Characteristics and source apportionment of VOC in a complex polluted city in China

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ABSTRACT

Volatile organic compounds (VOCs) are important precursors in the formation of ozone ($O_3$) and secondary organic aerosols. This study observed 56 VOCs species using an on-line monitor during Sep. 2017 to Aug. 2018 in a top polluted city in China, Handan, as well as $O_3$ and NOx to analyze the pollution characteristics, chemical reactivity of VOCs in different $O_3$ pollution levels, regional $O_3$ formation mechanism and source apportionment of VOCs. Our results showed that the daily concentration of VOCs had a wide range from 37.7 µg·m$^{-3}$ to 288.9 µg·m$^{-3}$, with the average of 112.0±45.5 µg·m$^{-3}$ during the observation period. The alkenes and other aromatics contributed more $O_3$ formation potential (OFP) of VOCs in medium polluted days in comparison with clean days. $O_3$ formation in Handan mainly occurred under the VOC-sensitive regime in spring and winter, while in summer and autumn, and daytime high $O_3$ episodes were NOx-sensitive. According to the ratio of i-butane/n-butane and i-propane/n-propane, the main sources of butane and propane were vehicular exhaust and liquid gasoline source in the observation period. The source apportionment of VOCs using PCA (principal components analysis) model were pursued for the four seasons, and the result show that vehicle emission, industrial production, solvent use, gasoline evaporation and combustion are important emission sources in Handan.

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 O$_3$ pollution gradually appears in Chinese cities (Wei, 2018). VOCs are important precursors for initiating the formation of ground-level O$_3$, secondary organic aerosol (SOA) and photochemical smog in atmospheric chemistry (Wei et al., 2016; Wang et al., 2017). The photochemical reaction mechanism of O$_3$ 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 O$_3$ 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 US EPA (USEPA, 1990). VOCs 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. (2018b) simulate the impact of VOCs emission of petrochemical industrial zone on the summertime O$_3$ 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, 2019). Handan was listed in the ten top 
polluted cities in China since 2013 (http://www.mee.gov.cn/hjzl/). PM$_{2.5}$ is the major air 
pollutant in Handan, but the O$_3$ concentrations showed a rapid increase in recent years. Since 
2016, O$_3$ has replaced PM$_{2.5}$ to be the major primary pollutant in summer in Handan. On 
November 11, 2018, Handan government promulgated the “The Volatile Organic 
Compounds Prevention and Control Action Plan” and set a target of 18 VOCs species 
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 O$_3$ pollution, formation process of heavy O$_3$ pollution episode, and source 
apportionment of VOCs in Handan, to provide policy-making support for future VOCs and 
O$_3$ 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’s about 10 m above the ground. This site, as show in Fig. 1, is located in the southern urban 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.

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

VOCs concentrations were observed using the instrument of GC 5000 volatile organic compound online chromatographic monitor manufactured by AMA instrument in 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 (PMAS) standard gas was diluted to $10^{-9}$ volume by DIM 200 for the following analysis. H₂ is derived from H₂ generator electrolysis distilled water by HG300. ZAG 300 can remove organic impurities by catalytic decomposition of hydrocarbons. At first, sample gas were 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. PMAS standard gases were used to calibrate the instrument by multi-point every month.
The MDL (method detection limits) of all VOCs species were 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 ($\mu$g·m$^{-3}$) of each compound was calculated from the mixing ratios in ppbv, using the following Eq. (1) (Wang et al., 2016):

$$C_i = \frac{M_i \times C_i'}{22.4} \times \frac{273.15}{273.15 + T} \times \frac{B_a}{101.325}$$

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 $B_a$ 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 widely 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 a 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>alkyne, of the concentrations of 63.1 $\mu$g·m$^{-3}$, 26.2 $\mu$g·m$^{-3}$, 18.2 $\mu$g·m$^{-3}$, 4.6 $\mu$g·m$^{-3}$, respectively.
Fig. 2. Box plots of VOCs in Sep. 2017-Aug. 2018 in Handan (µg·m⁻³) (the yellow, blue, green and red box chart represent alkanes, alkenes, aromatics, and alkyne, respectively).

Fig. 3(a) presents the seasonal variations of the four 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. Aromatics concentrations 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 alkenes (C>4) concentrations were very low (3.9 µg·m⁻³) in winter (in Fig. 3(b)). BTEX was the abundant group in aromatics, which accounted for 70.5%
in aromatics with the average concentration of 24.2 $\mu$g·m$^{-3}$. Light alkanes and short-chain alkenes contributed most of VOCs in winter.

