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 NOx 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 NOx-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 NOx) 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/). PM2.5 is the major air pollutant in Handan, but the O3 concentrations showed a rapid increase in recent years. Since 2016, O3 has replaced PM2.5

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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 Hebei Province; http://info.hebei.gov.cn/eportal/ui?pageld=1981538&amp;articleKey=14459367a&amp;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 (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.

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. NOx and meteorological parameters were measured at the same site. NOx was measured by 17i chemiluminescent NO-NO2-NOx 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).](image-url)
\[ C_i = \frac{M_i \times C'_i \times 273.15}{22.4 \times 273.15 + T} \times \frac{B_o}{101.325} \]  

(1)

where \( C_i \) is the concentration of VOCs species in \( \mu g \) \( m^{-3} \). The \( C'_i \) represents the volume concentration of corresponding VOCs species in ppb. \( M_i \) is molecular weight. \( T \) and \( B_o \) represent the temperature (°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 (37.7–288.9 \( \mu g \) \( m^{-3} \)), with the average of 112.0 ± 45.5 \( \mu g \) \( m^{-3} \). The concentration of 2-methylpentane (11.3 \( \mu g \) \( m^{-3} \)) was the highest among the 29 alkane species, due to the high concentration of 2-methylpentane in summer (the average reached 35.8 \( \mu g \) \( m^{-3} \)), followed by \( i \)-pentane (9.9 \( \mu g \) \( m^{-3} \)) and ethane (8.7 \( \mu g \) \( m^{-3} \)).

The BTEX had the highest concentration in aromatics (16.2 \( \mu g \) \( m^{-3} \)), accounting for 61.8% in total aromatics.

Toluene had the highest concentration (5.6 \( \mu g \) \( m^{-3} \)) 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 \( \mu g \) \( m^{-3} \), 26.2 \( \mu g \) \( m^{-3} \), 18.2 \( \mu g \) \( m^{-3} \), and 4.6 \( \mu g \) \( m^{-3} \), 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 concentration in autumn and winter were higher than that in the other two seasons. The concentrations of alkenes in winter was 2.5 times...
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 ≤ 4) accounted for 57.3% in total alkanes, and short-chain alkenes (C ≤ 4) accounted for 88.4% of total alkenes. The long-chain alkene (C > 4) concentrations were very low (3.9 µg 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 µg 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 Shijiazhuan). The VOCs concentrations in winter of Shijiazhuan was 1.3 times higher than that in Handan. Solvent use for pharmaceutical and chemical were major VOCs sources in Shijiazhuan (Chang et al., 2015). Düzce and Calgary had lower VOCs concentrations than that in Handan. Major VOCs species in

<table>
<thead>
<tr>
<th>City</th>
<th>Period</th>
<th>VOCs concentrations (µg m⁻³)</th>
<th>Major pollutants</th>
<th>Instrument/detector</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Handan, China</td>
<td>Spring</td>
<td>88.8</td>
<td>i-Pentane (13.8%), ethene (7.8%), ethane (7.7%), propane (7.6%)</td>
<td>GC 5000</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>105.2</td>
<td>2-Methylpentane (34%), i-pentane (15.3%), isoprene (3.7%), ethane (3.2%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>123.04</td>
<td>Ethene (11.3%), ethane (7.7%), n-dodecane (7.7%), toluene (5.7%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>136.6</td>
<td>Ethene (17.8%), ethane (12.1%), propane (8.2%), benzene (6.7%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Nov. 2014</td>
<td>27.6</td>
<td>Aromatics (44.2%), alkanes (40.9%)</td>
<td>GC-MS</td>
<td>(Wang et al., 2016)</td>
</tr>
<tr>
<td>Shijiazhuan, China</td>
<td>Jan. 2014–Apr. 2014</td>
<td>309.9</td>
<td>Aromatics (31%), halohydrocarbons (30.7%)</td>
<td>Agilent 6890N/5975B</td>
<td>(Chang et al., 2015)</td>
</tr>
<tr>
<td>Jinan, China</td>
<td>Jun. 2010–May 2012</td>
<td>53.1</td>
<td>Cyclopentane (14.3%), i-pentane (9.7%), toluene (9.5%), propane (8.1%)</td>
<td>airmo VOC</td>
<td>(Liu et al., 2014)</td>
</tr>
<tr>
<td>Hefei, China</td>
<td>Sep. 2016–Jan. 2017</td>
<td>57.31</td>
<td>Toluene (19.2%), chloroethene (14.2%), benzene (14.0%), dichloromethane (13.4%), 1,2,4-trimethylbenzene (13.3%)</td>
<td>GC-MS</td>
<td>(Hu et al., 2018)</td>
</tr>
<tr>
<td>Düzce, Turkey</td>
<td>Spring</td>
<td>13.5</td>
<td>BTEX (31.1%)</td>
<td>Thermal desorber GC-FID GC-MS</td>
<td>(Bozkurt et al., 2018)</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>11.6</td>
<td>BTEX (29.1%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Autumn</td>
<td>20.9</td>
<td>BTEX (39%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>29.8</td>
<td>BTEX (50.4%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bursa, Turkey</td>
<td>Mar. 17, 2006–May 10, 2006</td>
<td>86.0</td>
<td>Toluene (30%), m,p-xylene (7.4%), benzene (4.3%)</td>
<td>Agilent Model 6890</td>
<td>(Yurdakul et al., 2018)</td>
</tr>
<tr>
<td>Calgary, Canada</td>
<td>2010–2015</td>
<td>38.6</td>
<td>Ethane (15.1%), propane (12.3%), n-butane (9.7%)</td>
<td>GC-MS</td>
<td>(Bari and Kindzierski, 2018)</td>
</tr>
</tbody>
</table>
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 \( \text{O}_3 \) Pollution**

