Characteristics of VOCs and their Potentials for O₃ and SOA Formation in a Medium-sized City in Eastern China

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ABSTRACT

To understand the characteristics and environmental effects of volatile organic compounds (VOCs) in a typical medium-sized city in China, manual measurements including 56 species of the nonmethane hydrocarbons (NMHCs) were taken at three urban and suburban sites in Huai’an from April to September 2019, and automatic measurements including 106 species of VOCs were taken at the urban center in May and August 2019. Spatial and temporal characteristics of the VOC concentrations were analyzed. Positive matrix factorization (PMF) model was applied to apportion VOC sources. Ozone (O₃) formation potentials (OFPs) and secondary organic aerosol (SOA) formation potentials (SOAFPs) were calculated. The results show that the mean VOC concentration was much lower in the urban center than in the suburbs. Generally, proportions of both alkenes and aromatic hydrocarbons were higher and proportion of alkanes was lower in Huai’an than that in big cities, indicating emissions from solvent usage and industrial process play a more important role in the medium-sized city. The results of source apportionment show that solvent usage and industrial process together contributed 53%, and vehicle emission contributed 27% to the ambient VOCs. The dependence of VOC concentrations on temperature indicates that a considerable part of VOCs may come from fugitive emissions. The two-peak pattern of diurnal variation suggests near-surface emissions contributed a lot to the VOCs. Aromatic hydrocarbons were identified as the key component to the formation of O₃ and SOA. Furthermore, biogenic emission could contribute greatly (>20%) to the ambient VOCs during daytime in summer, which may have significant effects on O₃ formation. Aromatic hydrocarbons were identified as the key component to the formation of O₃ and SOA, which should be given more attention in developing air pollution control strategies.

Keywords: Volatile organic compounds, Ozone pollution, Source apportionment, OFP, SOAFP

1 INTRODUCTION

In the past decade, although the overall air quality has been greatly improved, it is still far from full attainment of the air quality standard (GB3095-2012). What makes the situation even tougher is the complex pollution featured by fine particles (PM₂.₅) and ozone (O₃). While the mean concentration of PM₂.₅ decreased from 72 µg m⁻³ in 2013 to 44 µg m⁻³ in 2019 in the key regions of China, the O₃ concentration in terms of the 90th percentile of daily maximum 8-hour moving averages (MDA8-90%) increased from 139 µg m⁻³ to 167 µg m⁻³ (MEE, 2013–2019). Due to the complexity of the generation processes of O₃ and PM₂.₅, as well as increasing marginal cost for the pollution control, great challenges will still remain for a long time in China.
VOCs are important precursors of both O₃ and PM₂.₅ (Li et al., 2020b; Wang et al., 2016), which are usually defined as any carbon compounds participating in photochemical reactions except CO, CO₂, H₂CO₃, metal carbides, metal carbonates and ammonium carbonate (U.S. EPA, 1988). Alkanes, alkenes, aromatics, halohydrocarbons and oxygenated compounds are the most common species of VOCs. In photochemical reactions, VOCs reacts with hydroxyl radical (OH) to form hydrogen peroxide radical (HO₂) and organic peroxy radical (RO₂). HO₂ and RO₂ then compete with O₃ for NO, destroying the photolysis cycle of NO₂-NO-O₃ and accumulating O₃ volume fraction (Atkinson, 2000). In addition, VOCs also generate SOA through gas-phase reaction, heterogeneous reaction and liquid-phase reaction (Grosjean, 1992; Hu et al., 2011; Kroll et al., 2007; Ye et al., 2018). Although most VOC emissions are from natural sources globally (Fares et al., 2013; Shalamzari et al., 2014), anthropogenic emissions are often dominating in cities where human activities are concentrated (Hu et al., 2019; Liu et al., 2008; Mozaffar and Zhang, 2020).

Characterizing VOCs in terms of both emissions and ambient concentrations are very difficult (Guo et al., 2017; Mozaffar and Zhang, 2020). Besides the intrinsic differences among different sources (Liu et al., 2008; Mo et al., 2015; Wu et al., 2020a), VOC emissions are also affected by many factors such as human activities, technologies, and meteorological conditions. Therefore, VOC emissions are varying with place and time, and consequently so does the chemical composition of ambient VOCs. Generally, alkanes are the most abundant VOCs in the atmosphere in most regions of China (Hui et al., 2021; Li et al., 2020b; Mozaffar and Zhang, 2020), however, some regions are found to be different. For example, in the BTH, aromatics were found to be the most abundant (Han et al., 2015; Mozaffar and Zhang, 2020; Sun et al., 2018; Wang et al., 2016). Furthermore, relative importance of different sources also varies in different regions. For example, the main sources in the BTH are motor vehicles, fossil fuel combustion, solvent utilization, and liquefied petroleum gas usage (Liu et al., 2016; Song et al., 2007; Wei et al., 2019), however, in the YRD, industrial emissions and biomass burning play a more critical role (An et al., 2020; Han et al., 2019; Zhang et al., 2018), while in the PRD, solvent usage has a greater contribution (Guo et al., 2017; Ling et al., 2011; Ou et al., 2015).

