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Sources of volatile organic compounds and policy implications for regional ozone pollution control in an urban location of Nanjing, East China

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Abstract. Understanding the composition, temporal variability, and source apportionment of volatile organic compounds (VOCs) is necessary for determining effective control measures to minimize VOCs and its related photochemical pollution. To provide a comprehensive analysis of VOC sources and their contributions to ozone (O_3) formation in the Yangtze River Delta (YRD) - a region experiencing highest rates of industrial and economic development in China, we conducted a one-year sampling exercise for the first time at an urban site in Nanjing (JAES site). Alkanes were the dominant group at the JAES site, contributing ~53% to the observed total VOCs, followed by aromatics (~17%), acetylene (~17%), and alkenes (~13%). We identified seasonal variability in TVOCs with maximum and minimum concentrations in winter and summer, respectively. A morning and evening peak and a daytime trough were identified in the diurnal VOCs patterns. We identified the source apportionments of VOCs and their contributions to photochemical O_3 formation using the Positive Matrix Factorization (PMF) and observation-based model together with a Master Chemical Mechanism (OBM-MCM). The PMF model identified five dominant VOC sources, with highest contributions from diesel vehicular exhausts (34 ± 5%), followed by gasoline vehicular exhausts (27 ± 3%), industrial emissions (19 ± 2%), fuel evaporation (15 ± 2%) and biogenic emissions (4 ± 1%). The results from the OBM-MCM model simulation inferred photochemical O_3 formation to be VOC-limited at the JAES site when considering both the reactivity and abundance of the individual VOC species in each source category. Further, VOCs from vehicular and industrial emissions were found to be the dominant control on O_3 formation, particularly the VOC species *m,p*-xylene, toluene and propene, which top priorities should be given to the alleviation of photochemical smog. However, when considering the reactivity and abundance of VOC species, the contribution of biogenic emissions to O_3 pollution was significantly reduced. Our results therefore highlight the need to consider both the abundance and reactivity of individual VOC species in order to develop effective control strategies to minimize photochemical pollution in Nanjing.

1. Introduction

Volatile organic compounds (VOCs) are key precursors of O_3 and secondary organic aerosols (SOA) - a major component of fine particulate matter ($PM_{2.5}$). VOCs significantly contribute to the formation of photochemical smog, atmospheric oxidative capacity, visibility degradation, and global climate (Jenkin and Clemitshaw, 2000; Seinfeld and Pandis, 2006), and some VOCs are also known to be toxic to human health. Therefore, in recent years, much research has focused on the impacts of VOCs due to their influence on atmospheric chemistry and impacts on human health (Shao et al., 2009 and references therein).

The Yangtze River Delta (YRD) region (Shanghai-Jiangsu-Zhenjiang region) is one of the fastest growing regions in China, having recently undergone rapid urbanization and industrialization. Rapid economic growth

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has been associated with increased photochemical smog and elevated concentrations of ground-level O_3 and fine particulate matter ($PM_{2.5}$). These conditions have been listed as the most important sources of pollution affecting the population in the YRD region, and are likely caused by increasing concentrations of VOCs. Therefore, it has been suggested that controlling VOC emissions is necessary for the effective alleviation of photochemical smog (Wang et al., 2009; Zhang et al., 2009; Cai et al., 2010; Kurokawa et al., 2013; Ding et al., 2016).

To further understand VOC characteristics and to develop effective policies towards lowering VOC emissions, a number of sampling campaigns have been conducted to investigate the components, mixing ratios, photochemical reactivity and emissions of VOCs over the YRD region (Mo et al., 2015; Pan et al., 2015; An et al., 2014; Cai et al., 2010; Shao et al., 2016; Xu et al., 2017). For example, based on continuous observation data collected from March, 2011 to February, 2012, An et al. (2014) identified clear seasonal VOCs variability in an industrial area of Nanjing, with maximum and minimum levels observed in summer and winter, respectively. VOC variability was also found to be strongly influenced by industrial emissions. In contrast, Mo et al. (2017) found no difference in VOC chemical compositions between residential, industrial and suburban areas of the coastal industrial city, Ningbo. By comparing the emission-based profiles and those extracted from the positive matrix factorization (PMF) model, the photochemical industry was identified as the highest contributor of ambient VOCs due to the unique industrial structure of Ningbo (Mo et al., 2015, 2016). Pan et al. (2015) conducted emissions measurements of open biomass burning in the rural area of the YRD region and examined the major contributors to O_3 pollution using a box model together with the Regional Atmospheric Chemical Mechanism. Overall, these studies were conducted in industrialized and/or rural areas of the YRD region and demonstrated the contributions of industrial emissions and biomass burning towards ambient VOC levels and their contributions to O_3 formation. However, VOC studies in urban areas of the YRD region are limited and could help to improve our understanding of the spatial variability of VOCs and their environmental impact, particularly as stricter policies on VOCs and/or photochemical smog have been implemented since 2013 (Fu et al., 2016). Furthermore, the sampling resolution and sampling duration of these studies were relatively low as the samples were collected using canisters. High-resolution VOC datasets can provide more detailed information on the temporal and spatial variability, source apportionments, and impact factors of VOCs.

In this study, we collected continuous one-year observational VOC data at an urban site in Nanjing in the YRD region. The seasonal and diurnal characteristics of VOCs were investigated, and their sources were identified and quantified using the PMF model. Furthermore, we used a box model together with a Master Chemical Mechanism (OBM-MCM) to identify the O_3-precursor relationships and the contributions of VOC sources to photochemical O_3 formation. Our results were compared with VOCs data from other Chinese megacities. Based on these findings, we summarized and proposed control strategies to minimize VOCs pollution and assessed their implications for Nanjing and the wider YRD region. The results provide useful information towards lowering photochemical pollution in the YRD region as well as other regions in China.

2. Methodology

2.1. Sampling campaign

We continuously measured VOC concentrations from January to December, 2016, at an observation station on the rooftop of an office building (~80 m above the ground level) of the Jiangsu Academy of Environmental Science (JAES). The station is located in an urban area of Nanjing, and is surrounded by heavy road traffic, residential buildings, a plant and flower market, and several auto repair shops (Fig. 1). Nanjing, located in the western part of the YRD region, is one of the most urbanized and industrialized areas in the world and consequently experiences severe air pollution. The site is located downwind of both Nanjing city center and the wider YRD region (Zhao et al., 2017; Zhou et al., 2017), and is therefore ideally placed to determine the combined impacts of VOCs from both local and regional atmospheric pollution.

