Pollution Characteristics and Key Reactive Species of Volatile Organic Compounds in Beijing-Tianjin-Hebei Area, China

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ABSTRACT

Volatile organic compounds (VOCs) are important precursors in the formation of ground-level ozone. In this study, the hourly mixing ratios of 61 ambient VOC species were monitored from 2018 till 2019 in 10 cities in the Beijing-Tianjin-Hebei (BTH) area of China, and the VOC distributions, speciation and photochemistry were also examined. The highest mixing ratios were found in the south, viz., Langfang (LF), Baoding (BD), Handan (HD) and Shijiazhuang (SJZ), and the lowest ones, in the north, viz., Chengde (CD) and Zhangjiakou (ZJK). In all of the cities, alkanes were the most abundant VOC component (50%), whereas ethane and propane were the most concentrated species. The mixing ratios of the VOCs exhibited a daily double peak as a result of the varying intensity of the photochemical reactions and the formation of the inversion layer. Additionally, the chemical reactivity of the VOCs was evaluated by calculating the loss rate of OH (L_{OH}) for each species. Our results indicated that the alkenes and aromatics possessed higher L_{OH} values as well as higher ozone formation potential (OFP) and secondary organic aerosol formation potential (SOA{\text{p}}) values than the alkanes. Based on the diagnostic ratios of propane/n-butane, propane/i-butane, cis-2-butene/trans-2-butene, toluene/benzene and xylene/ethylbenzene, motor vehicle emissions contributed significantly to the ambient VOCs in the area.

Keywords: VOCs; Ozone formation potential; Secondary organic aerosols formation; China.

INTRODUCTION

Volatile organic compounds (VOCs) play an essential role in the formation of ground-level ozone (O_3) and secondary organic aerosols (SOA) (Zhang et al., 2014). Researches had found that under suitable meteorological conditions such as high temperature, intense light, low humidity, low wind speed, etc., VOCs emitted from various sources can react with NO, and OH radicals to generate ozone and SOA (Hui et al., 2019; Li et al., 2020). By analyzing the VOCs pollution characteristics of a liquefied petroleum gas (LPG) during 1 day, Chen et al. (2001) found the alkanes with short carbon chain contributed 10% of ozone production in Santiago. Also, alkenes contributed 5%. In addition, Deng et al. (2019) measured VOCs from 28 August to 7 October 2016 and found that the alkenes and aromatics in Chengdu were the main factors in the formation of ground-level ozone with the total ozone formation potential (OFP) of 51.7% and 24.2%, respectively. Wang et al. (2018) found that alkanes were the most highly discharged components (58.67%) in Zhoushan city by analyzing the emissions inventory in 2015, in which aromatics was the main contributor of ozone formation, with 69.97% of total OFP. However, VOCs are prone to photochemical reactions in atmosphere, and lower sampling frequency can not reflect the true pollution characteristics. Therefore, a long-term and high sampling frequency analysis is essential to truly reflect the VOCs pollution characteristics in a large scale.

The BTH area, as China’s political center, contains 13 cities and is suffering the most serious air pollution. In BTH area, 6 cities ranked last 10 in China ambient air quality index in 2017, and 5 cities in 2016 and 2018. Currently, the characteristic of air pollution in this region has gradually changed from only particulate matter pollution in a city into a regional multi-pollutant (especially as PM_{2.5} and ozone)
pollution (He et al., 2013; Song et al., 2017). The ground-level ozone mixing ratio is growing rapidly with an average rate of 3.4% per year from 2002 to 2010 (Li et al., 2015). As a precursor of ozone, the pollution characteristics and sources of VOCs are important for improving regional air quality. In this study, 61 species of VOCs in 10 cities were measured in BTH area. The mixing ratio and composition of ambient VOCs were studied, and the loss rate of OH (L_{OH}) was calculated to estimate the chemical reactivity of VOCs. To determine their contribution in ozone and SOA formation, the OFP and secondary organic formation potential (SOAP) of VOCs were calculated based on the observed mixing ratios, and the sources of VOCs were initially determined by analyzing the relationship between VOCs. The results can provide the data foundation for introducing the pollution control strategies in northern China.