Characteristics of the VOCs also differ by the size of cities. In China, large cities generally include provincial capitals and municipalities, medium-sized cities include prefecture-level cities, and small cities include county-level cities and towns. Compared with large cities, medium-sized cities are usually less developed, with heavier industrial emissions of air pollutants, especially for VOCs. Unfortunately, due to limited measurements of VOCs, relevant studies are particularly scarce for medium-sized cities in China (Zhang et al., 2019). Considering the great number and remarkable VOC emissions of these cities, in-depth studies about the VOC characteristics are needed for coping with the VOC-related air pollution in a synergic and effective way.

Huai’an is a typical medium-sized developing city in the north of Jiangsu Province, located between 32°43′00″~34°06′00″ N and 118°12′00″~119°36′30″ E, as shown in Fig. 1. The city has a population of about 4.9 million. The GDP in 2019 was about 60 billion US dollars, of which industrial and service sectors accounted for 46.6% and 39.3%, respectively (HSB, 2019). Like most other cities in China, air quality of the city has improved notably during the past ten years. In particular, the annual concentration of PM₂.₅ has decreased from 68 µg m⁻³ in 2013 to 42 µg m⁻³ in 2019. On the contrary, the concentration of O₃ MDA8-90% increased significantly from 56 µg m⁻³ to 165 µg m⁻³ during the same period. In this study, based on ambient concentrations of VOCs measured in the year of 2019 at different sites in the city, temporal and spatial characteristics of the VOC concentrations, sources, and potential impacts on O₃ and SOA pollution were studied, and policy implications were discussed.

2 DATA AND METHODS

2.1 Data Sampling

Considering the features of social and economic activities, as well as natural factors such as dominant wind direction in the target area, three VOC sampling sites were selected in Huai’an city, as shown in Fig. 1. The Huai’an monitoring station (HMS) locates in the urban center, with a dense population and intensive traffic. The Huaiyin Normal University (HNU) locates in the northwest of the urban area (in the downwind direction), surrounded by industrial development.
zones with industries such as petrochemical, printing, shoemaking, garment processing, furniture manufacturing, and food processing. The Chuzhou monitoring station (CMS) locates in the southeast of the urban area, where the population density is relatively low, but close to an industrial development zone, namely the Chuzhou Electric Power Industrial Park.

Manual measurements of VOCs at the CMS, HNU and HMS were carried out simultaneously from April to September in 2019, a period when O3 pollution is most frequently occurred. Samples were collected for 5–10 days per month, 4–8 times a day, and three hours each time, by using SUMMA canisters according to the constant current sampling method (Wang and Austin, 2006b). The samples were analyzed by using a gas phase mass spectrometer (Agilent 7890B+5977B, NO.SMF-007) according to the EPA TO-15 (1999) method (Wang and Austin, 2006a). Blank samples were collected at each site in each month. To get high-resolution information of the VOCs, automatic measurements were carried out at the site of HMS in May and August, for 10 days per month, and more than 22 hours per day. An automatic gas chromatography system equipped with a mass spectrometer and a flame ionization detector (GC-MS/FID) was used to continuously analyze the VOCs. Totally 56 kinds of the NMHCs (NMHCs-56) were covered in the manual measurements, and 106 kinds of VOCs (VOCs-106) were covered in the automatic measurements, including the NMHCs, halohydrocarbons, and OVOCs. Detailed species of the VOCs measured in this study were listed in Table S1. Throughout the whole process of sampling and analysis, strict quality assurance and quality control were carried out in accordance with the requirements of standard methods (MEE, 2018a, b).

To test the consistency between the manual and automatic measurements, daily mean concentrations of the NMHCs-56 in May and August were calculated and compared, as shown in Fig. S1. The daily mean concentrations obtained by the two methods are basically consistent. The two-month mean concentrations of manual measurements (15.29 ppbv) is 11.28% higher than the automatic measurements (13.74 ppbv). The correlation coefficient between the manual and automatic measurements is 0.72. This verifies that the manual and automatic measurements are generally comparable with each other.