VOCs are important precursor of \( \text{O}_3 \) formation in atmospheric environment. It is report that the \( \text{O}_3 \) pollution 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). The \( \text{O}_3 \) pollution levels in four seasons in Handan were shown in Fig. 4. 160 \( \mu \text{g m}^{-3} \) and 215 \( \mu \text{g m}^{-3} \) 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 \( \text{O}_3 \) concentration being less than 160 \( \mu \text{g m}^{-3} \)), mild pollution (defined as the maximum 8-h \( \text{O}_3 \) concentration being between 160–215 \( \mu \text{g m}^{-3} \)), medium pollution (defined as the maximum 8-h \( \text{O}_3 \) concentration exceeding 215 \( \mu \text{g m}^{-3} \)). It can be seen there was no excessive \( \text{O}_3 \) 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 \( \text{O}_3 \) pollution in summer, with medium \( \text{O}_3 \) pollution account for 20.7% in total days. Therefore, this study only discussed \( \text{O}_3 \) pollution in summer.

\( \text{O}_3 \) is an important product of photochemical reaction of VOCs and \( \text{NO}_x \) in atmosphere. In order to determine the role of VOCs in \( \text{O}_3 \) photochemistry, we evaluated OFP for 55 VOCs (except acetylene). MIR (maximum incremental reactivity) considers the maximum number of \( \text{O}_3 \) molecules generated by given VOCs species, as well as the interaction between kinetic reactivity and mixtures. The calculation Eq. (2) is given as below:

\[
\text{OFP}(A) = \text{MIR}(A) \times C(A)
\]

where \( C(A) \) represents the mass concentration (\( \mu \text{g m}^{-3} \)) for species \( A \). The MIR (g-\( \text{O}_3 \) 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):

\[
\text{Prop-Equiv } (A) = \frac{C(A) \times \text{KOH}(A)}{\text{KOH}(\text{C}_x\text{H}_y)}
\]

where \( \text{KOH}(A) \) is the rate constant for the reaction of VOC species \( A \) with OH radical; and \( \text{KOH}(\text{C}_x\text{H}_y) \) is the rate constant for \( \text{C}_x\text{H}_y \) 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 alkanes > long-chain alkenes > short-chain alkenes > other aromatics > BTEX > short-chain alkanes. Prop-Equiv concentrations were long-chain alkenes > long-chain alkanes > BTEX > short-chain alkenes > other aromatics > short-chain alkanes. It should be noted that the OFP of long alkanes 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 alkanes and alkenes play an important role in \( \text{O}_3 \) formation in summer in Handan.

The OFP of long-chain alkenes and short-chain alkenes in medium pollution were 7.3 \( \mu \text{g m}^{-3} \) and 6.3 \( \mu \text{g m}^{-3} \) 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 \( \mu \text{g m}^{-3} \). But OFP of long-chain alkenes in \( \text{O}_3 \) 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 \( \text{O}_3 \) medium days.

![Fig. 4. The percentages of \( \text{O}_3 \) pollution days in the four seasons in Handan.](image-url)
Fig. 5. Chemical reactivity of major VOC components in different O₃ 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 O₃ 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 O₃. 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 \( \text{O}_3 \) formation among aromatic, which was consist with previous work (Tan et al., 2012; Kumar et al., 2017). It can be seen that the OFP of \( \text{i} \)-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 \( \text{O}_3 \) formation in summer. \( \text{NO}_x \) also had important effect on \( \text{O}_3 \) concentration, which verifies the assumption in the following sections.