METHODS

Sampling Site

VOCs sampling was collected 1–31 December 2018 as winter, 1–31 March 2019 as spring, 1–31 July 2019 as summer, and 1–30 September 2019 as autumn in 10 cities in BTH area: Baoding (BD), Cangzhou (CZ), Chengde (CD), Handan (HD), Hengshui (HS), Langfang (LF), Shijiazhuang (SJZ), the provincial capital of Hebei Province), Tangshan (TS), Xingtai (XT) and Zhangjiakou (ZJK). Among them, SJZ, TS, LF, BD, CZ, HS, XT and HD were regarded as the key cities as “air pollution transmission passage cities” by the Ministry of Ecology and Environment of China for controlling regional environmental quality and reducing heavy pollution. As the only 2 cities with relatively good air quality in BTH area, it has a long-term significance in studying the sources of pollutants and regional transmission in CD and ZJK (Wang et al., 2016; Chen et al., 2016). The BD sampling site is located in Dongfeng Park in the center of Baoding, near commercial, educational and residential areas. The CZ sampling site is located in Cangzhou Technical College, which is an educational area in the city. The CD sampling site is located in Chengde Petroleum College in High-tech Zone of Chengde, near Olympic Sports Center and several schools. The HD sampling site is located in Handan Ecological Environment Bureau, near residential areas. The HS sampling site is located in Hengshui College of Vocational Technology, near residential areas and botanical gardens. The LF sampling site is located in Langfang No. 10 Middle School, near the city’s education and residential areas. The SJZ sampling site is located in Shijiazhuang No. 9 Middle School, which belongs to the education, residential and commercial areas in the urban area. The TS sampling site is located in Tangshan Environmental Monitoring Center, near the education and residential areas. The XT sampling site is located in Xingtai No. 1 Middle School, and where are residential areas. The ZJK sampling site is located in Zhangjiakou Vocational and Technical School in High-tech Zone, near residential areas.

The sampling sites were all in urban area, which surrounded by cultural and educational areas, residential areas, and commercial areas. There are no obvious characteristic pollutant emission sources around the sites. The samples were collected on the rooftop of a 25-m-high building in environmental protection agency.

Sampling and Analysis of VOCs

Hourly integrated ambient VOC samples were measured using an online gas chromatograph (GC) with a flame ionization detector (FID) consisting of an airmoVOC C2–C6 analyzer and an airmoVOC C6–C12 analyzer (Chromatotec Inc.). A customized airmoOzone analytical system (ASS) was used to monitor a total of 61 VOC species, including alkanes (29 species), alkenes (15 species), alkynes (1 species) and aromatics (16 species) as shown in Table 1. The FID technology with H2 as the carrier gas was used in ASS process, in which the separation and detection sensitivity of VOC components can reach 0.01–100 ppbv level. The instruments are calibrated by primary standard gas that has been calibrated. The ASS complies with the non-interference standard of EN 14662-3:2015 (“Ambient air—Standard method for the

| Alkanes (29) | Alkenes and Alkynes (16) | Aromatics (16) |
|-------------|-------------------------|----------------|
| Ethane      | 2,3-Dimethylpentane      | Ethene         |
| Propane     | 2-Methylhexane           | Propylene      |
| t-Butane    | 2,2,4-Trimethylpentane   | \(\text{trans}-2\)-Butene |
| n-Butane    | n-Heptane               | 1-Butene       |
| Cyclopentane| Methylcyclohexane        | cis-2-Butene   |
| i-Pentane   | 2,3,4-Trimethylpentane   | 1,3-Butadiene  |
| n-Pentane   | 2-Methylheptane          | \(\text{trans}-2\)-Pentene |
| 2,2-Dimethylbutane | 3-Methylheptane  | 1-Pentene         |
| 2,3-Dimethylbutane | n-Octane          | cis-2-Pentene    |
| 2-Methylpentane | n-Nonane           | Isoprene        |
| 3-Methylpentane | n-Decane            | 2-Methyl-1-pentene |
| n-Hexane    | n-Undecane             | 1-Hexene        |
| Methylcyclopentane | n-Dodecane    | Isobutene | 1,2,4-Trimethylbenzene |
| 2,4-Dimethylpentane | \(\alpha\)-Pinene | 1,2,3-Trimethylbenzene |
| 2,2-Dimethylbutane | \(\beta\)-Pinene | 1,3-Diethylbenzene |
| Cyclohexane |                        | Acetylene       |

Table 1. The VOCs species measured in this study.
The measurement of benzene concentrations Part 3: Automated pumped sampling with in situ gas chromatography”, and the monitoring of BTEX and other VOCs is also internationally certified.