2.2 The PMF Model

The PMF model is a receptor model developed by Paatero and Tapper (1994), which has been widely used to identify sources of PM2.5 and VOCs (Huang and Hsieh, 2020; Hui et al., 2019; Shao et al., 2016; Tao et al., 2017; Yu et al., 2019). In this model, the samples and species data can be regarded as an $i \times j$ matrix ($x$), where $i$ represents the number of samples and $j$ represents the number of species. The goal of the model is to find the source spectrum matrix ($f$) and the contribution matrix ($g$) of the sources in each sample. The measured mass concentration of
species \( j \) in the \( i \)-th sample can be expressed as Eq. (1):

\[
x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}
\]

(1)

where \( e_{ij} \) is the residual error between the measured concentration of species \( j \) in the \( i \)-th sample and its analytical value. The solution of \( g_{ik} \) and \( f_{kj} \) are derived by minimizing the objective function \( Q \), which is defined as Eq. (2):

\[
Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left( x_{ij} - \frac{\sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right)^2
\]

(2)

where \( i \) represents the number of samples; \( j \) represents the number of species; \( p \) represents the number of factors; \( x_{ij} \) represents the concentration of the \( j \)-th species in the \( i \)-th sample; \( g_{ik} \) represents the contribution of the \( k \)-th factor to the \( i \)-th sample; \( f_{kj} \) represents the fraction of the \( j \)-th species in the \( k \)-th factor; \( e_{ij} \) represents the residue of the \( j \)-th species in the \( i \)-th sample; and \( u_{ij} \) represents the uncertainty of the \( j \)-th species in the \( i \)-th sample.

To make the PMF robust, samples and their species of VOCs were selected according to certain criteria. For example, samples missing important species, and species missed in most samples were not considered in the PMF. For running the PMF, it is critical to evaluate and describe the uncertainty of input data. In this study, the uncertainty \( (u_{ij}) \) of input component concentration \( x_{ij} \) is calculated as Eqs. (3) and (4) (Polissar et al., 1998).

When the \( x_{ij} \) is higher than the minimum detection limit (MDL):

\[
u_{ij} = \sqrt{\left( EF \times x_{ij} \right)^2 + \left( 0.5 \times MDL \right)^2}
\]

(3)

When the \( x_{ij} \) is lower than or equal to the MDL:

\[
u_{ij} = \frac{5}{6} \times MDL
\]

(4)

The MDL was determined for each species of VOCs, basing on the methods of sampling and analysis. EF represents the error fraction, which is related to the analysis error, chemical activity, and species concentrations. According to some suggested values in recent studies (Ji et al., 2020; Wu et al., 2020b; Xie et al., 2021), it was set to 0.15 for automatic measurements and 0.25 for manual measurements in this study.

2.3 Photochemical Activity Analysis of VOCs

To evaluate the potential effects of VOCs on the generation of \( O_3 \) and SOA, the OFPs and SOAFPs were calculated and analyzed in this study. The OFP represents the potential maximum contribution of specific VOC species to \( O_3 \) generation under the optimal reaction conditions, and is widely used to evaluate the role of VOCs in the formation of \( O_3 \) (Hanif et al., 2021; Liang et al., 2020; Mitchell et al., 2021). In this study, to identify the OFP of each species of VOCs, the maximum incremental reactivity (MIR) method (Carter, 1994) is used.

The OFP (\( \mu g \ m^{-3} \)) is defined as Eq. (5):

\[
\text{OFP}_i = C_i \times \text{MIR}_i
\]

(5)

where \( C_i (\mu g \ m^{-3}) \) is the concentration of the \( i \)-th VOC species in the atmosphere and \( \text{MIR}_i (\mu g \ \mu g^{-1}) \) is the maximum incremental reactivity, with values suggested by Carter (2010).

The SOAFP is estimated using the SOA yield method (Wu et al., 2017), which represents the potential maximum contribution of specific VOC species to SOA formation. This index estimates
SOA formation rates of individual VOC and is an indicator of the relative importance of different VOCs in SOA formation.

The SOAFP ($\mu g m^{-3}$) is defined as Eq. (6):

$$\text{SOAFP}_i = C_i \times Y_{SOA_i}$$  (6)

where $C_i$ ($\mu g m^{-3}$) is the concentration of the $i$-th VOC species in the atmosphere, and $Y_{SOA_i}$ (%) is the yield of SOA. The values of $Y_{SOA_i}$ used in this study were calculated by Wu and Xie (2018) basing on studies of multiple cities in China.

### 3 RESULTS AND DISCUSSION

#### 3.1 Species and Concentrations of VOCs

Based on the manual measurements, the mean concentrations of the NMHCs-56 at the HMS, CMS, and HNU were 14.91 ppbv, 22.36 ppbv, and 24.11 ppbv, respectively. The concentration was obviously lower in the center than that in the suburbs where industrial zones are located. Based on the automatic measurements at the HMS, the mean concentration of the VOCs-106 was 21.75 ppbv, and the mean concentration of the NMHCs-56 was 14.01 ppbv, which is comparable to the manually measured result mentioned above. The mean concentration of the NMHCs-56 accounted for about 64.4% of the VOCs-106, suggesting that the NMHCs-56 are the major species of the VOCs in this city.

