Characteristics of one-year observation of VOCs, NOx, and O₃ at an urban site in Wuhan, China

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ABSTRACT

A continuous online observation of ozone and its precursors (NOx, VOCs) was carried out in central urban Wuhan from September 2016 to August 2017. The concentration levels of ozone, NOx, VOCs and their variations in urban Wuhan were analyzed, as well as effects of VOCs on ozone photochemical generation and the main controlling factors for ozone production. During the observation period, the average concentrations of ozone and NOx in Wuhan was 22.63 and 30.14 ppbv, respectively, and the average concentration of VOCs was 32.61 ppbv (42.3% alkanes, 13.0% alkenes, 10.0% aromatics, 7.3% acetylene, 9.9% OVOCs, and 10.5% halohydrocarbons). Ozone concentration was higher in spring and summer as compared with autumn and winter, whereas VOCs and NOx concentrations were lower in spring and summer but higher in autumn and winter. Aromatics and alkenes, two of VOCs species, showed the highest contributions to ozone formation potential in Wuhan (35.7% alkenes, 35.4 aromatics, 17.5% alkanes, 8.6% OVOCs, 1.6% halogenated hydrocarbons, and 1.4% acetylene). Among all VOCs species, those with the highest contribution were ethylene, m-xylene, toluene, propylene and o-xylene. The contribution of these five compounds to the total ozone formation potential concentration was 43.90%. Ozone-controlling factors in Wuhan changed within one day; during the early morning hours (6:00–9:00), VOCs/NOx was low, and ozone generation followed a VOCs-limited regime. However, during the peak time of ozone concentration (12:00–16:00), the ratio of VOCs/NOx was relatively high, suggesting that ozone generation followed a NOx-limited regime.

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Introduction

With the development of industry and the service sector, China’s economy and urbanization process have rapidly developed in the past 20 years (Wang et al., 2015b). However, the processes of population growth and industrialization have increased the demand for energy, and the resulting environmental problems have become increasingly more serious (Chan and Yao, 2008; Hao and Wang, 2005; Shao et al., 2006). In large urban agglomerations, the rising trend of atmospheric pollutant concentration has been very significant (An et al., 2014; Barletta et al., 2005; Liu et al., 2008). In previous studies,
particulate matter pollution has been a research focus. In recent years, due to the continuous efforts of people of all walks of life, the particulate matter pollution situation in China has markedly improved but the ozone concentration has continued to rise and has become the priority domestic pollutant, after fine particulate matter, in many Chinese areas.

Ozone is not only the major oxidant in the troposphere but is also the main precursor of OH radicals and NOx radicals in the troposphere (Masclln et al., 2013; Wang et al., 2015a). Tropospheric ozone pollution may also cause climate change, which has adverse effects on humans and ecosystems (Mills et al., 2015; Tang et al., 2013). Tropospheric ozone is a secondary pollutant produced by the photochemical reaction of NOx and VOCs (Sillman, 1995). As the main precursor of ozone formation, the relationship between the concentra
tion changes of ozone and its precursor are non-linear. In previous studies, researchers have defined the effects of precursor changes on ozone concentration as either VOCs-limited or NOx-limited (Geng et al., 2008; Tie et al., 2007; Zhang et al., 2004b). In 1989, Seinfeld calculated by numerical simulation that the ozone formation in the Los Angeles urban area was under the control of NOx. The ratio of VOCs/NOx was greater than 8:1 (where the VOCs concentration used the carbon atom concentration). Seinfeld defined the ratio as the threshold of VOCs control and NOx control conversion to ozone formation in typical urban areas (Seinfeld, 1989), and researchers around the world then used this method to study the main control factors of photochemical reactions in their respective regions (An et al., 2015; Li et al., 2013; Ran et al., 2009; Trainer et al., 1993; Sillman, 2002; Ran et al., 2011; Li et al., 2013; Zou et al., 2015). According to previous studies, ozone production in typical urban areas is mainly controlled by NOx. However, recent studies have shown that the ozone control factor could change diurnally in many areas. In the morning, it is controlled by VOCs, then control changes to NOx at the peak time of ozone concentration (Li et al., 2013; Kanaya et al., 2009; Sillman and West, 2009; Zou et al., 2015).

Because large gaps exist in the photochemical reactivity between different VOCs, it is important to calculate the ozone formation potential of the relative contributions of various VOCs for controlling the ozone formation in a region. In previous studies, researchers have developed a variety of methods to calculate the ozone generating capacity of VOCs; the maximum incremental reactivity (MIR) and propylene-equivalent concentration method are most widely used.

Wuhan is the largest extra-large city in central China and an important transportation hub. In 2017, Wuhan’s gross domestic product (GDP) was 1.34 trillion yuan, ranking ninth in the country (2017 data from the Wuhan Bureau of Statistics). However, with the rapid development of Wuhan’s industrialization and urbanization in recent years, multiple atmospheric pollutants have become increasingly serious, especially ozone, which has become the second primary pollutant in Wuhan after fine particulate matter (Wuhan City 2017 Environmental Communiciqué). In past research, there was rarely long-term continuous on-line observation of ozone, NOx, and VOCs in the Wuhan area, especially VOCs data. Therefore, it is important for the study of the ozone pollution status in Wuhan to obtain long-term continuous observational data for ozone and its precursors. This study analyses the concentration and variation characteristics of ozone and its precursors in Wuhan (including diurnal, seasonal, and annual changes) and analyses the diurnal and seasonal varieties of ozone production in the region based on one year of continuous online observations. We summarize the overall information of the observed data and describe the characteristics of the changes in ozone and its precursors at various time periods. We classify VOCs species, use the propylene-equivalent concentration and MIR to evaluate the contribution and impact of various VOCs on ozone generation, and use the characteristic VOCs ratio method to evaluate the photochemical age of the air mass in Wuhan. Then, we discuss the ozone controlling factors and formation mechanism in Wuhan based on the changes of VOCs/NOx ratios.