The ASS calibration system consisted of internal and external parts. In order to ensure the reliability and accuracy of the data, internal calibration was performed once a day and external calibration was performed once a month. Benzene, butane and hexane were used as the internal standards, and the VOCs standard gases were used for external calibration.

The \( L_{OH} \), OFP and SOAp of VOCs

The variety of VOCs is numerous, as the precursors of ozone and SOA, the photochemical reaction rate and the effects on ozone and SOA formation will vary from species to species.

The loss rate of each VOC species reacting with OH is a parameter that qualitatively identifies the VOC’s chemical activity, which can be calculated by multiplying the VOCs concentration by its corresponding radical rate coefficient as shown in Eq. (1) (Luo et al., 2011; Chen et al., 2012; Li et al., 2015):

\[
L_{OH} = [\text{VOC}] \times K_{OH}
\]

where \( L_{OH} \) is the loss rates of the \( i^{th} \) VOC species react with OH; [VOC] is the concentration of the \( i^{th} \) VOC species (\( \mu g m^{-3} \)); \( K_{OH} \) is the rate coefficient of the reaction of \( i^{th} \) VOC species with OH and referred the research results of Carter (2010).

To quantify the contribution to ground-level ozone and SOA formation, it is essential to estimate the OFP and SOAp of a particular VOCs species. The effect of VOCs on ozone generation will vary depending on the species and the reaction rate of photooxidation reaction. In this study, the maximum incremental reactivity (MIR) analysis was used to assess the OFP of each component. Incremental reactivity is defined as the amount of ozone formed when a certain amount of VOCs are added to a VOCs mixture. The MIR method is superior to the concentration-based method to determine the relative contribution of each substance to OFP and can be calculated by Eq. (2):

\[
OFP_i = [\text{VOC}_i] \times MIR_i
\]

where OFP, is the OFP value of the \( i^{th} \) VOC species; [VOC] is the concentration of the \( i^{th} \) VOC species (\( \mu g m^{-3} \)); MIR, is the ozone generation coefficient of the \( i^{th} \) VOC species in the maximum incremental reaction of ozone. The MIR coefficient was referred the latest research results (Duan et al., 2008; Carter, 2010; Wang et al., 2020).

SOA is an important component of fine particles and is the suspended particulate in atmosphere generated by atmospheric oxidation of VOCs. The rate of SOA generation varies with VOCs. This study estimated the SOA formation potential of VOCs in atmosphere based on aerosol generation coefficient (FAC). The SOAp calculation formula is shown in Eqs. (3) and (4):

\[
[\text{VOC}]_S = [\text{VOC}]_O / (1 - F_{VOC})
\]

\[
SOAp_i = [\text{VOC}]_i \times FAC_i
\]

where SOAp, is the SOAp value of the \( i^{th} \) VOC species; [VOC] is the initial concentration of emission source of the \( i^{th} \) VOC species (\( \mu g m^{-3} \)); [VOC] is the oxidized concentration monitored by the ASS of the \( i^{th} \) VOC species (\( \mu g m^{-3} \)). The FAC and \( F_{VOC} \) coefficients were referred the research as Grosjean and Seinfeld (1989) and Grosjean (1992).

Identification of VOCs Sources

Correlation between individual VOCs species can be applied to determine the primary source of ambient VOCs. Xylene/ethylbenzene, toluene/benzene, cis-2-butene/trans-2-butane, propane/i-butane and propane/m-butane were selected to identify the source (Barletta et al., 2005; Liu et al., 2008a; Yuan et al., 2012).