About the composition of the VOCs, according to the automatic measurements at the HMS, alkanes accounted for the largest proportion (37.49%) followed by halohydrocarbons (22.04%), alkenes (13.92%), OVOCs (14.52%), and aromatic hydrocarbons (12.04%). However, according to the manual measurements of the NMHCs-56, the composition was different at different sites. At the HMS, proportion of alkanes (63.09%) was much higher than that at the other two sites (56.18% at the CMS and 44.32% at the HNU), while the proportion of aromatic hydrocarbons (14.96%) was significantly lower than at the other sites (23.35% at the CMS and 30.88% at the HNU). Alkenes accounted for a similar proportion (about 20%) at all three sites. The higher proportion of alkanes at the HMS indicates that vehicle emission and evaporation of oil and gas play a more important role in the center area than in the suburb. Table S2 lists the top ten species of the NMHCs-56 along with their concentrations and proportions at the three sites. In terms of individual species, propane was the most abundant at all the three sites, followed by ethane at the HMS and the CMS, and toluene at the HNU.

Table 1 presents a comparison of NMHCs measurements among different cities in China. Compared with big cities, the mean concentration of the NMHCs in Huai’an was generally lower. Significant difference in composition of the NMHCs can also be found. In the medium-sized cities, the proportion of alkanes was generally lower, and proportions of both alkenes and aromatic hydrocarbons were relatively higher. This suggests that emissions from traffic vehicles and gas evaporation have more impacts on the big cities and emissions from solvent usage and industrial process play a more important role in the medium-sized cities.

Fig. 2 shows the monthly variation in concentrations and proportions of the NMHCs-56 at the three sites. Generally, high values of monthly mean concentrations occurred in May and July. The concentration in June was relatively low because of the “Mei-yu” system, which brought much larger amount of rainfall in June (88 mm) than in May (19.8 mm) (CMSDC, 2021). On the whole, the monthly VOC concentrations were well correlated with the temperature, that is, higher in late spring and summer, and lower in early spring and autumn, except for June. One possible explanation is that higher temperature tends to increase VOC evaporation (Drozd et al., 2021), especially for fugitive emissions.

Fig. 3 shows the diurnal variation in concentrations of the VOCs based on automatic measurements in May and August, representing spring and summer, respectively. It shows an obvious two-peak pattern in both May and August. In May, the first peak value appeared between 8:00 and 11:00, and the second peak appeared around 21:00. This can be mainly attributed to two factors. One is the intense traffic emissions during rush hours, and the other is the diurnal variation of the
Planetary boundary layer (PBL) in terms of both height and diffusion intensity, which is generally going high and strong from sunrise till afternoon around 14:00–15:00, and later gradually becoming low and weak until next morning. In addition, higher temperature tends to enhance the photochemical reactions, which may also contribute to the valley of concentrations in sunny days.