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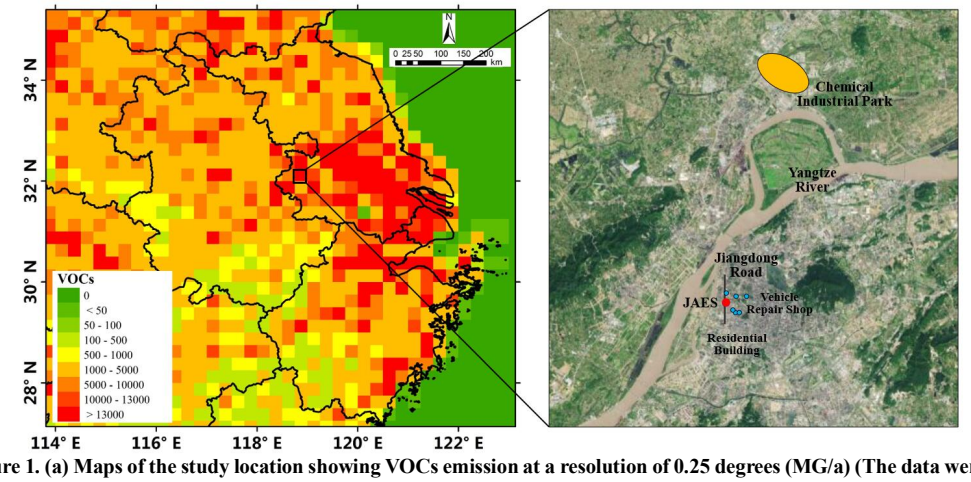

Figure 1. (a) Maps of the study location showing VOCs emission at a resolution of 0.25 degrees (MG/a) (The data were from MEIC emission inventory (www.meicmodel.org, last access date:15 September 2019)). (b) The location of the JAES sampling site is indicated by a red circle (The base map was from © Baidu Maps). The blue circles indicate vehicle repair shops, the yellow circle indicates chemical industry park and the black solid line indicates a heavy traffic road

Fifty-six VOC species including alkanes, alkenes, aromatics, and acetylene were measured at 1-h intervals using a PerkinElmer Online Ozone Precursor Analyzer based on a thermal desorption-GC system. First, the dried air samples were collected by a thermal desorption instrument and subsequently pre-concentrated onto a cold trap. The sampling flow was 15 mL/min. The sample was enriched after 600 mL of air sample, and the cold trap was heated to resolve the compounds adsorbed on to it. By applying the Dean's Switch technology, the low- and high-volatile components were injected into the Al_2O_3/Na_2SO_4 PLOT column (50 m × 0.22 mm × 1 μm) and the dimethyl siloxane column (50 m × 0.32 mm × 1 μm), respectively, and analyzed using a flame ionization detector (FID). The temperature increased from 46 °C for 15 min to 170 °C at a rate of 5 °C/min, and then to 200 °C at a rate of 15 °C/min. The samples were finally held at 200 °C for 6 min.

A calibration was performed daily for quality control. The calibration curves showed good linearity with a correlation coefficient of 0.99. Seven repeated analyses were performed to test the precision of the 56 species using a gas standard mixture with species concentrations ranging from 20 to 49 ppbC. The relative standard deviations of most of the 56 species were < 5%, representing an error of < 0.5 ppbC.

2.2. The PMF model for VOC source identification

In this study, the PMF (version 4.0) model was applied to the observed VOC data to identify potential VOC sources. A detailed description of the PMF model is provided by Yuan et al. (2009) and Ling et al. (2011). In brief, the PMF model is a receptor model, which can identify the sources and contributions of given species without prior input of their source profiles. In this study, a total of 25 species were selected as the input for the PMF model including species with high abundances as well as typical tracers of emission sources. Species with high percentages of missing values (> 25%) were excluded (*i.e.,* 1,3-butadiene, cis/trans-2-pentene, dimethylpentane, and trimethylpentane). The total concentration of the 25 selected species accounted for ~92% of the total measured VOC composition. Furthermore, we calculated the total reactivity of the selected 25 species to be ~90% of the total measured VOCs by combining the VOC concentrations and OH radical loss rates (L_{OH}) (Shao et al., 2009). The high abundance and total reactivity contributions suggests that the selected 25 species were appropriate for the PMF model simulation.

The PMF model was tested with a variety of factors, and the optimum source profiles and contributions were determined based on the correlation between modelled and observed data, the comparison of modelled profiles with the results from emission-based measurements, and other PMF model simulations (i.e., HKEPD, 2015;

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Wang et al., 2014; An et al., 2014; Liu et al., 2008a).

2.3. VOC contributions on O_3 formation using the observation-based model

In this study, we applied the observation-based model (OBM) coupled with the MCM (version 3.2), which consists of ~6000 reactions involving ~16,500 species without considering vertical and horizontal transport, to quantify the contributions of VOC emission sources to photochemical O_3 formation. This model has been widely used to identify the photochemical reactivity and photochemical products in different environments (Volkamer et al., 2007; Xue et al., 2014; Li et al., 2014; He et al., 2019). Detailed configurations of the model have been introduced in previous studies (Saunders et al., 2003; Lam et al., 2013). In this study, the hourly data of VOCs, trace gases (i.e., CO, NO_x, SO_2, and O_3), and meteorological parameters on 88 O_3 episode days (identified as hourly maximum O_3 concentrations > 80 ppbv per day) were used as the input for the model. To simulate each O_3 episode day, we ran the model for two-days using the mean diurnal variability of the input species during the whole sampling period to achieve a steady state for the unmeasured mixing ratios of species with a short lifetime, i.e., OH and HO_2 radicals (Wang et al., 2017; Sun et al., 2018).