RESULTS AND DISCUSSION

Spatial Pollution Characteristics of VOCs

Fig. 1 illustrated the annual average mixing ratio and major compositions of VOCs in 10 cities. The total VOCs’ mixing ratio in LF was highest with average values of 35.08 ppbv, followed by BD (32.48 ppbv), HD (31.30 ppbv), and SJZ (31.20 ppbv). The CD and ZJK were the least VOCs pollution cities with the average mixing ratio of 10.51 ppbv and 8.80 ppbv respectively. It can also be seen from Fig. 1, the cities with severe VOCs pollution were located in the southern part of BTH area, and the pollution in the southwest (such as SJZ) is more severe than in the southeast (such as CZ). Due to the altitude of northern BTH area is higher than the southern area (Xu et al., 2013), the main wind direction during the year caused by topographic conditions is the north wind, which spread atmospheric pollutants to the south of BTH area. Simultaneously, the formation of underlying airflow in the southwestern part is not conducive to spread the regional pollutants, and the south winds in summer and autumn make the pollutant transport channel of BTH area blocked and settled (Wu et al., 2018). In addition, the cities in southern BTH area are mostly traditional industrial cities. For examples, the textile, building materials and pharmaceutical industries in SJZ are all in the forefront of China; BD has a well-known large enterprise in the automobile manufacturing, machinery and electronics industries; chemical industry and steel industry in HD also have a high production capacity (Zhang et al., 2017).

The atmospheric pollutants emitted from these industries are mainly VOCs (Wang et al., 2013). Moreover, motor vehicle exhaust emissions in this area are also master reasons for the high mixing ratio of VOCs (Lang et al., 2012). In contrast, due to the rich forest resources and few industries, CD and ZJK had a lowest VOCs mixing ratio than other cities. At the same time, the higher terrain also makes it more advantageous in regional pollutant transmission (Wang et al., 2019).

The VOCs components in sampling cities were also illustrated in Fig. 1. It showed that the alkanes were the most...
significant VOCs component in all cities with the contribution of larger than 50%. The ethane is a critical composition of natural gas, and the familiar tracers of LPG are propane, n-butane and i-butane (Ling et al., 2011; Lyu et al., 2016). The mixing ratios of these species were relatively high (Table 2). Thus, the alkanes in ambient air are mainly derived from the use of natural gas and LPG. Alkenes were the second-highest contributor in HD and TS, in which the proportions of aromatics of HD (23%) and TS (22%) were higher than alkenes respectively as 16% and 18%. Ethane, propane and ethene are the main species of motor vehicle emissions and liquefied petroleum gas emissions. Benzene, toluene and m/p-xylene in aromatic hydrocarbons are mainly from motor vehicle emissions, and m/p-xylene is also related to industrial layout (Wang et al., 2016).

Table 2 showed the top 10 species in each city. As the representative species of alkanes, ethane and propane occupied the top 3 in each city. They usually come from exhaust of LPG vehicles and gasoline vehicles. Ethene, the representative substance of alkenes, was also in the forefront, usually from the chemical industry. Benzene, toluene and m/p-xylene have the highest mixing ratios in aromatics, but the total aromatics’ mixing ratio is usually lower than other components and the aromatics usually come from mobile sources and coating for building. Acetylene ranked in top 10 in most cities as the only alkynes measured in samplings and usually derived from gasoline vehicles and coal burning (Liu et al., 2008a). Overall, the sources of these species are very diverse, such as mobile sources, fuel evaporation, painting, stationary combustion sources, petrochemical industry, etc.

Fig. 1. The annual average mixing ratio distributions and compositions of VOCs in sampling cities.
Table 2. The 10 most abundant species measured in the sampling areas.

|   | BD     | CZ     | CD     | HD     | HS     | LF     | SJZ    | TS     | XT     | ZJK    |
|---|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| 1 | Propane| Ethane | Ethane | Ethane | Ethane | Propane| Ethane | Ethane | Ethane | Ethane |
| 2 | Ethan  | Propane| 1,3-Butadiene| Ethane| Ethane| Ethane| Ethane| Ethane| Ethane| Ethane|
| 3 | Ethane | Ethane | Ethane | Ethane | Ethane | Ethane | Ethane | Ethane | Ethane | Ethane |
| 4 | i-Butane| Acetylene| 3-Methyl-pentane| Isobutene| Acetylene| i-Butane| Propane| Ethane| Ethane| Ethane|
| 5 | Toluene| p-Ethyltoluene| Acetylene| Styrene| i-Butane| Acetylene| n-Hexane| i-Butane| n-Hexane| i-Butane|
| 6 | Toluene| o-Ethyltoluene| Propane| n-Butane| Propylene| Acetylene| Propylene| i-Butane| n-Butane| i-Butane|
| 7 | Propylene| Propylene| n-Hexane| Ethene| 2,3,4-Trimethylpentane| i-Butane| i-Pentane| Toluene| Propane| 2,3-Dimethylpentane|
| 8 | Benzene| 1,3,5-Trimethylbenzene| n-Pentane| n-Pentane| Benzene| i-Pentane| Toluene| Propane| 2,3-Dimethylpentane| i-Butane|
| 9 | n-Butane| Methylcyclopentane| i-Butane| Cyclopentane| cis-2-Butene| Cyclohexane| i-Pentane| Propane| i-Pentane| i-Butane|
| 10 | m/p-Xylene| 1,3-Diethyl-benzene| n-Butane| Acetylene| cis-2-Butene| 2-Butene| Styrene| m/p-Xylene| o-Xylene| Benzene|
Fig. 2. The seasonal characteristics of VOCs mixing ratio and components in sampling cities.