### Table 1. Comparison of NMHCs measurements in different cities in China.

<table>
<thead>
<tr>
<th>City</th>
<th>Time</th>
<th>Number of species</th>
<th>NMHCs Conc(^{(a)}) (ppbv)</th>
<th>Alkanes Prop(^{(b)}) (%)</th>
<th>Alkenes Prop(^{(b)}) (%)</th>
<th>Aromatics Prop(^{(b)}) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing</td>
<td>2019.3</td>
<td>59</td>
<td>39</td>
<td>62</td>
<td>21</td>
<td>17</td>
<td>(Zhang et al., 2021a)</td>
</tr>
<tr>
<td>Beijing</td>
<td>2016.1, 4, 7, 10</td>
<td>56</td>
<td>28</td>
<td>59</td>
<td>30</td>
<td>11</td>
<td>(Liu et al., 2020)</td>
</tr>
<tr>
<td>Shijiazhuang</td>
<td>2019.5–2019.9</td>
<td>56</td>
<td>38</td>
<td>67</td>
<td>23</td>
<td>10</td>
<td>(Wang et al., 2021)</td>
</tr>
<tr>
<td>Tianjin</td>
<td>2014.11–2015.10</td>
<td>56</td>
<td>29</td>
<td>63</td>
<td>19</td>
<td>18</td>
<td>(Liu et al., 2016)</td>
</tr>
<tr>
<td>Xi’an</td>
<td>2019.1, 7</td>
<td>56</td>
<td>48</td>
<td>57</td>
<td>31</td>
<td>12</td>
<td>(Sun et al., 2021)</td>
</tr>
<tr>
<td>Taiyuan</td>
<td>2015.4–2015.12</td>
<td>40</td>
<td>36</td>
<td>50</td>
<td>27</td>
<td>23</td>
<td>(Li et al., 2020a)</td>
</tr>
<tr>
<td>Shanghai</td>
<td>2016.8–2016.9</td>
<td>56</td>
<td>19</td>
<td>59</td>
<td>15</td>
<td>26</td>
<td>(Zheng et al., 2019)</td>
</tr>
<tr>
<td>Shanghai</td>
<td>2017.5</td>
<td>56</td>
<td>24</td>
<td>63</td>
<td>15</td>
<td>22</td>
<td>(Liu et al., 2019)</td>
</tr>
<tr>
<td>Nanjing</td>
<td>2016.5–2017.2</td>
<td>55</td>
<td>19</td>
<td>67</td>
<td>14</td>
<td>19</td>
<td>(Wu et al., 2020b)</td>
</tr>
<tr>
<td>Nanjing</td>
<td>2018.7–2018.8</td>
<td>49</td>
<td>24</td>
<td>56</td>
<td>21</td>
<td>23</td>
<td>(Fan et al., 2021)</td>
</tr>
<tr>
<td>Nanjing</td>
<td>2016.1–2016.12</td>
<td>56</td>
<td>26</td>
<td>53</td>
<td>30</td>
<td>17</td>
<td>(Zhao et al., 2020)</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>2016.7–2016.8</td>
<td>56</td>
<td>35</td>
<td>63</td>
<td>17</td>
<td>20</td>
<td>(Zheng et al., 2021b)</td>
</tr>
<tr>
<td>Guangzhou</td>
<td>2014.10–2014.11</td>
<td>56</td>
<td>34</td>
<td>49</td>
<td>25</td>
<td>26</td>
<td>(He et al., 2019)</td>
</tr>
<tr>
<td>Xiamen</td>
<td>2016.8, 12</td>
<td>51</td>
<td>16</td>
<td>60</td>
<td>14</td>
<td>26</td>
<td>(Hong et al., 2019)</td>
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<tr>
<td>Chengdu</td>
<td>2018.6–2019.1</td>
<td>52</td>
<td>36</td>
<td>56</td>
<td>31</td>
<td>13</td>
<td>(Xiong et al., 2021)</td>
</tr>
<tr>
<td>Chengdu</td>
<td>2016.10–2017.9</td>
<td>56</td>
<td>42</td>
<td>57</td>
<td>26</td>
<td>17</td>
<td>(Song et al., 2018)</td>
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<tr>
<td>Chongqing</td>
<td>2015.8–2015.9</td>
<td>46</td>
<td>30</td>
<td>50</td>
<td>34</td>
<td>16</td>
<td>(Li et al., 2018)</td>
</tr>
<tr>
<td>Wuhan</td>
<td>2017.1–2017.2</td>
<td>56</td>
<td>53</td>
<td>63</td>
<td>16</td>
<td>21</td>
<td>(Zheng et al., 2021)</td>
</tr>
<tr>
<td>Huai’an</td>
<td>2019.5, 8</td>
<td>56</td>
<td>20</td>
<td>55</td>
<td>22</td>
<td>23</td>
<td>This study</td>
</tr>
</tbody>
</table>

Notes: (a) mean concentration of the NMHCs; (b) proportion of the category accounted in the total concentration of the NMHCs.

![Fig. 2. Monthly variation in concentrations and proportions (marked on the bars) of the NMHCs-56 at the three sites.](image_url)
In August, the diurnal variation was similar to that in May, but the peaks appeared about two hours earlier. This is possibly because of the differences in daily human activities as well as the development of convective boundary layer, which tend to start earlier in August than in May. Such two-peak pattern can be hardly seen in the diurnal variations of both the OVOCs and the halohydrocarbons. For the OVOCs, secondary formation by photochemical reactions is an important source, which may compensate to a large extent to the decrease caused by the developed PBL around noon. For the halohydrocarbons, industrial emissions are generally the main source (Fu et al., 2020; Ji et al., 2020) and usually with high stacks, and thus the surface concentration is generally low under stable PBL at night. However, in the daytime, with the development of unstable PBL, the halohydrocarbons in the upper layer can be transported to the lower layer, resulting in the increase of near-surface concentration, which caused the inconspicuous diurnal variation of the halohydrocarbons. In addition, the concentrations of the halohydrocarbons in spring were larger than those in summer. This is mainly because of the generally more stable atmosphere in spring and stronger photochemical reaction in summer.

