasonality, following the order of winter > autumn > summer > spring, with the values being 0.5 times higher during winter than spring.

A high incidence of O₃ pollution was observed during summer, with the OFP of alkenes and other aromatics simultaneously increasing during medium pollution days. As the concentration of the O₃ rose, the chemical reactivity of isoprene, *i*-pentane, and ethene notably climbed as well. The diurnal variation in the VOC/NO_x ratio indicates that the O₃ during spring and winter generally formed in VOC-sensitive regimes, whereas high diurnal concentrations during summer and autumn, including an episode during which the 8-h concentration exceeded the Stage II limit specified by NAAQS, were generated in NO_x-sensitive regimes.

The removal rate for ethylbenzene exceeded that of benzene: The ethylbenzene/acetylene ratio increased with the photochemical age, but the benzene/acetylene ratio displayed the opposite trend. The ambient ratios for *i*-butane/*n*-butane and *i*-pentane/*n*-pentane revealed that vehicular exhaust and liquid gasoline were the primary sources of butane and propane, respectively, during the observation period.

PCA identified the major VOC sources in Handan as industrial emissions, solvents, evaporated gasoline, and vehicular emissions. Their respective contributions varied slightly by season: High temperatures were conducive to gasoline and solvent evaporation during summer and autumn, and biogenic emissions were also more prominent during summer. During winter, however, the fraction from combustion increased significantly.

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DISCLAIMER

The authors declared that there are no conflict interest of reference to any companies or specific commercial products.

SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <https://doi.org/10.4209/aaqr.2019.11.0608>

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