Fig. 3. The daily variation of the VOCs concentration in sampling cities.

**OH Loss Rate of VOCs**

To determine the objects that control VOCs, attention must be paid to their chemical reactions in atmosphere rather than the mixing ratio of VOCs. The loss rate contributions of the different VOCs components during sampling were shown in Table 3. From the perspective of the city, 5 cities (BD, CZ, HD, LF and SJZ) with higher mixing ratio of VOCs also have higher $L_{OH}$ (> 10). The $L_{OH}$ of LF (21.90) was twice higher than the average of all cities (10.47), which is due to the higher proportion of alkenes (28.2%) than other cities (Fig. 2). The $L_{OH}$ in ZJK (3.82), TS (4.79) and XT (5.88) were the lowest. It can be seen from Fig. 2 that TS and XT had lower levels of alkenes and aromatics, and the reaction activity of alkenes and aromatics was higher than alkanes. Simultaneously, the lowest total mixing ratio of VOCs leads to the lowest $L_{OH}$ of ZJK. In terms of component contribution, the alkanes (13.70%) with the highest mixing ratio of components is far less reactive than alkenes (73.06%). While the aromatics have a lower mixing ratio, the reactivity (12.93%) is comparable to that of alkanes. For alkanes, TS (20.35%) and LF (8.98%) were the highest and lowest cities; for alkenes, LF (86.87%) and TS (55.68%) respectively were the highest and lowest cities; for aromatics TS (23.84%) and LF (3.77%) were the highest
and lowest cities, respectively. It was related to their mixing ratio (Fig. 2). It should be noted that the isoprene has the highest $K_{\text{OH}}$ coefficient, and which accounted for about 25% of the total $L_{\text{OH}}$ of the alkenes. It is well known that isoprene is the most abundant plant source of VOCs emissions, and plant emissions also contribute to the pollution of VOCs (Chen et al., 2014). The oxidation reaction with OH radicals is the most essential way to reduce emissions for most VOCs (Parrish et al., 2007; Alvim et al., 2018). The complex chemical reactions of VOCs in the atmosphere will directly lead to the generation of ozone and SOA. Therefore, the OFP and SOAp of VOCs were studied.

**Ozone and SOA Formation Potential of VOCs Species**

The $L_{\text{OH}}$ can only qualitatively identify the reaction species. To determine the contribution to the formation of ground-level ozone, the estimation of OFP for a particular VOCs species is essential.
Table 3. The total OH loss rate and contribution of VOCs groups.

| Sites | \(k_{\text{OH}} (s^{-1})\) | Total VOCs | Contribution of VOCs groups (%) |
|-------|------------------|------------|-------------------------------|
|       |                  | Alkanes    | Alkenes                       | Aromatics       | Alkynes          |
| BD    | 13.02            | 14.11      | 63.18                         | 22.63           | 0.08             |
| CZ    | 14.72            | 11.49      | 75.67                         | 12.46           | 0.38             |
| CD    | 9.00             | 9.26       | 83.12                         | 7.50            | 0.12             |
| HD    | 13.74            | 14.19      | 64.04                         | 21.52           | 0.26             |
| HS    | 7.60             | 13.76      | 79.32                         | 6.41            | 0.51             |
| LF    | 21.90            | 8.98       | 86.87                         | 3.77            | 0.38             |
| SJZ   | 10.27            | 12.51      | 78.97                         | 7.78            | 0.74             |
| TS    | 4.79             | 20.35      | 55.68                         | 23.84           | 0.13             |
| XT    | 5.88             | 20.07      | 67.22                         | 12.58           | 0.13             |
| ZJK   | 3.82             | 12.26      | 76.55                         | 10.80           | 0.39             |