Fig. 3. Seasonal variations of VOCs and its components concentrations in winter. Long-chain alkanes (C>4), other aromatics refer to aromatics except BTEX in this study.

Table 1 presents the comparison of VOCs concentrations and the other reported cities (Wang et al., 2016; Chang et al., 2015; Liu et al., 2014; Hu et al., 2018; Bozkurt et al., 2018; Yurdakul et al., 2018; Bari and Kindzierski, 2018). VOCs concentrations in Handan were higher than Chinese cities 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 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 (see Table 1).

Table 1 Comparison of VOCs concentrations in Handan and in other cities.
<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>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 (12.1%), Propane (8.2%), Ethane (17.8%), Ethane (12.1%), Propane (8.2%), Toluene (6.7%)</td>
<td>GC-MS</td>
<td>(Chang et al., 2015)</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>2014.11</td>
<td>27.6</td>
<td>Aromatics (44.2%), alkanes (40.9%)</td>
<td>Agilent 6890N-5975B</td>
<td>(Wang et al., 2016)</td>
</tr>
<tr>
<td>Shijiazhuang, China</td>
<td>2014.01-2014.04</td>
<td>309.9</td>
<td>Aromatics (31%), halohydrocarbons (30.7%), Cyclopentane (14.3%)</td>
<td>Airmo VOC</td>
<td>(Liu et al., 2014)</td>
</tr>
<tr>
<td>Jinan, China</td>
<td>2010.06-2012.05</td>
<td>53.1</td>
<td>i-Pentane (9.7%), Toluene (9.5%), Propane (8.1%), Toluene (19.2%), Chloroethene (14.2%), Benzene (14.0%),</td>
<td>Airmo VOC</td>
<td>(Liu et al., 2014)</td>
</tr>
<tr>
<td>Hefei, China</td>
<td>2016.09-2017.11</td>
<td>57.31</td>
<td>Dichloromethane (13.4%),1,2,4-Trimethylbenzene (13.3%)</td>
<td>Airmo VOC</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</td>
<td>(Bozkurt et al., 2018)</td>
</tr>
<tr>
<td></td>
<td>summer</td>
<td>11.6</td>
<td>BTEX (29.1%)</td>
<td>GC-FID GC-MS</td>
<td>(Bozkurt et al., 2018)</td>
</tr>
<tr>
<td>Bursa, Turkey</td>
<td>autumn</td>
<td>20.9</td>
<td>BTEX (39%)</td>
<td></td>
<td>(Yurdakul et al., 2018)</td>
</tr>
<tr>
<td></td>
<td>winter</td>
<td>29.8</td>
<td>BTEX (50.4%)</td>
<td></td>
<td>(Yurdakul et al., 2018)</td>
</tr>
<tr>
<td>Calgary, Canada</td>
<td>2010-2015</td>
<td>38.6</td>
<td>Toluene (30%), m, p-Xylene (7.4%), Benzene (4.3%)</td>
<td>Agilent Model 6890</td>
<td>(Bari and Kindzierski, 2018)</td>
</tr>
</tbody>
</table>

**Chemical reactivity of VOC in different level of O₃ pollution**

VOCs are important precursor of O₃ formation in atmospheric environment. It is report that the O₃ concentration and exceeding-standard days in 2018 obviously increased compared to those in 2017 (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 daily maximum O$_3$-8h concentration less than 160 µg·m$^{-3}$), mild pollution (defined as daily maximum O$_3$-8h concentration being between the 160-215 µg·m$^{-3}$), medium pollution (defined as daily maximum O$_3$-8h concentration exceeding 215 µg·m$^{-3}$). It can be seen there was no excessive 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 O$_3$ pollution in summer, with medium O$_3$ pollution account for 20.7% in total days. Therefore, this study only discussed O$_3$ pollution in summer.

Fig. 4. The percentages of O$_3$ pollution days in the four seasons in Handan.

O$_3$ is an important product of photochemical reaction of VOCs and NOx in atmosphere. In order to determine the role of VOCs in O$_3$ photochemistry, we evaluated OFP for 56 VOCs. MIR (maximum incremental reactivity) considers the maximum number of 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:
\[
\text{OFP}(A) = \text{MIR}(A) \times C(A) \quad (2)
\]

Where \( C(A) \) represents the mass concentration (\( \mu g \cdot m^{-3} \)) for species \( A \). The MIR (\( g \ O_3/g \) VOCs) value for each species can be found by Carter (Carter, 1994). Prop-Equiv method put all VOCs species on a base line 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 follow 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 \( C_3H_6 \) 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 quiet high, with 28.3%~37.5% of total VOCs
concentrations (see Fig. 6). Therefore, long alkanes 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 alkanes in O₃ pollution days were lower than the others two pollution levels. The proportion of Propy-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.