To simulate O_3 formation, we used the model to calculate the relative incremental reactivity (RIR) to assess the sensitivity of O_3 photochemical formation to changes in the concentrations of its precursors (Carter and Atkinson, 1989; Cardelino and Chameides, 1995). The RIR is defined as the percent change in O_3 production per percent change in precursors and is calculated as shown in Eq. (1), while the average RIR of precursor *X* is calculated as shown in Eq. (2).

$$RIR^S(X) = \frac{\left[P^S_{O_3-NO}(X) - P^S_{O_3-NO}(X-\Delta X)\right]/P^S_{O_3-NO}(X)}{\Delta S(X)/S(X)} \quad (1)$$

$$\overline{RIR} = \frac{\sum_1^N [RIR^S(X) P^S_{O_3-NO}(X)]}{\sum_1^N P^S_{O_3-NO}(X)} \quad (2)$$

where the superscript *S* is the specific sample day; *S(X)* represents the measured concentration of precursor *X*, including the amounts emitted at the site and those transported to the site; *ΔS(X)* is a hypothetical change in the concentration of precursor *X* (10% *S(X)* in this study); and *N* is the number of evaluated days. $P^S_{O_3-NO}$ is the O_3 formation potential, which is the net O_3 production and NO consumed during the evaluation period.
Furthermore, to investigate the relative importance of the precursor species to photochemical O_3 formation, the RIR-weighted values and the relative contributions of different precursors were calculated as shown in Eq. (3) and Eq. (4), taking into consideration both the reactivity and abundance of VOC species (Ling et al., 2011; Ling and Guo, 2014).

$$RIR\text{-}weighted(X) = \overline{RIR}^X \times conc(X) \quad (3)$$

$$Contribution(X) = \frac{\overline{RIR}^X \times conc(X)}{\sum[\overline{RIR}^X \times conc(X)]} \quad (4)$$

where *X* represents the specific precursor, $\overline{RIR}^X$ is the average RIR value of precursor *X*, and *conc(X)* is the concentration of precursor *X*.

3. Results and discussion

3.1 VOCs observation statistics

Table 1 shows the average concentration and standard deviation of fifty-six VOC species concentrations measured at the JAES site. The annual average total VOC (TVOC) concentrations in 2016 was 25.7 ± 19.1 ppbv, with highest contributions from alkanes (13.6 ± 10.5 ppbv, ~53%), followed by aromatics (4.4 ± 4.0 ppbv, ~17%), acetylene (4.5 ± 5.5 ppbv, ~17%) and alkenes (3.2 ± 3.3 ppbv, ~13%). Annually, the most abundant 10 species were acetylene, propane, ethane, ethylene, butane, toluene, *i*-pentane, *i*-butane, propylene and benzene, with a combined contribution of ~77% of the TVOC. This observed VOC composition suggests that VOCs at the JAES site are predominantly sourced from combustion emissions (*i.e.*, vehicular emissions). Alkenes are mainly associated with vehicular emissions and are more photochemically reactive relative to alkanes and aromatics.

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The alkenes were found to have higher mixing ratios during weekdays relative to the weekends (2.9 ± 0.1 vs 3.5 ± 0.2 ppbv for weekdays and weekend, respectively, $p < 0.05$), further confirming the dominant contribution of vehicular emissions to VOC levels at the JAES site.

Table 1. The average range and standard deviation of VOC species concentrations measured at the JAES site from January to December 2016.

Species	Average ± Standard deviation (ppbv)	Species	Average ± Standard deviation (ppbv)
Alkanes	**13.64 ± 10.53**	**Alkenes**	**3.24 ± 3.28**
ethane	3.63 ± 2.68	ethene	1.72 ± 2.00
propane	3.70 ± 3.01	propylene	0.92 ± 1.16
i-butane	1.03 ± 0.87	1-butene	0.12 ± 0.16
n-butane	1.55 ± 1.26	cis-2-butene	0.06 ± 0.09
cyclopentane	0.08 ± 0.10	trans-2-butene	0.16 ± 0.11
i-pentane	1.15 ± 1.24	1-pentene	0.03 ± 0.03
n-pentane	0.61 ± 0.60	cis-1-pentene	0.02 ± 0.03
2,2-dimethylbutane	0.02 ± 0.02	trans-2-pentene	0.02 ± 0.03
2,3-dimethylbutane	0.05 ± 0.07	isoprene	0.14 ± 0.20
2-methylpentane	0.26 ± 0.29	*n*-hexene	0.05 ± 0.03
3-methylpentane	0.16 ± 0.21	**Aromatics**	**4.40 ± 4.01**
n-hexane	0.40 ± 0.45	benzene	0.80 ± 0.70
methylcyclopentane	0.26 ± 0.27	toluene	1.40 ± 1.35
cyclohexane	0.10 ± 0.16	ethylbenzene	0.50 ± 0.62
2,4-dimethylpentane	0.03 ± 0.01	*m/p*-xylene	0.70 ± 0.71
2,3-dimethylpentane	0.03 ± 0.02	*o*-xylene	0.25 ± 0.24
2-methyhexane	0.06 ± 0.09	styrene	0.12 ± 0.17
3-methylhexane	0.07 ± 0.10	*n*-propylbenzene	0.03 ± 0.03
heptane	0.09 ± 0.11	*i*-propylbenzene	0.03 ± 0.04
methylcyclohexane	0.07 ± 0.09	*m*-ethyltoluene	0.11 ± 0.14
2,2,4-trimethylpentane	0.02 ± 0.03	*p*-ethyltoluene	0.05 ± 0.07
2,3,4-trimethylpentane	0.02 ± 0.01	*o*-ethyltoluene	0.04 ± 0.05
2-methylheptane	0.02 ± 0.02	1,3,5-trimethylbenzene	0.04 ± 0.06
3-methylheptane	0.02 ± 0.02	1,2,4-trimethylbenzene	0.15 ± 0.21
octane	0.04 ± 0.06	1,2,3-trimethylpentane	0.10 ± 0.14
nonane	0.02 ± 0.02	*m*-diethylbenzene	0.03 ± 0.06
decane	0.04 ± 0.04	*p*-diethylbenzene	0.04 ± 0.08
undecane	0.04 ± 0.07	**Acetylene**	**4.47 ± 5.49**
dodecane	0.09 ± 0.20	--	--

The TVOC level in this study was lower than previous measurements from an industrial site in Nanjing, in which 43.5 ppbv TVOC was reported (An et al., 2014). However, the high TVOC levels are likely due to the proximity of the observation site (~3 km northeast) to the Nanjing chemical industry area, as well as several iron, steel, and cogeneration power plants (within 2 km) (An et al., 2014). The variability in land-use between these two studies have also resulted in distinct VOC component profiles. In the industrial area, the relative contributions of alkenes and aromatics were as high as 25% and 22%, while the contribution of alkynes was only 7% (An et al., 2014).