Fig. 5(a) showed the total OFP of VOCs in the 10 sampling cities. The OFP value is roughly divided into three levels: BD, HD, and LF are the highest (> 300 µg m\(^{-3}\)); CZ and SJZ are relatively high (> 160 µg m\(^{-3}\)); CD, HS, TS, XT, ZJK are relatively low (< 160 µg m\(^{-3}\)). The reason for this phenomenon might be the OFP contribution of alkanes was relatively small, and alkenes had the largest contribution of OFP and followed by aromatics. To determine the major contributing species of ozone formation in BTH area, Fig. 6(a) showed the contribution of each species to total OFP. Ethene has the highest contribution rate to OFP (13.52%). Its high reactivity (MIR = 9.07) and high mixing ratio (10.8% of total mixing ratio) ensure that it is the largest contributor to ozone formation. The OFP contribution of propylene (6.82%), \(m/p\)-xylene (4.20%) and toluene (3.85%) preceded only by ethene, but their mixing ratio only respectively accounted for 3.50%, 1.08% and 2.14% in total mixing ratio.

The formation of SOA also varies with the type of VOCs and the rate of reaction. Therefore, calculating the SOAp of VOCs has practical application value for studying the formation and controlling of SOA in air pollution. Fig. 5(b) showed the total SOAp of VOCs groups. Typically, VOCs above 6 carbon atoms can be oxidized to SOA (Liu et al., 2019), so aromatics have relatively high SOAp, which was much larger than alkanes and alkenes. The characteristics of SOAp was different from that of OFP, only BD and HD at the first level, which was caused by the higher content of aromatics in the 2 cities than other cities. To determine the major contributing species of SOA formation in this region, Fig. 6(b) showed the contribution of each species to total SOAp. Toluene had the highest contribution to SOAp (15.20%). It was mainly due to its high FAC value (5.40). The values of SOAp of ethylbenzene (8.37%), \(m/p\)-xylene (6.93%) and 1,3,5-trimethylbenzene (6.37%) were after toluene.

In summary, the most important components of VOCs for OFP and SOAp were alkenes and aromatics, which is consistent with the results of Lin et al. (2015). Therefore, it is necessary to control the emission of alkenes and aromatics to control ozone and SOA pollution.

Diagnostic Ratios of VOCs

Table 4 demonstrated the ratio of specific VOCs species in sampling cities. To identify the main sources of alkanes with short carbon chain (less than 5 carbon), the correlation between propane, and \(n\)-butane and \(i\)-butane was studied.
cis-2-Butane and trans-2-butane were studied to determine the main sources of alkenes with short carbon chain. Previous studies had shown that the ratio of 1 represents a major source of vehicle emissions (Liu et al., 2008b). As shown in Table 4, the ratios of BD, CZ, HD, HS, LF, SJZ and TS are all around 1. It indicates that the reactive 2-butene in these cities is mainly derived from vehicle emissions.

Toluene and benzene are often derived from the emission of vehicle and the evaporation of fuel, while toluene is also a tracer of paint solvents. The ratio of toluene to benzene (T/B) is generally used to explore the characteristics of the source of aromatics (Nelson and Quigley, 1984; Hui et al., 2019; Tohid et al., 2019; Zhang et al., 2019). Research had found that the T/B value is equal to 2 representing the VOCs mainly come from the motor vehicle emissions (Barletta et al., 2008). The value of T/B in BD, CZ, HD, LF, SJZ in Table 4 indicated that the motor vehicle emissions was the main source. In CD, HS, XT, ZJK, the value of T/B were all far less than 2, which illustrated the VOCs were also affected by using organic solvents (Barletta et al., 2008; Wang et al., 2016) which was consistent with the result of light alkanes and alkenes.

In addition, the ratio of xylene/ethylbenzene (X/E) is generally used to illustrate the aging of air masses (Han et al., 2017). The reaction rate of m/p-xylene with OH radicals is faster than ethylbenzene. When m/p-xylene reacts rapidly with OH radicals, X/E decreases significantly. Then, the residence time of VOCs in the atmosphere decreases, and the air mass begins to age (Huang et al., 2015). The diagnostic ratio of typical urban areas of X/E is about 2.5. When the ratio is significantly lower than 3, the long-distance transmission of VOCs has a greater impact on local pollution (Yurdakul et al., 2018). Table 4 showed that the X/E value of BD, LF, SJZ, and TS were comparable to the ratio of typical urban areas, indicating that these cities were greatly affected by transmission in other areas. The lower X/E value indicated that VOCs in CD, HS, XT and ZJK were mainly affected by local emission.