1. Experiments

1.1. Site description

The observation period of this study was from September 2016 to August 2017; a one-year continuous online observation period with a time resolution of 1 hr was adopted. The monitoring site is located on the rooftop of the building of the School of Resources and Environmental Sciences, Wuhan University (114°37′E, 30°53′N). The monitoring site is approximately 15 m above the ground, with an open field and stable air flow. The location of the site is in the university city, on the southeast side of Wuhan City, and there is no obvious air pollution source within 2 km. The underlying surface conditions are similar to those in the Wuhan urban area, and the monitoring data can basically represent the pollution of urban Wuhan. Fig. 1 shows the annual variation of meteorological elements and ozone, VOCs, and NOx during the observation period. Fig. 2 and Table S1 show the statistics of meteorological elements for each season at the site during the observation period. In spring, autumn and winter, the prevailing wind directions of this observation site are west and southwest, whereas the dominant wind direction in summer is west and southeast. The average values of wind speed, temperature, and humidity during the observation period were 1.28 m/s, 18.57°C, and 71.67%, respectively.

1.2. Measurement instruments

The VOCs data were measured by the atmospheric volatile organics rapid online continuous automatic monitoring system (TH-300B Tianhong China). The system sampling frequency is 1 hr. The TH-300B monitoring system consists of the following components: the carrier gas system, electronic cryogenic pre-concentration sampling system, GC-FID/MS (gas chromatography–flame ionization detector/mass spectrometer detector) analysis system and recording system. Before the measurements, the sampling tubes should be set outdoors and the sampling port should be set about 1 m from the vertical height of the roof. A particulate removal device consisting of a PTFE membrane bracket which had a 47 mm diameter and 2 µm pore should be placed at the sample inlet of the concentrator to remove particulate matter from the gas.
sample. Real-time ambient air samples were collected by the sampling system and enter the enrichment system in 5 min, the sampling flow (FID&MS) was 60 mL/min, anti-blowing flow was 180 mL/min. At low temperature (about −150 °C), the C2–C4 hydrocarbons in the air samples were captured by the PLOT column. Other VOCs compounds were captured by the deactivated quartz capillary column and rapidly heated. In the analysis, the compounds were fed into the analysis system, the gas chromatography separation of the C2–C4 hydrocarbons was detected by the flame ionization detector, the remaining VOCs compounds were detected and identified by the mass spectrometer detector; the entire process can be achieved by the automatic operation of the control software. The entire system was also equipped with an automatic backflushing and automatic calibration system. During the observation period, a total of 100 VOCs were collected and classified into six categories: alkanes, alkenes, aromatic hydrocarbons, alkyne (acetylene), OVOCs, and halohydrocarbons. In addition, in order to ensure the authenticity and accuracy of the measurement data, the experimental instruments should be regularly inspected and calibrated. We injected different concentrations of standard gas, and 5-point calibration curves were generated in the process, there was an obvious linear response relationship because the linear correlation coefficient was basically higher than 0.999. The detection limit range of the TH-300B monitoring system for all VOCs can be found in Table S2. The quantitative accuracy of the 90% target was less than 25% among all the detected VOC components except for a small amount of VOC components. The quantitative repeatability of the sample usually does not exceed 5%. The accuracy of the

Fig. 1 – Time series of meteorology parameters (air temperature, RH), trace gases (O3, NOx) and different groups of VOCs from September 2016 to August 2017 at Wuhan.

Fig. 2 – Wind rose diagrams for the frequencies of wind direction in each season from September 2016 to August 2017 at Wuhan.
sample was determined by the relative error between the measured and guaranteed values, and then the relative error of the target is less than 30%. The working state and response of the TH-300B monitoring system were calibrated at 11:00 in every observation period day; the FID used external standard method and the MS used internal standard method.

Nitrogen oxides were measured by the chemiluminescence method using the NO-NO₂-NOX analyzer (42i Thermo USA). The ozone concentration is measured by an O₃ analyzer (49i Thermo USA) that uses UV spectrophotometry. The working principle of them are mentioned in many references, we don’t repeat here. The meteorological parameters, such as temperature, humidity, wind direction, and wind speed, were provided by the Hubei Provincial Meteorological Observatory Automatic Observatory.

2. Results and discussion

2.1. Characteristics of ozone NOx and VOCs

The distribution of ozone, NOx, and VOCs in different seasons is shown in Table 1. A significant seasonal variation in ozone concentration can be seen; the lowest level was reached in winter and the highest level in summer. In addition, the range of changes in ozone concentration was largest in late summer and early autumn, which was significantly higher than in other periods of the year. This may be due to differences in other meteorological conditions, such as sunshine and ambient temperature, and the emitted intensity of atmospheric pollutant discharge in different seasons (Blommer et al., 2009; Blommer et al., 2010). The seasonal variation of the concentrations of NOx and VOCs were negatively correlated with the ozone concentration. The NOx and VOCs concentrations reached the highest level in winter and the lowest level in summer.

To better understand this phenomenon, Table S3 shows the Pearson correlation coefficient between ozone and its precursors. We can clearly see that there was a significant correlation between the concentration of O₃ and its precursors. It should be noted that during the observation period, there was a significant negative correlation between the concentration of ozone and the concentrations of its precursors in Wuhan. NO, NO₂, NOx as precursors of ozone, their negative correlation with ozone concentration was significant, but lower than the negative correlation between the concentration of ozone and VOCs. As a typical secondary pollutant, ozone is mainly produced by photochemical reactions of its precursor pollutants such as VOCs and NOx in the atmosphere. NO₂ generates NO and O atoms by photolysis, and then O atoms react with O₂ to ozone. In addition, NO can react with ozone to NO₂ and oxygen. Through the above chemical reactions, a dynamic equilibrium is formed between NO, O₃, and NO₂. When VOCs are present in the atmosphere, it could generate RO₂ radicals, and RO₂ radicals will react with NO so that NO was consumed, thereby breaking the dynamic equilibrium between NO, O₃, and NO₂, increasing the ozone concentration. Despite there is a complex series of chemical reactions between ozone, NOx, and VOCs, the negative correlation between ozone and its precursors is always present.