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The alkane, alkene, and aromatic concentrations from the industrial site were 1.4, 3.4, and 2.2 times higher than the concentrations of this study, respectively, while alkyne concentrations were ~30% lower. Given the large variability observed between the two sites, it is crucial to assess the spatial variability of ambient VOCs across the city through a collaboration of multiple research groups using available real-time and online VOC monitoring systems.

Table S1 compares reported ambient VOCs from continuous measurements of ≥1 year in several megacities in a number of countries, including China. Continuous online measurements of ambient VOCs have only been available in China since 2010, unlike many developed countries whereby online VOC measurements have been available since the year 2000. In China, such measurements are only concentrated in a few megacities, including Beijing, Guangzhou, and Shanghai. The TVOC level reported in Nanjing was close to levels measured in Shanghai (another megacity in the YRD, East China, 27.8 ppbv) (Wang et al., 2013), Tianjin (a megacity in North China, 28.7 ppbv) (Liu et al., 2016), and Wuhan (a megacity located in central China, 24.3 ppbv) (Lyu et al., 2016), but was considerably lower than Beijing (north China, 35.2 ppbv) (Zhang et al., 2017) and Guangzhou (south China, 42.7 ppbv) (Zou et al., 2015). Alkanes were the dominant hydrocarbon group in all the cities; however, some differences in relative contributions of the four classes were observed. The contribution from aromatics was highest in Shanghai (31%) relative to the other cities, which is likely explained by the large petrochemical and steel industry in Shanghai (Wang et al., 2013, Huang et al., 2011). In comparison, the contribution of aromatics in Guangzhou (Zou et al., 2015) and the industrial area in Nanjing (An et al., 2014) were 24% and 22%, respectively, while in other cities the contribution ranged between 17-19%. The current ambient VOCs concentrations in Chinese megacities are generally comparable to the urban VOCs levels in developed countries during the year 2000. Chinese megacities are therefore experiencing much higher ambient VOCs contamination, given the remarkable decrease in VOC emissions in developed countries over the last two decades (European Environment Agency, 2016; U.S. EPA, 2017; Pan et al., 2015). High VOCs levels in Chinese megacities are known to impact ambient ozone and secondary particle pollution, as well as cause adverse impacts on human health.

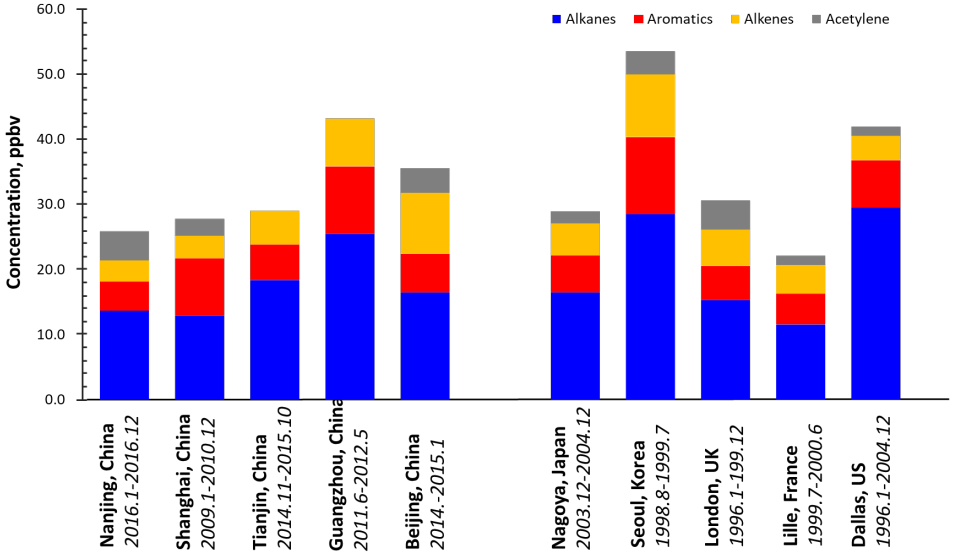

Figure 2. Comparison of annual average concentrations of ambient VOC in different cities based on real-time online continuous measurements of at least one year.

3.2 Temporal variability

In this study, ambient VOCs showed significant seasonal variability, with relatively high monthly average concentrations in winter (40.2 ± 24.0 ppbv) and spring (23.8 ± 15.0 ppbv), and low concentrations in summer

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(18.5 ± 14.6 ppbv) and autumn (20.1 ± 12.2 ppbv). As shown in Fig. S1, the highest monthly average concentration was observed in December, followed by January. High pollution levels during the winter period are usually expected and is explained by atmospheric temperature inversions caused by cooler weather, which inhibits particle dispersion. Lower concentrations during the summer period are due to both favorable diffusion conditions and photochemical degradation of VOCs.

High wintertime VOCs pollution were also reported in Shanghai (Wang et al., 2013), Guangzhou (Zou et al., 2015), and Tianjin (Liu et al., 2016), though some differences in the monthly VOCs variability were also observed. Except for the winter months, similar (and relatively stable) ambient VOCs levels in the remaining months were observed for Guangdong (Fig. 3). In Shanghai, relatively high ambient VOCs were also observed in June-July. The peak value in June can be explained by chemical and petrochemical industrial sites located upwind of the monitoring site (Wang et al., 2013). VOCs concentrations in Tianjin showed significant monthly variability. Highest concentrations were reported in autumn and lowest concentrations were reported in summer. The observed monthly variability is affected by several factors including the type and level of emissions and local meteorological conditions.