(a) Clean period

(b) Mild pollution
Fig. 5. Chemical reactivity of major VOCs compositions in different O3 pollution level in Handan.

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. Isopene, 2-Methylpentane and o-xylene have high Prop-Equiv concentrations with strong chemical reaction activity in summer. 2-Methylpentane, isopene, ethene and i-pentane are major contributors to form O3. In particular, the concentration of isopene accounted for 3.4%-4.1% of VOCs, while its OFP accounted for 30%-35% in total OFP. Toluene and xylene were the top contributors of O3 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 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 µg·m⁻³) was not significantly higher than that in mild pollution (249.2 µg·m⁻³). It...
implies that VOCs were not the main factor of medium O_3 formation in summer. NOx also had important effect on O_3 concentration, which verifies the assumption in the following sections.

(a) Clean period

(b) Mild pollution
Fig. 6. Percentages of the concentrations, OFP and Prop-Equiv concentrations of major VOCs under different levels of O₃ pollution in Handan.

**Regional O₃ formation mechanism**

The concentration variations and hourly change-rates of O₃ can better illustrate diurnal variations and formation processes of O₃. 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 O₃ at time \(t\), \([X]_{t-1}\) represents the concentrations for the last hour before time \(t\).

The ratio of VOCs and NOx can be used to qualitatively evaluate the relationship between O₃ and its precursors (VOCs and NOx). Assessing the city is VOC-sensitive or NOx-sensitive is necessary to effectively control O₃ pollution. Under typical atmospheric
conditions, the reaction rate constants between NOx 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/NOx 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/NOx and VOC(OFP) /NOx ratios, change-rate of O\(_3\) in four seasons for one year. In spring and winter, the VOC/NOx ratios were more than 5.5 from 10:00 LT to 16:00, and the ratio of the other time of the day were less 5.5. This illustrates that O\(_3\) formation mainly occurred under the VOC-sensitive regime. At this time, the reaction rate of NO\(_2\) with OH is higher than VOCs with OH, and the reaction can remove OH from VOC oxidation cycle. Under this condition, reducing NOx emission will bring more O\(_3\). In summer, the ratio reached a relatively high level during 7:00 LT to 22:00 LT, with the average of 12:1. Except the period from 5:00 LT to 8:00 LT, the ratio was greater than 5.5 in autumn with average of 9:1. In those two seasons the O\(_3\) formation was under NOx-sensitive, that is, reducing NOx is beneficial to the reaction of peroxide radicals (HO\(_2\) and RO\(_2\)) and hinders the formation of O\(_3\).

The maximum ratio of VOC/NOx and VOC(OFP) /NOx appeared in 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 O\(_3\) pollution frequency. The VOC(OFP) /NOx ratio is 1.3 times of VOC/NOx in summer. Fig. 7 presents the change-rate of O\(_3\) began to increase at 7:00LT, 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 LT to 18:00 LT. In the high $O_3$ episode, the $O_3$ chemistry was under NOx-sensitive, which is similar to previous studies in Guangzhou (Zou et al., 2015) and Pearl River Delta region (Li et al., 2013).
Fig. 7. The diurnal variation of $O_3$ concentration, VOC/NOx and VOC(OFP)/NOx ratios, change-rate of $O_3$ in different seasons in Handan (the blue line is the VOC (ppbc)/NOx (ppb) ratio of 5.5:1).

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 $O_3$ 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. NOx average concentration in medium pollution days were 14 µg·m⁻³ higher than clean period. Therefore it can be concluded that NOx and VOCs dominated the O₃ formation, especially in medium pollution. Whether there is regional O₃ transmission remains to be proved.

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

**Ambient ratios: Photochemical characteristics and source**

The change in concentrations ratio of special hydrocarbon can reflects their atmospheric photochemical processes, and effect of atmospheric physical transmission is eliminated by their ratio, so we can calculated photochemical age of air masses (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 massed was estimated as following Eq. (11) (Roberts et al., 1984):
\[
\begin{align*}
\frac{1}{[\text{OH}](K_{\text{toluene}} - K_{\text{benzene}})} \times & \left[ \ln \left( \frac{[\text{toluene}]}{[\text{benzene}]}_{t=0} \right) - \ln \left( \frac{[\text{toluene}]}{[\text{benzene}]} \right) \right] \\
(11)
\end{align*}
\]

Where \([\text{OH}]\) is the 24-hour averaged concentration of OH, i.e., \(3 \times 10^6\) molecules \(\text{cm}^{-1} \text{s}^{-1}\).