To better reflect the ozone concentration change and its formation process in Wuhan, we analyzed the daily change rate in different seasons of ozone and its precursors (VOCs, NOx). The calculation is as Eq. (1):

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

[X] represents the concentration of ozone and its precursors (VOCs, NOx) at time t, and [X]_{t+1} represents the concentration of ozone and its precursors one hour after time t.

Fig. 3 shows the seasonal variations of ozone and its precursor concentrations and their time-to-hour change rate. From Fig. 3a, the daily change of ozone concentration shows a distinct unimodal pattern, with the maximum occurring at approximately 15:00–16:00 every day. Ozone is a product of photochemical reactions, and its generation is mainly affected by light and temperature. This single peak change pattern can be mainly attributed to changes in the solar radiation intensity during the day. From the perspective of seasonal changes, the ozone concentration is highest in summer and lowest in winter because the photochemical reaction intensity in summer is significantly higher than in winter; in addition, the NOx concentration in winter is significantly higher than in summer, and the NO₂ concentration is also higher than in summer. The higher NO₂

Table 1 – Month average concentration of VOCs categories, NOx and ozone in each season at Wuhan (ppbv).

<table>
<thead>
<tr>
<th>Season</th>
<th>Month</th>
<th>Alkanes</th>
<th>Alkenes</th>
<th>Aromatics</th>
<th>OVOCs</th>
<th>Halohydrocarbons</th>
<th>TVOCs</th>
<th>NOx</th>
<th>O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spring</td>
<td>March</td>
<td>15.22</td>
<td>6.27</td>
<td>3.73</td>
<td>3.27</td>
<td>4.69</td>
<td>33.17</td>
<td>40.2</td>
<td>18.91</td>
</tr>
<tr>
<td></td>
<td>April</td>
<td>16.15</td>
<td>5.11</td>
<td>2.80</td>
<td>3.07</td>
<td>3.71</td>
<td>30.83</td>
<td>35.7</td>
<td>25.16</td>
</tr>
<tr>
<td></td>
<td>May</td>
<td>15.70</td>
<td>5.00</td>
<td>2.41</td>
<td>3.71</td>
<td>3.32</td>
<td>30.14</td>
<td>37.2</td>
<td>31.58</td>
</tr>
<tr>
<td>Summer</td>
<td>June</td>
<td>12.73</td>
<td>4.22</td>
<td>1.99</td>
<td>3.53</td>
<td>3.00</td>
<td>25.47</td>
<td>26.8</td>
<td>30.65</td>
</tr>
<tr>
<td></td>
<td>July</td>
<td>8.16</td>
<td>3.15</td>
<td>1.43</td>
<td>3.25</td>
<td>2.03</td>
<td>18.02</td>
<td>13.9</td>
<td>34.33</td>
</tr>
<tr>
<td></td>
<td>August</td>
<td>10.00</td>
<td>3.87</td>
<td>1.98</td>
<td>3.75</td>
<td>2.58</td>
<td>22.19</td>
<td>13.9</td>
<td>31.83</td>
</tr>
<tr>
<td>Autumn</td>
<td>September</td>
<td>11.73</td>
<td>4.49</td>
<td>3.15</td>
<td>5.59</td>
<td>3.91</td>
<td>28.87</td>
<td>14.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>October</td>
<td>16.54</td>
<td>6.71</td>
<td>3.88</td>
<td>4.51</td>
<td>4.18</td>
<td>35.82</td>
<td>17.4</td>
<td>14.27</td>
</tr>
<tr>
<td></td>
<td>November</td>
<td>20.91</td>
<td>9.11</td>
<td>4.66</td>
<td>2.30</td>
<td>5.52</td>
<td>42.50</td>
<td>42.2</td>
<td>9.32</td>
</tr>
<tr>
<td>Winter</td>
<td>December</td>
<td>26.55</td>
<td>12.82</td>
<td>5.55</td>
<td>1.82</td>
<td>5.44</td>
<td>52.18</td>
<td>57.5</td>
<td>8.15</td>
</tr>
<tr>
<td></td>
<td>January</td>
<td>20.91</td>
<td>10.33</td>
<td>4.54</td>
<td>1.25</td>
<td>3.90</td>
<td>40.93</td>
<td>37.5</td>
<td>13.87</td>
</tr>
<tr>
<td></td>
<td>February</td>
<td>17.06</td>
<td>8.19</td>
<td>2.61</td>
<td>1.65</td>
<td>2.29</td>
<td>31.79</td>
<td>43.5</td>
<td>14.69</td>
</tr>
</tbody>
</table>
concentration in winter will cause more OH radicals to be consumed by the reaction with NO₂, which reduces the ozone production (Geng et al., 2008). Regardless of the effect of transport, the negative rate of change in ozone concentration indicates that chemical loss dominates the change in ozone concentration, and the positive rate of change in ozone concentration indicates that the photochemical production of ozone plays a major role in the change of concentration (Zou et al., 2015). In general, the effect of vertical transport of ozone concentration is difficult to estimate but cannot be ignored. Due to the small wind speed at the observation point, we can assume that the change in ozone concentration here only comes from the chemical effect; however, the transport could also have an impact on the daily changes in ozone concentration. Although there was a slight difference in the change rate of ozone concentration during the four seasons, the times for negative values were all at approximately 16:00. At this time, the photochemical process began to weaken due to the weakening of the light intensity, thereby causing a decrease of the OH radical concentration. At approximately 20:00, light completely disappeared and OH radicals stopped producing; however, NOx titration continued to consume ozone. From 00:00 to 08:00, the ozone concentration was relatively stable, and the rate of change was almost maintained at 0. After 08:00, due to the diffusion of the atmospheric boundary layer and the continuous increase in photochemical reactions, the rate of change in ozone concentration had a significant upward trend (it had always been positive) and reached a peak at approximately 12:00. The peak value of the ozone change rate in summer was the highest during the
monitoring period and the lowest in winter; the difference was significant. The photochemical reaction intensity and ozone production in summer were significantly higher than in winter.