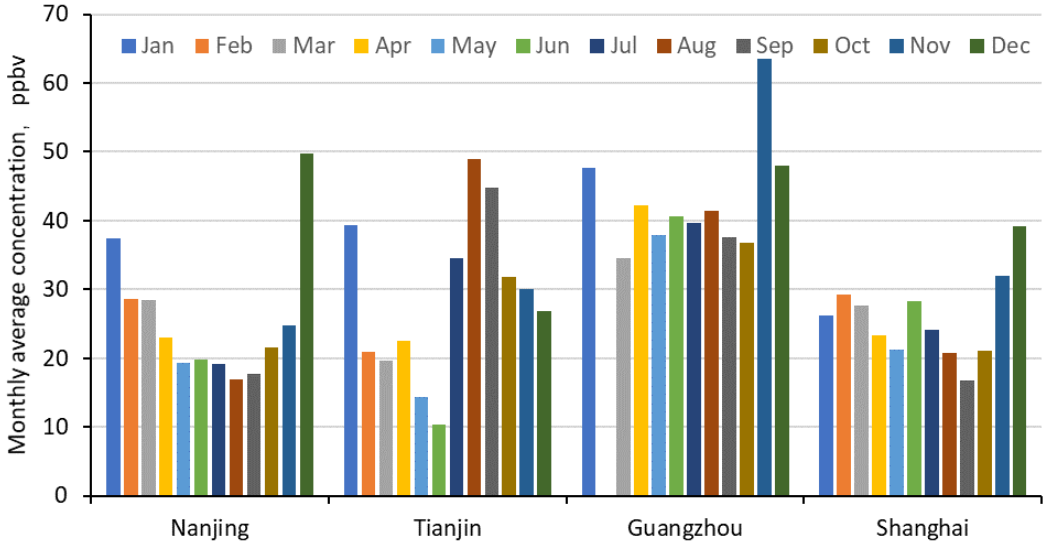

Figure 3. Monthly variability of ambient VOCs at the JAES site and three other Chinese cities, Shanghai (Wang et al., 2013), Guangzhou (Zou et al., 2015), and Tianjin (Liu et al., 2016).

Figure S3 shows the diurnal trends in ambient VOCs for each month. The diurnal patterns were generally similar for all the months. The observed peak at approximately 8-9 am (local time) corresponds with the city's morning traffic rush. The concentration begins to decrease after 9 am, with lowest concentrations observed at approximately 3 pm. The observed decline was likely due to reduced vehicle emissions, growth of the inversion top, and enhanced photochemical VOC degradation. After 3 pm, the concentrations begin to increase gradually as a result of increased vehicle emissions during the evening rush hour, as well as a reduction in the atmospheric mixing height under evening meteorological conditions. The second evening VOCs peak was less prominent than the morning peak. Evening concentrations were generally higher than the daytime concentrations, and the amplitudes of diurnal variability were larger in autumn and summer compared to winter and spring.

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3.3 Source apportionment of VOCs

In this study, we applied the PMF model to apportion the sources of VOCs at the sampling site. Figure 4 illustrates the source profiles of the VOCs produced by the PMF model. The model identified five VOCs sources, including biogenic emissions (Source 1), fuel evaporation (Source 2), gasoline vehicular exhausts (Source 3), diesel vehicular exhausts (Source 4), and industrial emissions (Source 5). Source 1 was identified as biogenic emissions due to the high loading of isoprene – a typical tracer of biogenic emissions (Yuan et al., 2012; Lau et al., 2010). Source 2 was represented by high proportions of 2-methylpentane, 3-methylpentane, *i*-pentane, and cyclopentane. Pentanes are mainly associated with gasoline emissions. However, the low contributions of incomplete combustion tracers in this profile suggests that the VOCs are sourced from fuel evaporation (An et al., 2015); thus, Source 2 was identified as fuel evaporation. Source 3 and Source 4 were identified as vehicular exhausts due to their high loadings of incomplete combustion tracers, i.e., C_2-C_4 alkanes and alkenes (Guo et al., 2011a, b). Higher proportions of n/i-pentane, n-hexane, and methylcyclopentane in Source 3 relative to Source 4 indicates VOCs sourced from gasoline vehicular exhausts (Ling et al., 2011; Guo et al., 2011b; Liu et al., 2008b). Source 4 was identified as diesel vehicular exhausts due to the high percentages of ethyne, ethane, and propene, as well as C_2-C_4 alkenes (Ou et al., 2015; Liu et al., 2008c; Cai et al., 2010). Furthermore, high concentrations of aromatics were identified in Source 5. Aromatics are frequently observed in the profiles of solvents used in a variety of industries, including shoe making, paint, printing, and petroleum (Guo et al., 2016; Lau et al., 2010; Yuan et al., 2009; Song et al., 2008). In addition, the profile of Source 5 was consistent with the chemical profiles of the measured industrial emissions at the industrial site in Nanjing. Therefore, Source 5 was identified as industrial emissions.

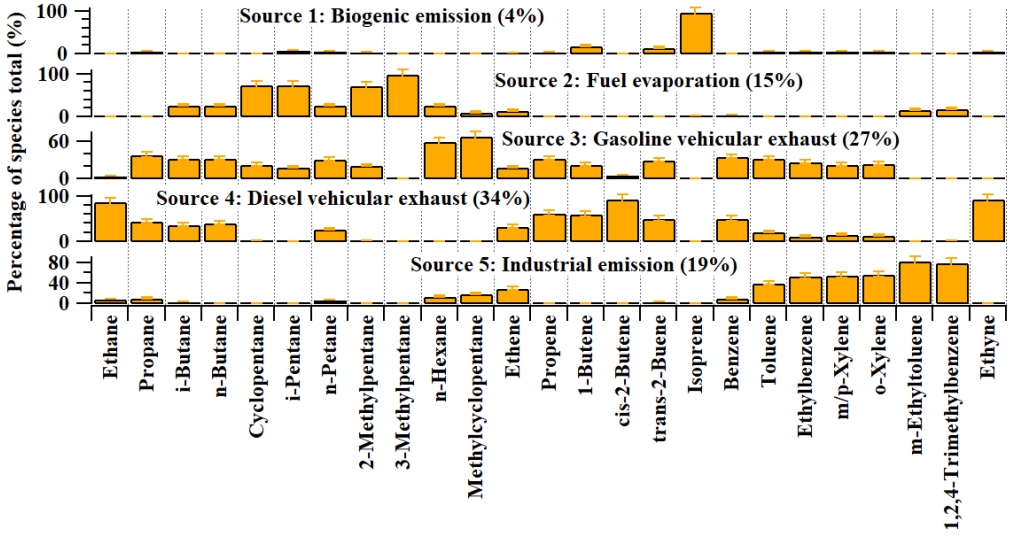

Figure 4. Source profiles of VOCs identified using the PMF model and the relative contributions of the individual VOC species.