\(K_{\text{toluene}}\) and \(K_{\text{benzene}}\) represent the coefficients for the reaction of OH with toluene and benzene, the value were \(5.63 \times 10^{-12}\) molecules \(\text{cm}^{-1} \text{s}^{-1}\) and \(1.22 \times 10^{-12}\) molecules \(\text{cm}^{-1} \text{s}^{-1}\), 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 \([\text{toluene}/\text{benzene}]_{t=0}\) were estimated from the 5th percentile of the observation at 7:00 am 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 (Gouw et al., 2005). As shown in Figs. 9(a), the scatterplot of benzene versus acetylene painted by photochemical age (Eq. (11)). A good correlation of benzene and acetylene with correlation coefficient of 0.7. The ethylbenzene an acetylene are positively correlated (in Figs. 9(b)), however the correlation coefficient \((r=0.54)\) is less than that of benzene and acetylene. We also found that the ethylbenzene/acetylene decreased with increasing photochemical age \((\text{slope}=8.06)\), while the ratio of benzene and acetylene increased with photochemical age \((\text{slope}=2.1)\). The reason is that the removal efficiency of ethylbenzene in the atmosphere is faster than toluene, the removal rate of ethylbenzene is about six time larger than benzene. The scatterplot of propane versus n-butane and i-butane were also colored by photochemical age (Figs. 9(c) and Figs. 9(d)). The two figures shows good correlation of both n-butane and i-butane with propane, especially correlation coefficient of n-butane with propane is 0.93, that 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 main from vehicular exhaust and LPG (in Figs. 10(a)), this is relative to the actual situation, LPG is the fuel for taxis and private cars in Handan. As shown in Figs. 10(b), the slope of the correlation of i-pentane and n-pentane (-0.29) in summer was quiet 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).
Fig. 9. Scatterplots versus acetylene of benzene and ethylbenzene, propane versus n-butane and i-butane. The scatter points are painted by photochemical age.

Fig. 10. Correlations between compounds (i-butane/n-butane and i-propane/n-propane) with similar atmospheric lifetimes.

**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 calculate procedures of PCA can refer to in 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 KMO (Kaiser-Meyer-Olkin) detected by input data were 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. Table 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. 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 from solvent use. Toluene and xylene are widely used as in printing, furniture and adhesives (Buzcu and P.Fraser, 2006; Ling et al., 2011), and long-chain alkane may 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 marks 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 Table 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 is 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%).

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>biomass (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></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>biomass combustion (5.1%)</td>
<td></td>
</tr>
</tbody>
</table>
CONCLUSIONS

In this study, we pursued online observation of VOC concentrations, as well as gaseous pollutants of \(O_3\) and NOx, from Sep. 2017 to Aug. 2018 in Handan, one of the top polluted cities in China, to understand the characteristics of VOCs pollution, chemical reactivity of VOCs, VOCs contributions in \(O_3\) formation, and risk assessment.

Our results showed that the VOCs concentrations in Handan was 112.0 \(\mu g \cdot m^{-3}\) on annual average, which was higher than Chinese city (Beijing, Jinan, Heifei) and foreign cities (Düzce and Calgary). The abundance of major VOCs compositions were alkanes > aromatics > alkenes > alkyne. VOCs concentrations had obviously seasonal variation of winter > autumn > summer > spring, that the concentrations in winter were 0.5 times higher than in spring.

Summer has a high incidence of \(O_3\) pollution. The OFP of alkenes and other aromatics increased during medium pollution days simultaneously. As the degree of \(O_3\) pollution increase, the chemical reactivity of isoprene, i-pentane and ethene increased obviously. VOC/NOx ratio diurnal variations indicate that, \(O_3\) formation in spring and winter were under VOCs-sensitive regime most of the day, while in summer, autumn daytime and high \(O_3\) episode (\(O_3\)-8h exceeded the Stage II of NAAQS), they were mainly under NOx-sensitive.
The removal rate of ethylbenzene is higher than benzene, at high photochemical age, the value of ethylbenzene/acetylene was lower than that in low photochemical age, but the benzene/acetylene was opposite. Through the ambient ratio (i-butane/n-butane, i-pentane/n-pentane) analysis showed that main source of butane and propane were vehicular exhaust and liquid gasoline source in observation period.

The PCA model results showed that the major sources apportionment of VOCs were industrial, solvent use, evaporation and vehicle emission in four seasons in Handan. In addition, there are slightly different in four seasons. Due to high temperature in summer and autumn, the evaporation about solvent and gasoline is more obvious. Biogenic emissions were prominent in summer. In winter, the contribution of combustion increased significantly.

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DISCLAIMER

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

REFERENCES