Compared with ozone, the diurnal variation of ozone precursor concentration showed the opposite double-peak pattern. The appearance time of the peak value was basically the same as the morning and evening traffic peak times. The minimum value appearance time was basically the same as the appearance time of the ozone peak; the concentration of precursors varied from season to season (highest in winter and lowest in summer) but the trend was consistent. As shown in Fig. 3d, f, the change rates of NOx and VOCs were relatively stable before 08:00, reaching the first peak of the day at 8:00, and the concentrations of NOx and VOCs peaked at the same time. During the period from 09:00 to 16:00, the change rates of NOx and VOCs were negative, and both concentrations gradually decreased. The lowest value of ozone precursors appeared at approximately 16:00, which was basically the same as the time when ozone peaks appeared; from the arrival of the evening rush hour, VOCs and NOx rates gradually increased, as did their concentrations. The second peak of VOCs concentration and change rate appeared earlier than that of NOx; this outcome may be due to the effect of the titration reaction with ozone, which made the NOx peak appear somewhat delayed.

Ozone precursors have higher concentrations at night and lower daytime concentrations (we set the daytime period as 07:00–19:00 and the nighttime period as 20:00–06:00). For VOCs, the maximum of average concentration during the day was 40.76 ppbv in winter, and the minimum was 21.26 ppbv in summer. The maximum of average concentration at night was 47.01 ppbv in winter, and the minimum was 22.69 ppbv in summer. The order of the average nighttime concentration of VOCs in descending order was winter, autumn, spring, and summer. The order of the average nighttime concentration of VOCs was the same as that during the day. The daily range of VOCs concentration in different seasons was winter (19.33 ppbv), spring (18.42 ppbv), autumn (14.43 ppbv), and summer (7.30 ppbv). For NOx, the maximum of average concentration during the day was 37.48 ppbv in winter, and the minimum was 16.51 ppbv in summer. The maximum of average concentration at night was 58.33 ppbv in winter, and the minimum was 20.26 ppbv in summer. The average daily and nighttime concentrations of NOx were in the order of winter > spring > autumn > summer; the highest daily range of NOx concentration was in winter (52.32 ppbv), the lowest was in summer (14.11 ppbv).

It can be seen from Tables S4a, b and S5 that the concentrations of major VOCs in Wuhan during the observation period were not the same as those in other cities. Some species had higher concentrations than other regions, and some species had lower concentrations than other regions, there was no rules to follow. Therefore, we can conclude that for the same VOCs species, the difference in observation time, observation location, and observation methods would lead to a certain impact on the final measured concentration. In addition, differences between city activities and energy structure could also affect the pollution status of VOCs. (An et al., 2012).

### 2.2. The effect of VOCs on ozone formation

#### 2.2.1. Overall characteristics of VOCs

Table S6 lists the concentrations of 100 VOCs species obtained during the observation period. The top 10 VOCs in the concentration categories were propane, ethane, ethylene, acetylene, acetone, n-butane, methylene chloride, isobutane, isopentane, and toluene (from large to small), accounting for 71.6% of the total VOCs concentration (Fig. 4).

The diurnal variations of various types of VOCs are shown in Fig. 5. Because many types of VOCs are observed and their chemical structures are different, the chemical reactivity of VOCs varies greatly. Therefore, these six types of VOCs did not exactly exhibit the same daily variation pattern. However, their daily trends were basically the same, with a bimodal distribution in all seasons. By comparing all kinds of VOCs in different seasons, we found that the highest diurnal change of alkanes concentration was in winter (11.10 ppbv), the minimum (4.95 ppbv) was in summer. The maximum concentration diurnal difference of aromatics occurred in winter (4.01 ppbv), the minimum was in summer (1.49 ppbv). The maximum concentration diurnal range of aromatics appeared in spring (1.85 ppbv), the minimum was in summer (1.02 ppbv). The maximum concentration diurnal difference of acetylene appeared in winter (1.36 ppbv), the minimum was in summer (0.46 ppbv). The maximum concentration diurnal range of OVOCs appeared in autumn (1.28 ppbv), the minimum was in winter (0.49 ppbv). The maximum concentration diurnal range of halohydrocarbons appeared in spring (1.44 ppbv), the minimum was in summer (0.55 ppbv).

#### 2.2.2. VOCs reactivity and ozone formation potential

Previous studies have found that the trend of increased surface layer ozone concentration is closely related to the emission of VOCs. Changes in the concentration of VOCs have a significant impact on the photochemical production of ozone. Due to the large difference in photochemical reactivity of each VOCs species, the contributions of different VOCs species to the photochemical generation of ozone are not the same. To better understand the characteristics of VOCs species observed in the atmosphere and determine their role in the photochemical generation of ozone to make an effective ozone control strategy, this study used two methods to analyze and describe the reactivity and ozone formation potential of various VOCs species.