Vehicular exhausts were found to be the most significant contributor to the TVOCs at the JAES site, with average contributions of ~34% and ~27% for diesel and gasoline exhausts, respectively, followed by industrial emissions (19%), fuel evaporation (~15%), and biogenic emissions (~4%). Our results are in contrast to previous results observed at industrial sites in Nanjing (An et al., 2014; Xia et al., 2014a). An et al. (2014) found that industrial activities were the most significant source of VOCs, contributing 45%-63% (mainly aromatic VOCs), followed by vehicle emission at 34%-50%. Similarly, Xia et al. (2014a) reported solvent usage and other industrial sources to account for most (31%) of the VOCs in a suburban site in southwestern Nanjing, close in proximity to Nanjing's industrial zone. Fossil fuel/biomass/biofuel combustion were the second highest contributors at 28%,

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while the average contribution of vehicular emissions was 17%, mainly from the northern center of Nanjing (Xia et al., 2014a). Combined, these results infer vehicular emissions to be a major component of urban emissions in Nanjing. The observed spatial variability in the contributions of VOC sources infers the complex emissions characteristics of VOCs in Nanjing, likely due to the city's unique industrial structure. These results also demonstrate that local emissions are dominant contributors to ambient VOCs levels in Nanjing.

The dominant contribution of vehicular emissions to ambient VOCs in Nanjing is consistent with the urban/central areas of other large cities, including Hong Kong, Guangzhou, Shanghai, and Beijing, as identified and quantified by the PMF model (Guo et al., 2011a; Yuan et al., 2009; Wang et al., 2015; Zhang et al., 2013; Cai et al., 2010). In addition, our results are in agreement with the anthropogenic VOC source emission inventory of Jiangsu Province in 2010 (Xia et al., 2014b), indicating vehicular emissions and industrial emissions (i.e., solvent usage and industrial process source) to be the two dominant sources of VOCs in the region. However, the contributions of vehicle related emissions (i.e., ~25%) and industrial emissions were lower and higher than those quantified by the PMF model in this study, respectively. The observed discrepancy between the two studies may be due to differences in source categories, measured VOC species, and/or sampling locations and methods used in the different models. For example, the VOC sources in Jiangsu province were categorized into vehicular related emission (~26%), industrial solvent usage (~25%), fossil fuel combustion (~24%), industrial processes (~22%) and biomass burning (~3%). Further, vehicle related emissions only included emissions from motor vehicles and ships, and the volatilization of fuel, while solvent usage included organic solvents volatilized from a variety of industries (the industrial produce process of electronic equipment manufacturing, furniture manufacturing, printing, packaging, inks, adhesives, etc. and other dry cleaning, catering, and architectural decoration processes). Higher vehicular emission contribution in this study may also be due to the increasing number of vehicles from 2010-2014 as a result of increased urbanization and industrialization (Statistical yearbook of Nanjing, 2014).

Figure 5 illustrates the mean diurnal variability of all identified source at the JAES site. These trends were influenced by the variability in emission strength, mixing height, and the concentrations and photochemical reactivity of individual species in each source profile. For example, we observed a typical diurnal pattern with a broad peak between 9 am–6 pm for biogenic emissions, as the emission rate of isoprene from vegetation is largely depended on ambient temperature and sunlight intensity. Higher levels of diesel and gasoline vehicular emissions were observed in the evening and early morning due to a reduced mixing height and increased emissions from the morning and evening rush hour. Lower concentrations observed during daytime hours were likely due to decreased emissions, increased mixing height and enhanced photochemical loss (Yuan et al., 2009). The diurnal pattern of fuel evaporation was also similar to the vehicular emissions trends, except the amplitude was much weaker, with a difference between maximum and minimum values of ~6 $\mu g/m^3$. We identified higher concentrations of industrial emissions at night and in the early morning, with values remaining fairly stable during daytime hours. This finding is consistent with other observations in urban and rural areas (Yuan et al., 2009).

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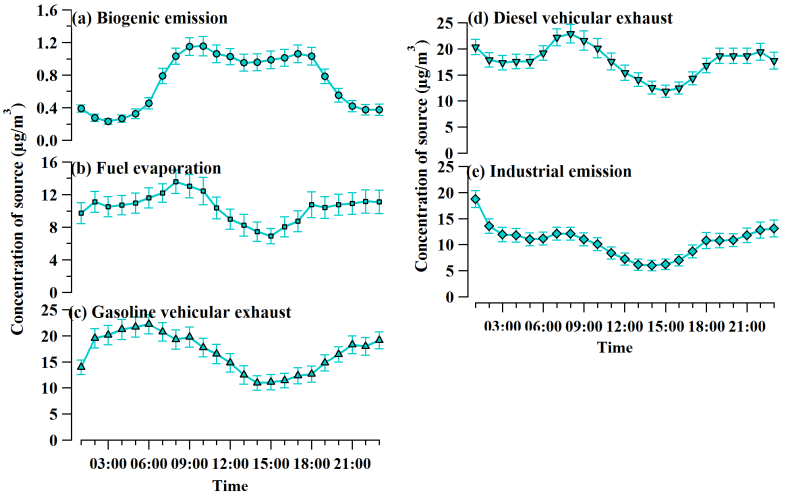

Figure 5. Diurnal patterns in source concentrations of the five identified sources

3.4 Contributions of VOC sources to O3 formation

To highlight the relative contributions of the different emissions on VOC abundance during the 88 O_3 episode days, we extracted and averaged the contributions of the different sources from the PMF model. We found that the contributions of gasoline vehicular exhausts had significantly increased during O_3 episode days, with a mean average percentage of 41 ± 5%.

Figure 6 shows the O_3 isopleth plot illustrating the relationship between VOCs and NO_x concentrations on the O_3 mixing ratio. The plot is the output from the OBM-MCM model, and is based on the mean diurnal variability of observed air pollutants on O_3 episode days. Based on the current scenario (with 100% VOCs and 100% NO_x), the O_3 mixing ratio decreased with the reduction of VOCs and increased with the reduction of NO_x, indicating that O_3 formation in this site is VOC-limited and is consistent with previous results observed in Nanjing (Wang et al., 2009; Zhang et al., 2009; Cai et al., 2010; Kurokawa et al., 2013; Ding et al., 2016). O_3 formation was found to be VOC-limited until NO_x had decreased to a mixing ratio of 45%. Furthermore, O_3 formation becomes NO_x-limited when the NO_x mixing ratios are reduced by > 70%. Overall, the O_3 isopleth results suggest that minimizing VOC emissions would be effective at reducing O_3 formation at the JAES site.