Fig. 4 shows the variation in proportions of the VOC categories with concentration of the VOCs-106. It is interesting to note that, with the concentration of the VOCs-106 increases, the proportion of alkanes increases significantly, and the proportion of halohydrocarbons decreases significantly. However, the proportions of alkenes, aromatic hydrocarbons, and OVOCs generally keep stable. These features may be attributed to the combined effect of atmospheric stability and height of emission sources. Usually, lower sources tend to have larger impact on the surface concentrations in stable condition than in unstable condition, and higher sources have a reverse effect. So, higher concentrations of the VOCs-106, as shown in Fig. 4, generally correspond to more stable conditions, since VOCs are mainly dominated by lower sources. Therefore, it can be inferred that alkanes are mainly emitted from lower sources (such as vehicle emissions and gas evaporation) and halohydrocarbons mainly come from higher sources (such as organized emissions of petrochemical enterprises). The other categories generally have mixed sources.

### 3.2 Source Apportionment of VOCs

Based on the manual measurements from April to September at the HMS, CMS and HNU, VOC source apportionment was conducted by using the model of PMF5.0 (U.S. EPA, 2014). In order to ensure robust runs of the model, 28 species were selected, considering the detection rates (ratio of samples detected to the total) and the source-indicative meanings. The factor profiles directly obtained from the PMF are presented in Fig. S2. The definition of each PMF factor is described in
Fig. 4. Variation in proportions of the VOC categories with their total concentration at the HMS.

Fig. 5 compares relative contributions of different sources to the VOCs at the three sites in Huai'an. Generally, solvent usage, vehicle emission, and industrial process were the top three sources, accounting for about 80% in total, followed by gas (i.e., diesel and gasoline) evaporation, accounting for 8%–9%. Contributions of fossil fuel combustion, biomass burning, and biogenic emission were relatively small, less than 6% each. Significant differences were found among different sites. For example, the proportion of vehicle emission at the HMS was significantly larger than that at the CMS and the HNU, while the industrial process and fossil fuel combustion at the HMS were less than those at the CMS and the HNU.

Characteristics of the VOC source contributions in Huai'an are quite different from that in many big cities. For example, the proportion of vehicle emission in Huai'an (about 27%) was obviously lower than that in Beijing (~45%) (Wei et al., 2019; Zhang et al., 2017; Zhang et al., 2020), Shanghai (34%) (Liu et al., 2019; Zheng et al., 2019) and Guangzhou (43%) (Zhang et al., 2021b), while the proportion of solvent usage and industrial process in Huai'an (totally about 55%) was higher than that in the big cities as mentioned above, generally between 35% and 50%. These differences are mainly caused by the degree of social economic development. As a developing city such as Huai'an, its traffic density is generally lower and contributes less to the VOCs, but solvent usage and industrial enterprises may have higher emissions as a result of relatively backward technologies in both production processes and pollution control.

Fig. 6 illustrates the average diurnal variation in relative contributions of different VOC sources at the HMS in May and August. Obvious differences are found in the diurnal variations between the two months. In general, the diurnal variation of each source contribution in May was relatively flat, while there was a large fluctuation in August. This may be mainly due to seasonal difference in meteorological conditions, which tend to be more stable in May than in August. In addition, some seasonal changes in human activities may be another reason.

In both months, relative contributions of vehicle emission and gas evaporation increased in the morning and evening, which may be related to heavy traffic in the rush hours. The contribution of solvent usage was relatively large during nighttime, especially in May, possibly because of the stable nighttime PBL and no photochemical depletion. In August, however, there were two obvious peaks of solvent usage around 10:00 and around 16:00–18:00, respectively. Yet the reason is not clear, we speculate it may be a result of abnormal emission from relevant sources. For industrial process, the diurnal variation was relatively small in May, and in August the daytime contribution was apparently lower than nighttime contribution. This is possibly because of higher mixing layer and stronger atmospheric diffusion ability during the daytime in summer.
Fig. 5. Relative contributions of different sources to the ambient VOCs at the three sites in Huai’an city.

Fig. 6. Diurnal variations in relative contributions of the VOC sources in May and August (based on automatic measurements at the HMS).

It is worth noting that biogenic emission showed a significant diurnal variation in both months. This emission usually peaks around noon, when the solar radiation is intensive. In addition, compared with May, the biogenic emission is much stronger in August, as a result of more intensive solar radiation and high leaf area index (Eschenbach and Kappen, 1996; Gast et al., 2020). As shown in Fig. 6(b), relative contribution of biogenic emission could be more than 20% at 14:00. This suggests that, although the average contribution of biogenic emission is relatively small, it may play an important role in the photochemical reactions during daytime in summer.