The first method was the propylene-equivalent concentration (Chameides et al., 1992). This method can estimate the photochemical activity of each VOCs species based on its kinetic reactivity (Zou et al., 2015). The principle is to compare all VOCs on an equal basis. This method is established on the assumption that VOCs in the troposphere mainly react with OH radicals and ignore the reaction mechanism and its associated uncertainties (Middleton et al., 1990). The calculation is as Eq. (2):

$$C_{j,\text{Propy-Equiv}} = C_{j,C} \times \frac{k_{j,\text{OH}}}{k_{\text{Propy-OH}}}$$

where $j$ represents a specific VOCs species, $C_{j,C}$ represents the carbon atom concentration (ppbC) of species $j$, and $k_{j,\text{OH}}$ (cm$^3$/molecule·sec) and $k_{\text{Propy-OH}}$ (cm$^3$/molecule·sec) refer to the
chemical reaction rate constants of species \( j \) and propylene with OH radicals, respectively. The chemical reaction rate constants for OH radicals of all VOCs species can be found in the 2003 study of Atkinson and Arey (Atkinson and Arey, 2003).

The second method was the MIR weighted concentration, which is defined as the maximum ozone concentration variation caused by the extraction or addition of VOCs compounds with unit mass concentration in a given air mass. This method considers the chemical reaction mechanisms of various VOCs species and the effects of VOCs/NO\(_x\) ratio changes on ozone formation (Atkinson, 2000). It can be used to estimate the contributions of all VOCs compounds to ozone production based on the VOCs mechanistic reactivity (Zou et al., 2015). The calculation is as Eq. (3):

\[
C_{j,\text{MIR}} = \text{MIR}_j \times \frac{C_{j,\text{ppbv}} \times m_j}{M}
\]

where \( C_{j,\text{ppbv}} \) (ppbv) represents the actual volume fraction concentration of species \( j \), \( M \) represents the relative molecular mass of ozone, \( m_j \) represents the relative molecular mass of species \( j \), and \( \text{MIR}_j \) (g O\(_3\)/g) represents the MIR constant of

![Graph](image)

Fig. 4 – Top 10 species that most contributed to the concentration of VOCs at Wuhan.

![Graph](image)

Fig. 5 – Diurnal variations of the VOCs concentrations during different seasons at Wuhan.
species $j$. This constant can be obtained by reference to the research of Carter in 1991 (Carter, 1991). The concentration, OH reaction rate constant, and the MIR constant of each VOCs species can be seen in Table S6.

Fig. 6 shows the percentage of VOCs species contribution over the year obtained by different concentration representations. The ppbC concentration contribution was ranked in the order of alkanes (49.3%), aromatics (21.0%), alkenes (9.9%), OVOCs (9.2%), halohydrocarbons (6.5%), and acetylene (4.1%). Alkenes and aromatics made the largest absolute contribution of the propylene-equivalent concentration and the MIR concentration; the combined ratios of the two were 72.6% and 71.1%, respectively. It can be seen that although alkanes contributed the most to the non-weighted ppbv and non-weighted ppbC concentrations due to their lower chemical reactivity, their contributions to propylene-equivalent concentration and MIR concentration were relatively low, 21.4% and 17.5%, respectively. In contrast, although the non-weighted concentrations of alkenes and aromatics were much less than those of alkanes, their chemical reactivity was relatively high, and their contributions to the propylene-equivalent concentration and the concentration of the MIR were greatly increased.

The volume concentration and carbon atom concentration range of VOCs in different seasons were 1.43–22.33 ppbv and 2.85–78.20 ppbC, respectively. As shown in Fig. 7a, b, the alkanes are the species that contributes most to the volume concentration and carbon atom concentration of VOCs in any season, and their proportions both fluctuate by approximately 50%. As shown in Fig. 7c, when the propylene-equivalent concentration was used to compare the activity of various types of VOCs, it was found that alkenes and aromatics replaced the alkanes as the highest contributing species. The propylene-equivalent concentration of each type of VOCs varies in different seasons. The alkenes maximum propylene-equivalent concentration appeared in winter (13.67 ppbC), the minimum occurred in spring (7.33 ppbC). The maximum of propylene-equivalent concentration aromatics appeared in autumn (14.38 ppbC), the minimum occurred in summer (5.69 ppbC). The maximum of propylene-equivalent concentration of alkanes appeared in winter (8.33 ppbC), the minimum occurred in summer (3.66 ppbC). The maximum OVOCs propylene-equivalent concentration appeared in autumn (2.31 ppbC), the minimum occurred in winter (1.06 ppbC). Note that the ratios of the propylene-equivalent concentration to the non-weighted ppbC concentration for each season were 0.22 (spring), 0.27 (summer), 0.27 (autumn), and 0.24 (winter). This was similar to the discovery by Ran in the Shanghai urban area, which indicated that the chemical reactivity of major VOCs compounds in urban Wuhan is lower than that of propylene (Ran et al., 2009). As shown in Fig. 7d, the MIR method, similar to the propylene-equivalent concentration method, was used to compare the contribution of various types of VOCs to MIR concentration. It was also found that alkenes and aromatics replaced alkanes to become the most-contributing VOCs species. The concentration range of alkenes was 19.17 (summer)–21.18 ppbv (winter), the MIR concentration range for aromatics was 17.79 (summer)–40.49 ppbv (autumn), the MIR concentration range for alkanes was 10.50 (summer)–21.18 ppbv (winter) and the MIR concentration ranges for OVOCs was 6.19 (winter)–11.06 ppbv (autumn).

Table 2 lists the top 20 VOCs compounds and their contribution rates based on the propylene-equivalent concentration method and MIR concentration method during the observation period. It can be seen from the table that whether
the propylene-equivalent concentration or the MIR concentration calculation method was used, the results obtained by them were similar: 16 among the top 20 VOCs were the same, the difference being in the order. Although both methods can be used to calculate the contribution of each VOCs compound to the ozone formation potential (OFP), the two methods are essentially different, and this difference led to the different order of the same VOC in the calculation results of the two methods. The propylene-equivalent concentration method estimates the reactivity of various VOCs based on its kinetic mechanism, ignoring the reaction mechanism between VOCs with peroxy radicals and NO; when using this method to

Fig. 7 – VOCs profiles based on different scales during different seasons at Wuhan.