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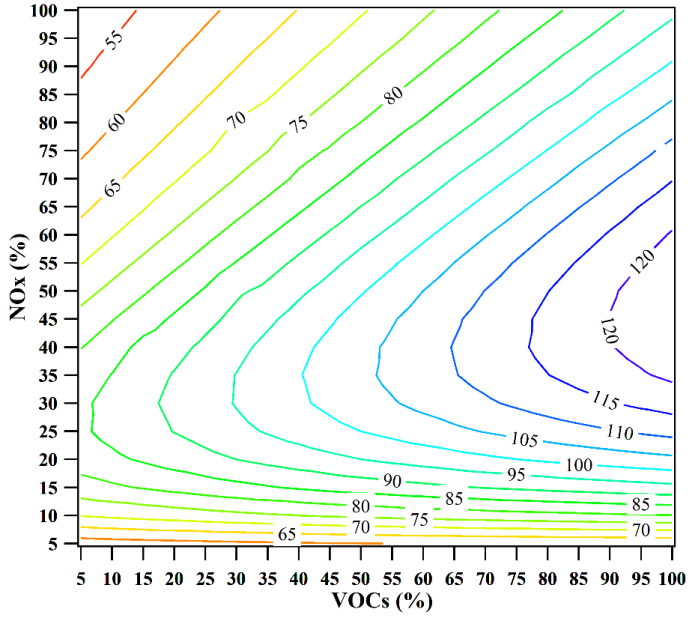

Figure 6. The ozone isopleth in terms of the percentage change of VOCs and NO_x. The ozone mixing ratios are in ppbv.

To further investigate the formulation and implementation of VOCs and their emissions, we simulated the RIR values of each source for all of the O_3 episode days using the OBM-MCM model (Fig. 7). The RIR value represents the percentage change in O_3 production per percent change in the precursors. Positive RIR values indicate reduced O_3 formation with reduced source concentration, while negative values would indicate the opposite. A larger absolute RIR value indicates a stronger impact of a particular source on O_3 formation. Our results infer positive VOC RIR values and negative NO RIR values (-0.34 ± 0.09), indicating O_3 formation to be VOC-limited, which is consistent with the O_3 isopleth analysis. This observation is also consistent with previous results in industrial, traffic, residential and commercial areas of Nanjing (Zhang et al., 2018; An et al., 2015). However, the RIR values of each source were found to vary day-to-day due to the variability in the mixing ratios of VOCs and NO_x, as well as changes in meteorological parameters. Figure 7a shows the mean RIR values of the different emission sources. Diesel vehicular exhausts were found to have the largest RIR value of 0.14 ± 0.01, followed by industrial emissions (0.13 ± 0.02), biogenic emissions (0.12 ± 0.01), gasoline vehicle exhausts (0.11 ± 0.01), and fuel evaporation (0.03 ± 0.01). Therefore, VOC species in diesel vehicular exhausts and industrial emissions had the highest impact on O_3 photochemical formation at the JAES site. Furthermore, we calculated the relative contributions of the different sources based on the reactivity and abundance of individual VOC species. Our results showed that vehicle exhausts were the highest contributors to O_3 formation at ~68%, with diesel and gasoline vehicular exhausts contributing 42% and 26%, respectively. This was followed by industrial emissions (22%), biogenic emissions (5%), and fuel evaporation (5%). Our results further demonstrate the need to minimize VOC emissions from vehicle exhausts in order to lower O_3 formation and photochemical pollution.

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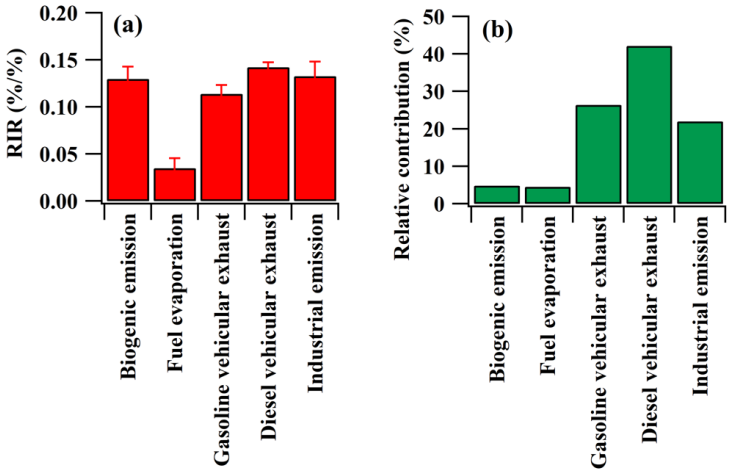

Figure 7a. The average RIR values of VOC sources, and (b) the relative contributions of different VOC sources to photochemical O_3 formation.

To further investigate the relative importance of individual VOC species in each source, we calculated the RIR values and relative contributions of individual VOC species to photochemical O_3 formation. Figure 8 illustrates the 10 VOC species with highest RIR and RIR-weighted values at the JAES site. Based on the mass concentrations of individual species in each source, we found that *m,p*-xylene and toluene in industrial emissions and gasoline vehicular emissions, propene and toluene in diesel vehicular emissions, and *i*-pentane in fuel evaporation to be the dominant species contributing to photochemical formation in each VOC source. Thus, only a small number of VOCs species can be monitored for effective control on local O_3 formation. Though the photochemical reactivity of *i*-pentane, propane and *n*-butane were lower than alkenes and aromatics, their high RIR-weighted values indicate that high concentrations of VOCs with low photochemical reactivity can still significantly contribute towards O_3 formation. This finding further confirms that both VOC reactivity and abundance should be considered for effective control on O_3 formation. Isoprene in biogenic emissions also shows high RIR-weighted values when considering both its reactivity and abundance. Currently, the majority of the VOCs control measures are focused on anthropogenic emissions, yet the contributions of biogenic emissions on O_3 formation are also significant (section 3.5). This feature highlights the need to minimize VOCs from biogenic emissions for effective control on O_3 formation.