By fitting the X/E ratio with ozone concentration, the condition of aging of air masses at each site can be further confirmed (Xu et al., 2011). The results of the period with strong photochemical action (1:00–3:00 p.m.) showed different correlations between ozone concentration and X/E.

| Sites | Propane/n-Butane | Propane/i-Butane | cis-2-Butene | Toluene/ Benzene | Xylene/Ethylbenzene |
|-------|-----------------|-----------------|--------------|-----------------|--------------------|
| BD    | 2.47            | 2.37            | 0.93         | 1.93            | 2.10               |
| CZ    | 2.87            | 2.59            | 0.95         | 1.88            | 1.81               |
| CD    | 1.63            | 1.70            | 0.39         | 0.66            | 0.77               |
| HD    | 2.15            | 2.85            | 1.13         | 1.47            | 0.92               |
| HS    | 2.38            | 2.16            | 1.17         | 0.89            | 0.83               |
| LF    | 2.15            | 2.75            | 1.35         | 1.72            | 2.32               |
| SJZ   | 2.78            | 2.10            | 1.22         | 2.47            | 2.59               |
| TS    | 1.43            | 0.96            | 1.11         | 1.22            | 2.33               |
| XT    | 0.7             | 0.75            | 0.42         | 0.87            | 0.69               |
| ZJK   | 3.16            | 4.67            | 0.56         | 0.77            | 0.88               |

Table 4. The ratios of specific species.
ratio in different cities (Table 5). In CZ, CD, HD, HS, XT and ZJK, ozone concentration and X/E ratio showed a significant negative correlation. The ozone concentration increases with the aging of the air mass, indicating that the regional transport process has a great influence on pollutants. However, there were insignificant correlations between the ozone concentration and the X/E ratio, indicating that the local emissions in BD, LF, SJZ and TS was the main source of pollution.

**CONCLUSIONS**

VOCs encompass an array of reactive and potentially hazardous pollutants that are present in the atmosphere. In this study, the characteristics and sources of 61 VOCs in the BTH area of China were investigated from 2018 till 2019, and the key reactive species in ozone and SOA formation were analyzed. The severest pollution was observed in LF, followed by BD, HD and SJZ, and the mildest, in CD and ZJK. The most abundant VOCs, in descending order, were alkanes, alkenes, aromatics and alkynes. The mixing ratio for alkanes exceeded 50% in every city, and only HD and TS displayed a higher proportion of aromatics than alkenes. Alkenes accounted for the smallest fraction (≤ 6.9%) of the VOCs. The chemical reactivity of the VOCs was estimated by calculating the LCH, and alkenes were identified as the most reactive components. Alkenes contributed the largest percentage of the OFP, with BD, HD and LF exhibiting the maximum OFP values, whereas aromatics contributed the largest percentage of the SOAp, with BD and HD exhibiting the maximum SOAp values.

The propane/n-butane and propane/i-butane, and cis-2-butane/trans-2-butane ratios indicated that vehicle emissions were the main source of light alkanes in the cities and also of active 2-butane in BD, CZ, HD, HS, LF, SJZ and TS, respectively. Furthermore, organic solvents in CD, HS, XT and ZJK can not be ignored as a contributing factor. The X/E ratio showed air masses aging in most of the cities, confirming that both short-range transport and local emission were responsible for the VOC pollution in this area.

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**Table 5.** The correlations (r values) of propane/n-butane, propane/i-butane and ozone/(X/E).

| Sites | Propane/n-Butane | Propane/i-Butane | Ozone/(X/E) |
|-------|------------------|------------------|-------------|
| BD    | 0.85             | 0.87             | -0.08       |
| CZ    | 0.87             | 0.89             | -0.59       |
| CD    | 0.93             | 0.90             | -0.76       |
| HD    | 0.85             | 0.85             | -0.68       |
| HS    | 0.88             | 0.86             | -0.61       |
| LF    | 0.89             | 0.85             | -0.44       |
| SJZ   | 0.88             | 0.91             | -0.18       |
| TS    | 0.93             | 0.96             | -0.21       |
| XT    | 0.90             | 0.85             | -0.79       |
| ZJK   | 0.86             | 0.87             | -0.92       |
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