<table>
<thead>
<tr>
<th>OH reactivity rank</th>
<th>Species</th>
<th>%</th>
<th>Number b</th>
<th>Species</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>m/p-Xylene</td>
<td>8.1</td>
<td>3</td>
<td>Ethene</td>
<td>15.5</td>
</tr>
<tr>
<td>31</td>
<td>Isoprene</td>
<td>7.9</td>
<td>16</td>
<td>m,p-Xylene</td>
<td>9.1</td>
</tr>
<tr>
<td>7</td>
<td>Ethene</td>
<td>5.9</td>
<td>10</td>
<td>Toluene</td>
<td>8.2</td>
</tr>
<tr>
<td>16</td>
<td>Propene</td>
<td>5.8</td>
<td>12</td>
<td>Propene</td>
<td>6.4</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>5.0</td>
<td>21</td>
<td>o-Xylene</td>
<td>4.7</td>
</tr>
<tr>
<td>34</td>
<td>trans-2-Pentene</td>
<td>4.7</td>
<td>14</td>
<td>Ethylbenzene</td>
<td>3.3</td>
</tr>
<tr>
<td>36</td>
<td>Styrene</td>
<td>4.0</td>
<td>19</td>
<td>i-Butene</td>
<td>2.8</td>
</tr>
<tr>
<td>23</td>
<td>1,2,4-Trimethylbenzene</td>
<td>3.8</td>
<td>1</td>
<td>Propane</td>
<td>2.7</td>
</tr>
<tr>
<td>14</td>
<td>o-Xylene</td>
<td>3.6</td>
<td>6</td>
<td>n-Butane</td>
<td>2.7</td>
</tr>
<tr>
<td>48</td>
<td>cis-2-Butene</td>
<td>3.3</td>
<td>9</td>
<td>i-Pentane</td>
<td>2.7</td>
</tr>
<tr>
<td>11</td>
<td>Ethylbenzene</td>
<td>3.2</td>
<td>37</td>
<td>1,2,4-Trimethylbenzene</td>
<td>2.5</td>
</tr>
<tr>
<td>28</td>
<td>1-Butene</td>
<td>2.8</td>
<td>28</td>
<td>1-Butene</td>
<td>2.2</td>
</tr>
<tr>
<td>6</td>
<td>i-Pentane</td>
<td>2.8</td>
<td>24</td>
<td>Propionaldehyde</td>
<td>2.0</td>
</tr>
<tr>
<td>54</td>
<td>trans-2-Butene</td>
<td>2.7</td>
<td>34</td>
<td>cis-2-Butene</td>
<td>2.0</td>
</tr>
<tr>
<td>57</td>
<td>1,3,5-Trimethylbenzene</td>
<td>2.6</td>
<td>33</td>
<td>Isoprene</td>
<td>2.0</td>
</tr>
<tr>
<td>1</td>
<td>Propane</td>
<td>2.3</td>
<td>8</td>
<td>i-Butane</td>
<td>1.9</td>
</tr>
<tr>
<td>3</td>
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<td>Butenone</td>
<td>1.9</td>
</tr>
<tr>
<td>29</td>
<td>Propionaldehyde</td>
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<td>35</td>
<td>trans-2-Pentene</td>
<td>1.8</td>
</tr>
<tr>
<td>52</td>
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<td>1.6</td>
<td>40</td>
<td>trans-2-Butene</td>
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<tr>
<td>9</td>
<td>i-Butane</td>
<td>1.4</td>
<td>29</td>
<td>Acrolein</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Table 2 – Relative contributions to ozone formation by the top 20 VOCs species based on the Propy-Equiv and the MIR scales at Wuhan.
estimate the OFP, compounds with high OH reaction rates, such as isoprene, could thus be overestimated (Zou et al., 2015). The MIR method takes into account the chemical mechanism of the VOC/NOx ratio and its effect on ozone production but the method may also introduce some mechanisms and estimation uncertainties (Dimitriades, 1996; Ran et al., 2009). As shown in Fig. 8, there are 5 alkene compounds in the top 10 VOCs that contribute most to the propylene-equivalent concentration; the other 5 are aromatics. The contributions of the two compounds to the propylene-equivalent concentration were 27.6% and 24.5%, of which the most critical active species were m/p-xylene (8.1%), isoprene (7.9%), ethylene (5.9%), propylene (5.8%), and toluene (5.0%). Among the top 10 VOCs that contributed most to the concentration of OFP, there were four aromatics, three alkenes, and three alkanes. The contributions of the three types of VOCs to the OFP concentration were 25.3%, 24.7%, and 8.1%, of which the most critical active species were ethylene (15.5%), m/p-xylene (9.1%), toluene (8.2%), propylene (6.4%), and o-xylene (4.7%). It can be seen that the key active species of VOCs in urban Wuhan are m/p-xylene, toluene, ethylene, and propylene. In addition, although the non-weighted concentration of isoprene was low, it entered the top 20 in both the propylene-equivalent concentration and the MIR concentration ranking. Therefore, it is also necessary to pay attention to isoprene emissions when formulating ozone control strategies.