3.3 Reactivity Characteristics of VOCs

3.3.1 OFPs of VOCs

Based on the manual measurements, the OFPs of VOCs at the three sites were calculated. The total average of OFPs was 97.35 µg m⁻³ at the HMS, 179.61 µg m⁻³ at the CMS, and 273.25 µg m⁻³.
at the HNU. The value at the HMS was much lower than that at the two suburb sites. This indicates that the VOCs in the suburbs may play a more important role in O\textsubscript{3} generation than in the city center. Fig. S3 shows the monthly OFPs and the proportions of different VOC categories at the three sites. Generally, OFPs were dominated by aromatic hydrocarbons, followed by alkenes and alkanes. However, relative importance among the three categories may differ in specific time and place, especially for aromatic hydrocarbons and alkenes. For example, alkenes were the largest contributor to the OFPs in April and May at the HMS and the HNU, but it was in July at the CMS.

Table 2 lists the top ten species of the VOCs along with their OFPs and proportions at the three sites based on manual measurements. The m/p-xylene and toluene were the two most important species at all three sites, followed by ethylene, o-xylene, Isoprene, and so on, with different order at different sites. It is found that among the top ten species, the composition profiles are similar at the CMS and the HNU, and both are quite different from that of the HMS.

### 3.3.2 SOAFPs of VOCs

Based on the manual measurements, the SOAFPs of different VOC species were calculated. Table 3 presents the top five species and their SOAFPs at the three sites. The total average SOAFPs was 0.55 \( \mu \text{g m}^{-3} \) at the HMS, 1.21 \( \mu \text{g m}^{-3} \) at the CMS, and 1.92 \( \mu \text{g m}^{-3} \) at the HNU. It is obviously that the VOCs contributed much less to the SOA formation in the urban center than in the suburbs. This implies that industrial emissions play a more important role than traffic emissions in the formation of secondary PM\textsubscript{2.5}.

Aromatic hydrocarbons have a dominant contribution to the SOAFPs, which accounted for more than 85% of the total SOAFPs at each of the three sites (85.60% at the HMS, 92.58% at the CMS, and 94.49% at the HNU), followed by alkanes (13.38% at the HMS, 7.04% at the CMS, and 94.49% at the HNU), and then alkenes (1.02% at the HMS, 0.44% at the CMS, and 0.38% at the HNU). This is quite different from the case of OFPs, which is dominated by both aromatic hydrocarbons and alkenes. Among the aromatic hydrocarbons, as shown in Table 3, xylene (including m/p-xylene 5.07\% at the HNU) and alkenes (1.02\% at the HMS, 0.44\% at the CMS, and 0.38\% at the HNU).

### Table 2. Top ten species of the NMHCs-56 along with their OFP concentrations (Conc, \( \mu \text{g m}^{-3} \)) and proportions (Prop, \%\%) at the three sites based on manual measurements.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Species</th>
<th>Conc/Prop</th>
<th>Conc/Prop</th>
<th>Conc/Prop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HMS</td>
<td>CMS</td>
<td>HNU</td>
</tr>
<tr>
<td>1</td>
<td>M/p-xylene</td>
<td>18.25/18.74</td>
<td>38.60/21.49</td>
<td>82.88/30.33</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>13.51/13.88</td>
<td>36.92/20.56</td>
<td>44.33/16.22</td>
</tr>
<tr>
<td>3</td>
<td>Ethylene</td>
<td>11.81/12.13</td>
<td>20.91/11.64</td>
<td>33.44/12.24</td>
</tr>
<tr>
<td>4</td>
<td>O-xylene</td>
<td>6.43/6.60</td>
<td>16.01/8.91</td>
<td>27.39/10.02</td>
</tr>
<tr>
<td>5</td>
<td>Isoprene</td>
<td>5.67/5.83</td>
<td>15.38/8.56</td>
<td>22.37/8.19</td>
</tr>
<tr>
<td>6</td>
<td>Trans-2-butene</td>
<td>5.16/5.30</td>
<td>9.77/5.44</td>
<td>12.88/4.71</td>
</tr>
<tr>
<td>7</td>
<td>N-hexane</td>
<td>4.84/4.97</td>
<td>7.47/4.16</td>
<td>9.19/3.36</td>
</tr>
<tr>
<td>8</td>
<td>Isobutane</td>
<td>4.07/4.18</td>
<td>5.93/3.30</td>
<td>8.65/3.17</td>
</tr>
<tr>
<td>9</td>
<td>Propylene</td>
<td>4.01/4.12</td>
<td>5.10/2.84</td>
<td>6.35/2.32</td>
</tr>
<tr>
<td>10</td>
<td>N-butane</td>
<td>3.89/4.00</td>
<td>4.58/2.55</td>
<td>5.08/1.86</td>
</tr>
<tr>
<td>SUM</td>
<td></td>
<td>--</td>
<td>77.65/79.76</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>160.66/89.45</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>252.55/92.43</td>
<td>--</td>
</tr>
</tbody>
</table>