**Regional \( \text{O}_3 \) Formation Mechanism**

The concentration variations and hourly change rates of \( \text{O}_3 \) can better illustrate diurnal variations and formation processes of \( \text{O}_3 \). The value of change rate can be calculated using following Eq. (4):

\[
\frac{d[X]}{dt} = [X]_t - [X]_{t-1}
\]

where \([X]_t\) is the concentration of \( \text{O}_3 \) at time \( t \), \([X]_{t-1}\) represents the concentrations for the last hour before time \( t \).

The ratio of VOCs and \( \text{NO}_x \) can be used to qualitatively evaluate the relationship between \( \text{O}_3 \) and its precursors (VOCs and \( \text{NO}_x \)). Assessing whether the city is VOC-sensitive or \( \text{NO}_x \)-sensitive is necessary to effectively control \( \text{O}_3 \) pollution. Under typical atmospheric conditions, the reaction rate constants between \( \text{NO}_x \) and OH (1.7 \( \times 10^{10} \)) is 5.5 times that of VOC and OH (3.1 \( \times 10^9 \)) (Tang et al., 2006). When the emission ratio of VOC/\( \text{NO}_x \) is 5.5, photochemical reactions of \( \text{O}_3 \) 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 \( \text{O}_3 \) concentration, VOC/\( \text{NO}_x \) and VOC(OFP)/\( \text{NO}_x \) ratios, change rate of \( \text{O}_3 \) in four seasons.

**Fig. 7.** The diurnal variation of \( \text{O}_3 \) concentration, VOC/\( \text{NO}_x \) and VOC(OFP)/\( \text{NO}_x \) ratios, change rate of \( \text{O}_3 \) in different seasons in Handan (the blue line is the VOC (ppbc)/\( \text{NO}_x \) (ppb) ratio of 5.5:1).
Winter regime, which is similar to previous studies in this season. The VOC(OFP)/NOx appeared around 13:00 LT in each season and their trends formation of O3 are similar. The maximum ratio of VOC/NOx was higher than VOCs with OH, and the reaction can remove O3 from VOC oxidation cycle. Under this condition, reducing NOx emission will bring more O3. 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 O3 formation was under the NOx-sensitive regime, that is, reducing NOx is beneficial to the reaction of peroxy radicals (HO2 and RO2) and hinders the formation of O3.

The maximum ratio of VOC/NOx and VOC(OFP)/NOx appeared around 13:00 LT in each season and their trends are similar. The VOC(OFP)/NOx ratio is 1.5 times of VOC/NOx in the four seasons. We also find that the ratio of VOC(OFP)/NOx and VOC/NOx will decrease with the increase of O3 pollution frequency. The VOC(OFP)/NOx ratio is 1.3 times of VOC/NOx in summer. Fig. 7 presents the change rate of O3 began to increase at 07:00 LT, reaching a maximum three hours later. At about 15:00 LT, the O3 concentrations reached the maximum in all the four seasons, which is a typical process of O3 accumulation in atmosphere. The O3 concentration is much higher in summer than that in the other three seasons, especially from 12:00 to 18:00 LT. In the high-O3 episode, the O3 chemistry was under the NOx-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/NOx ratio during clean period, mild pollution and medium pollution days in summer. The diurnal variation trend and value of VOC/NOx ratio in mild pollution and medium pollution days were similar. The VOC/NOx in clean period were highest in the three pollution levels, however, the O3 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. NOx average concentration
in medium pollution days were 14 μg m⁻³ higher than clean period. Therefore, it can be concluded that NO₂ 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):

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

(5)

where [OH] is the 24-h average concentration of OH, i.e., 3 × 10^6 molecules cm⁻³ s⁻¹. \( K_{\text{toluene}} \) and \( K_{\text{benzene}} \) represent the coefficients for the reaction of OH with toluene and benzene, the values were 5.63 × 10⁻¹² molecules cm⁻³ s⁻¹ and 1.22 × 10⁻¹² molecules cm⁻³ s⁻¹, respectively (Atkinson and Arey, 2003). \([\text{toluene}] / [\text{benzene}] \) is ratio between toluene and benzene of observation. The ratio \([ [\text{toluene}] / [\text{benzene}] ]_{0} \) is the initial concentration ratio. The concentrations of toluene and benzene in ratio \([\text{toluene}] / [\text{benzene}] \) 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. 8. The diurnal variation of VOC (ppbc)/NO₃ (ppb) ratio in different O₃ pollution levels in Handan (the black line is the VOC (ppbc)/NO₃ (ppb) ratio of 5.5:1).](image-url)
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., 2016; 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 \( O_3 \) 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 \( O_3 \) formation, and the associated source apportionment.

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

Table 2. Source apportionment of VOCs in four seasons.

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