2.2.3. VOCs ratios and ozone formation

In previous studies (Guo et al., 2007; Lyu et al., 2016), researchers have used ratios between VOCs with different photochemical reactivity to determine the transport and aging processes of contaminated air masses. For example, using the more reactive VOCs species versus the less reactive VOCs species, because the VOCs species with higher reactivity would be continuously consumed in the atmospheric chemical reactions, the ratio of the two species will change following the photochemical process. It can be found that if the ratio is higher, the photochemical age of the contaminated air mass is shorter, and the contaminated air mass could be mainly from local emissions; if the ratio is lower, the photochemical age of the contaminated air mass is longer, and the contaminated air mass may come from long-distance transport (Guo et al., 2007). In this study, we compared ethene and ethane, m/p-xylene and ethylbenzene (ethene and m,p-xylene are the two most important species that contribute most to the MIR concentration in Wuhan: 24.6%). By consulting the literature, it can be seen that ethene can stay in the atmosphere for approximately 1.4 days, ethane for approximately 56 days, m/p-xylene for approximately 0.6 to 1 days, and ethylbenzene for approximately 2 days (Warneck, 2000). Fig. 9 shows the daily variation of the ratio of selected characteristic VOCs species and ozone concentration. The daily average value of ethene/ethane was 0.62, and the daily average value of m/p-xylene/ethylbenzene was 0.87. For the same VOCs species ratio, the results observed in the Hong Kong urban area by Guo were 0.7 (ethene/ethane) and 1.8 (m, p-xylene/ethylbenzene) (Guo et al., 2007), and the observations by Lyu from 2013 to 2014 in urban Wuhan were 0.65 (ethene/ethane) and 1.33 (m,p-xylene/ethylbenzene) (Lyu et al., 2016). The observations in Hong Kong indicated that the photochemical pollution in the area mainly originates from the discharge of local pollutants. The observations in urban Wuhan from 2013 to 2014 indicated that the pollutants in the area were affected by transport from other areas. Previous studies have shown that the ratio of characteristic VOCs species is largely influenced by sampling point location, sampling period, and local pollutant emission characteristics (Lyu et al., 2016). The observations obtained in this study are all lower than the observations in the above two places. Considering the above factors, some contaminated air masses coming from other areas may have entered the Wuhan urban area. Both kinds of ratios showed fluctuating daily changes during daytime, whereas they increased in a stable manner at night and early morning. The two ratios began to decline rapidly at approximately 9:00 and reached the lowest level in

Fig. 8 – Top 10 species of VOCs that contribute most to the Propy-Equiv and MIR scales and their contributions to mixing ratios at Wuhan.
the afternoon, starting at approximately 16:00 in the afternoon, and then gradually rose and returned to the high value at night. The increase of the ratios in the early morning may be due to the emission of large amounts of VOCs by motor vehicles during the morning traffic rush hour. The decline of the ratio from morning to afternoon clearly shows the process of air mass aging, and the main reasons for the increase of the ratio at afternoon and night are the weakening of photochemical reactions and large-scale emissions of VOCs during late traffic peak hours. The daily change trend of ozone is opposite to the daily change trend of the characteristic VOCs ratios. The ozone concentration increased during the photochemical aging of the air mass and reached its maximum value in the afternoon. At night, due to the weakening of the photochemical reaction and the depletion of ozone by NO titration, the ozone concentration rapidly decreased. It can be seen that the change of ozone concentration in urban Wuhan is closely related to the photochemical reaction at the observation site, which is consistent with the research results by Lyu.

In this study, we also selected the volume fraction ratio of ethane/acetylene and acetylene/CO to the change the trend of the photochemical age of air masses in urban Wuhan throughout the year. Previous observations in tunnels have shown that the value of ethane/acetylene in the exhaust gas of fresh motor vehicles is 0.47 (Duffy and Nelson, 1996; Na, 2006). Because acetylene is more active than ethane, it consumes faster than ethane in atmospheric photochemical reactions. The value of ethane/acetylene changes as the reaction progresses. The larger the ratio, the longer the photochemical age of the air mass. As shown in Fig. 9, the average annual ethane/acetylene ratio in urban Wuhan is 1.92, and the ratio of each month is higher than 0.47, which indicates that there was a relatively obvious degeneration and aging phenomenon in urban Wuhan. Previous studies have shown that when the acetylene/CO value is less than approximately 5.3–6.9 × 10⁻³, the photochemical age of the air mass is longer (Guo et al., 2007; Touaty and Bonsang, 2000). However, due to the differences between the emission source structure of various regions, the ratio (5.3–6.9 × 10⁻³) cannot be used alone to explain the degree of aging of the air mass. Therefore, in this study, the acetylene/CO value (3.82 × 10⁻³) in the early morning peak period (6:00–8:00) with weak photochemical reaction in winter was chosen as the threshold for judging the photochemical age in urban Wuhan. When the ratio acetylene/CO value was less than 3.82 × 10⁻³, the air mass was denatured and aging and photochemical age were longer; the larger the value, the fresher the air mass and the shorter the photochemical age. As seen from Fig. 9, the photochemical age of winter air masses in urban Wuhan was relatively short, and the photochemical ages of air masses were longer in the other seasons.

Since toluene is the third-ranked VOC in contributions to the concentration of MIR in urban Wuhan, we chose the toluene/benzene ratio to evaluate the contribution of vehicle exhaust emissions to the contaminated air mass. It is generally considered that toluene/benzene is less than 2.0, which indicates that the influence of motor vehicle exhaust on the air mass is significant; the larger the value, the smaller the impact of motor vehicle emissions on the air mass and the greater the impact of VOCs emissions from solvent evaporation on the air mass (Chan et al., 2006). The average value of toluene/benzene in urban Wuhan was 1.44 throughout the year, which indicates that the motor vehicle emissions significantly contributed to the polluted air mass in the Wuhan urban area. Fig. 9 shows that the toluene/benzene values in spring and summer are significantly higher than those in autumn and winter. This can be attributed to the higher temperature in spring and summer, which results in an increase in the volatilization of solvents and LPG and thus makes the impact of other emission sources more significant than motor vehicle exhaust. The average values of toluene/benzene in autumn and winter were lower than in the entire year, which indicated that the polluted air mass in winter was greatly influenced by the emission of motor vehicles.