### Table 3. Top five species of the VOCs along with their SOAFP concentrations (Conc, \( \mu \text{g m}^{-3} \)) and proportions (Prop, \%\%) at the three sites based on manual measurements.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Species</th>
<th>Conc/Prop</th>
<th>Conc/Prop</th>
<th>Conc/Prop</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>HMS</td>
<td>CMS</td>
<td>HNU</td>
</tr>
<tr>
<td>1</td>
<td>M/p-xylene</td>
<td>0.17/30.08</td>
<td>0.35/28.97</td>
<td>0.75/38.98</td>
</tr>
<tr>
<td>2</td>
<td>Toluene</td>
<td>0.12/22.13</td>
<td>0.33/27.53</td>
<td>0.40/20.71</td>
</tr>
<tr>
<td>3</td>
<td>O-xylene</td>
<td>0.08/15.32</td>
<td>0.20/16.69</td>
<td>0.36/18.63</td>
</tr>
<tr>
<td>4</td>
<td>Ethylbenzene</td>
<td>0.05/9.51</td>
<td>0.13/11.01</td>
<td>0.23/11.90</td>
</tr>
<tr>
<td>5</td>
<td>N-dodecane</td>
<td>0.03/4.66</td>
<td>0.06/5.25</td>
<td>0.04/2.33</td>
</tr>
<tr>
<td>SUM</td>
<td></td>
<td>--</td>
<td>1.08/89.45</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.78/92.55</td>
<td>--</td>
</tr>
</tbody>
</table>
and o-xylene) was the dominant component, followed by toluene, ethylbenzene, n-dodecane (at the HMS), and styrene (at the CMS and the HNU), totally accounted for more than 80% of the total SOAFPs at each site. This result indicates that aromatic hydrocarbons are the most important contributor to the SOA formation, especially those species emitted from solvent usage.

4 CONCLUSIONS

As a medium-sized developing city, Huai’an sees a generally lower concentrations of the ambient VOCs, compared with big developed cities. Furthermore, the composition of the VOCs differs remarkably. In particular, proportions of alkenes and aromatic hydrocarbons are higher and proportion of alkanes is lower in Huai’an than that in big cities. This indicates that emissions from solvent usage and industrial process play a more important role in the medium-sized city, while emissions from vehicles and gas evaporation have more impact on big cities. This is also confirmed by the results of the source apportionment. Solvent usage and industrial process totally contributed about 55% to the ambient VOCs in Huai’an, much higher than reported results of most big cities, while vehicle emissions contributed about 27% in Huai’an, significantly lower than that in many big cities such as Beijing, Shanghai, Guangzhou, and Chongqing. These findings suggest that more attentions should be paid on solvent usage and industrial process in medium-sized cities instead of vehicle emissions.

It should be noted that even within the medium-sized city, ambient concentrations of the VOCs may have remarkable spatial differences. Generally, the average concentration was much lower in the urban center than that in the suburbs. In addition, proportions of alkanes were significantly higher, and proportions of both alkenes and aromatic hydrocarbons were significantly lower in the urban center than that in the suburbs. This implies that the emissions of VOCs are highly localized, and regional transport may be not that important, at least for a major part of VOCs.

Temporal variation is also remarkable in the ambient VOC concentrations and the source contributions. This can be mainly attributed to changes in emission intensities and meteorological conditions. In particular, the obvious dependence of VOC concentrations on temperature indicates a big part of VOCs may come from fugitive emissions. The two-peak pattern of diurnal variation reveals the combined effect of changes in emissions and the PBL, and suggests that near-surface emissions are major contributors to most species of the VOCs. However, a big part of halo-hydrocarbons and OVOCs may be emitted from elevated stack sources or formed by photochemical reactions. The biogenic emission can have a high contribution to the VOCs during daytime in summer, which may play a very important role in O₃ formation since many of its species such as isoprene and terpenes are highly active in photochemical reactions.

Generally, aromatic hydrocarbons are the most important contributor to the OFPs, followed by alkenes and alkanes, although their relative importance may change especially between aromatic hydrocarbons and alkenes. The SOAFPs were absolutely dominated by aromatic hydrocarbons, which accounted for more than 85% of the total SOAFPs. These findings indicate that aromatic hydrocarbons are the key species to the formation of both O₃ and secondary PM₂.₅, and should be a top priority for the pollution control.

ADDITIONAL INFORMATION

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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SUPPLEMENTARY MATERIAL

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REFERENCES