### 2.3. Relationship between the variation of VOCs/NOx ratios and the ozone formation regime

In previous studies (Seinfeld, 1989; Geng et al., 2008; Ran et al., 2009; Li et al., 2013; Zou et al., 2015), researchers have defined the influence of precursors on ozone production as NOx-
limited and VOCs-limited. It is important for controlling ozone pollution in the region to understand if ozone generation is limited by NOx or limited by VOCs. Using the ratio of VOCs/NOx to determine if ozone production is controlled by VOCs or NOx in a certain area is a qualitative analysis of the relationship between atmospheric ozone concentration and its precursors (Sillman, 2002). The reaction of ozone photochemical formation begins with the reaction of OH radicals with VOCs, during which VOCs compete with NOx for OH radicals. When the concentrations of VOCs and NOx reach a certain ratio, the concentration of ozone production will reach the highest level and the reaction rate of OH radicals with VOCs and NOx will be equal. When the ratio of VOCs/NOx is small, the reaction between OH radicals and NOx is dominant and ozone generation is relatively sensitive to the concentration of VOCs. When the ratio of VOCs/NOx is large, the reaction between OH radical and VOCs is dominant and ozone generation is sensitive to NOx concentration. The method of judging whether ozone generation was affected by VOCs or NOx via the VOCs/NOx ratio was first proposed by Seinfeld. He calculated the results using a numerical simulation method based on the 1980 Los Angeles (United States) photochemical smog event. The method of judging whether ozone generation was affected by VOCs or NOx by the VOCs/NOx ratio was first proposed by Seinfeld in 1989. He calculated that 8:1 was the switching threshold for determining the ozone concentration in typical urban areas affected by VOCs or NOx; the number was calculated by the method of numerical simulation based on the Los Angeles photochemical smog event in 1980 (Seinfeld, 1989). In this study, only the VOCs/NOx ratio was used to determine whether ozone generation in urban Wuhan was controlled by VOCs or NOx; no model was used for simulation.

Fig. 10 shows the daily variation of VOCs/NOx ratios in different seasons during the observation period. As shown in the figure, the average VOCs/NOx ratio was approximately 6.16 during the early morning traffic hours (6:00–9:00) in summer, autumn and winter, which was less than 8:1 and thus proved that the ozone generation in this period was limited by VOCs; during 12:00–16:00, when the ozone concentration peaked, the average VOCs/NOx ratio was approximately 11.61, which was greater than 8:1 and thus proved that ozone generation was limited by NOx during this period. The average value of the VOCs/NOx ratio during the early morning traffic hours (6:00–9:00) in spring was approximately 3.25 and approximately 4.37 during the period from 12:00 to 16:00 in spring, and these values were significantly less than 8:1. Therefore, the spring ozone production in urban Wuhan was limited by VOCs. This observation is similar to that of Zou’s 2015 study in the suburbs of Guangzhou.

Note that this study only used the VOCs/NOx ratio method to determine the main control factor for ozone production in urban Wuhan based on one-year observational data. The

![Fig. 10](image-url)  
*Fig. 10 – The diurnal patterns of VOC/NOx ratios calculated in three different ways, as well as ozone concentrations, for each season from autumn 2016 to summer 2017 at Wuhan. Blue level lines represent the VOC(ppbC)/NOx ratio of 8:1.*
threshold chosen was the observation obtained in Los Angeles in the 1990s. This could not be fully applicable to Wuhan, and more numerical models (e.g., OBM models based on observations) should thus be used to simulate the effects of VOCs and NOx on ozone generation in the future to obtain more accurate results.

3. Conclusions

This study conducted continuous online observations of ozone, NOx, and VOCs in the Wuhan urban area from September 2016 to August 2017. The observations showed that the average concentration of ozone in urban areas in Wuhan was 22.63 ppbv throughout the year and that the concentrations of ozone in spring and summer were significantly higher than those of autumn and winter. Concentrations of NOx and VOCs were opposite to those of ozone. The concentrations in autumn and winter were significantly higher than those in spring and summer. The annual average concentration of NOx was 30.14 ppbv, and the average concentration of VOCs was 32.61 ppbv throughout the year. Alkenes comprised the highest proportion of the total VOCs species, 42.29%, and the proportions of alkenes, aromatics, acetylene, OVOCs, and halogenated hydrocarbons were 13.0%, 10.0%, 7.3%, 9.9%, and 10.5% of the total VOCs, respectively. The 10 highest volume fractions of all VOCs species were propane (16.5%), ethane (13.1%), ethylene (8.0%), acetylene (7.2%), acetone (7.0%), n-butane (5.2%), dichloromethane (3.9%), isobutane (3.5%), isopentane (3.3%), and toluene (2.9%), which cumulatively accounted for 71.6% of the total VOCs concentration.

Propylene-equivalent concentration and maximum incremental reactivity concentration were used to evaluate the activity of VOCs species and their contribution to ozone formation potential in urban Wuhan. The results showed that aromatics and alkenes contributed the most to the propylene-equivalent concentration, 36.6% and 36.0%, respectively. Similarly, aromatics and alkenes were also the VOCs species that had the highest contributions to ozone formation potential, 35.4% and 35.7%, respectively. The most important reactive VOCs components in the atmosphere in Wuhan were m-xylene, toluene, ethylene, and propylene.

The daily average of ethylene versus ethane and m,p-xylene versus ethylbenzene in the urban area of Wuhan were 0.62 and 0.87, respectively. The lateral comparison results showed that the ratio in Wuhan was low, indicating that the photochemical age of the air mass in Wuhan city is relatively long and that part of it may be derived from external transport. The annual average values of ethane/acytene and acetylene/CO were 1.92 and 2.95, respectively, indicating that there is obvious air mass aging in the urban areas of Wuhan. In winter, the photochemical age of air masses was short, and the photochemical ages of other seasons were longer. The annual average of toluene/benzene was 1.44, indicating that motor vehicle emissions significantly contributed to the polluted atmosphere in Wuhan.

We calculated the daily variations of VOCs/NOx ratios in each season and found that the main controlling factors for ozone production in summer, autumn, winter were diurnal changes that were VOCs-limited in the early morning but NOx-limited in the peak ozone period. However, the ozone concentration in spring was only limited by VOCs throughout a day.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2018.12.002.

References