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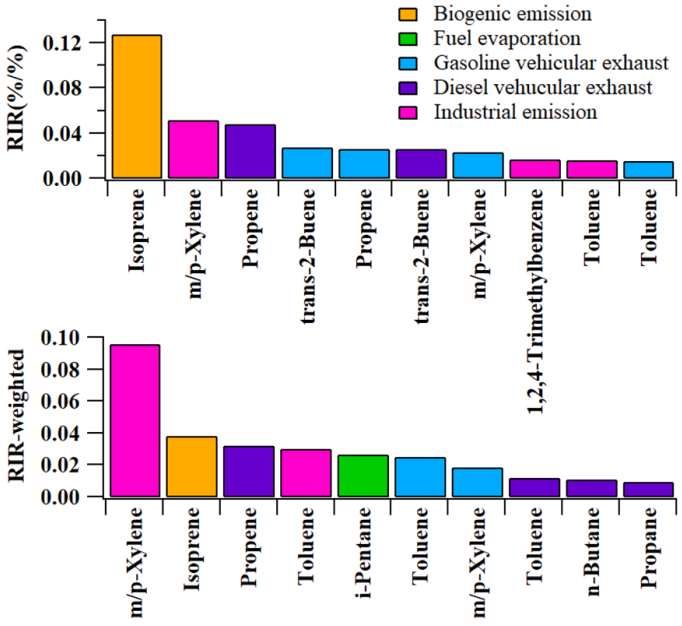

Figure 8. The average RIR values and RIR-weighted values of the top 10 VOC species in the different source categories.

3.5 Policy summary and implications

To effectively control photochemical pollution, the Prevention and Control of Atmospheric Pollution Act was passed in 1987 and amended recently in 2015. As a result, a series of measures to prevent and control VOCs levels have been and are being implemented by central and local governments, including the implementation of new laws and regulations, and the advancement of technology. The results of this study suggest that photochemical O_3 formation within the urban areas of Nanjing city are VOC-limited, which is consistent with observations in the urban locations of other regions, including the North China Plain, the Yangtze River Delta and the Pearl River Delta. Minimizing VOC emissions and their concentrations should therefore be prioritized in order to alleviate O_3 pollution. The prevention and control of VOC pollution has been listed as one of the key tasks of "the Blue Sky" Project initiated in 2012 by the Department of Environmental Protection of Jiangsu Province. Furthermore, the administrative measures on the Prevention and Control of Volatile Organic Compounds Pollution in Jiangsu (Order No. 119 of the Provincial Government) was enacted on March 6, 2018 and implemented on May 1, 2018, with the aim to control VOC emissions in Jiangsu Province.

In order to achieve these goals, various measures have been implemented (Table S2), including: 1) investigating the current pollution status and identifying the progress of VOCs prevention and control in Jiangsu Province (Provincial Office of the Joint Conference on the prevention and control of air pollution [2012] No. 2); 2) conducting a strict industry access system, under the Advice on Promoting Air Pollution Joint Prevention and Control Work to Improve Regional Air Quality (Office of the State Council [2010] No. 33); 3) strengthening the remediation on existing sources of VOCs and reducing VOC emissions from these sources, under the Guidelines for the Implementation of Leak Detection and Repair (LDAR) in Jiangsu Province (Trial) (Provincial Office of Environmental Protection [2013] No. 318); 4) strengthening the VOC monitoring capacity, under the Guidelines for Control of Volatile Organic Compounds Pollution in Key Industries in Jiangsu Province (Provincial Office of Environmental Protection [2013] No. 128); 5) improving standards on VOC emissions for key industries, including standards for surface coating of the automobile manufacturing industry (DB32/2862-2016), the chemical industry (DB32/3151-2016), and furniture manufacturing operations (DB32/3152-2016), which are

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still effective since their enforcement; 6) implementing the Pilot Measures for Volatile Organic Compounds Discharge Charges (Ministry of Finance [2015] No. 71) on October 1, 2015 to raise awareness of emissions reduction in factories and to control VOC emissions from industrial sources; 7) encouraging the public to live a low-carbon life and to supervise and make recommendations in accordance with the laws, under the Measures for Public Participation in Environmental Protection in Jiangsu Province (Trial) (Provincial Regulation of Environmental Protection Office [2016] No. 1).

Based on the VOC source apportionment results in this study, we identified vehicular emissions and industrial emissions to be the two major VOC sources contributing to photochemical O_3 formation. Other measures and/or regulations have been conducted in the Jiangsu Province to effectively control VOCs emissions from vehicles and industry. For vehicular emissions, the Regulations on Prevention and Control of Vehicle Exhaust Pollution in Nanjing was amended in July 2017, and subsequently in March, 2018 (http://hbt.jiangsu.gov.cn/col/col1590/index.html). The new regulation not only focusses on vehicle emissions, but also incorporates a number of additional topics, including optimizing the function and distribution of urban areas, limiting the number of vehicles in the region, promoting new green energy vehicles, and improving the quality of fuel. It is advised to promote intelligent traffic management, implement a priority strategy for public transportation, and construct more efficient traffic systems to promote pedestrian and bicycle use. Further studies should be conducted to estimate and manage the increasing quantity of vehicles on the road. As of January 1, 2017, these regulations specify that all new and used vehicles should meet the fifth phase of vehicle emission standards, including vehicle manufacturing, selling, registering and importing. For the vehicles already on the road, an environmental protection examination should be monitored annually, based on the standards of GB 14622-2016, GB 18176-2016, GB 19755-2016, and HJ 689-2014. Penalties are issued if qualified vehicles excessively emit pollutants due to poor maintenance.

For industrial emissions, various policies have been implemented to reduce VOC emissions, particularly in chemical industries: including, 1) investigations on the VOC emissions of the chemical industry and the establishment of an archive system for VOC pollution control, particularly the inspection of industry information, products and materials, unorganized emission of storage, and exhaust gas treatment facilities, under the Plan for Investigation of Volatile Organic Pollutant Emissions in Jiangsu Province, mentioned in the Provincial Office of Environmental Protection [2012] No. 183; 2) exhaust gas remediation in the chemical industry park, under the Technical Specifications for Prevention and Control of Air Pollution in Chemical Industries in Jiangsu Province (Provincial Office of Environmental Protection [2014] No. 3), which states the establishment of the long-term supervision of exhaust gas remediation in the chemical industry park of Jiangsu Province; 3) a pilot project on the leak detection and repair (LDAR) technology in the chemical industry park, under the notification on carrying out the technical demonstration and pilot work of leak detection and repair (LDAR) in petrochemical and chemical industries (Provincial Office of Environmental Protection [2015] No. 157). The TVOC removal efficiency of organic exhaust vents should be >95%, and higher for areas of excessive environmental pollution at >97% (GB 31571-2015).

Overall, though measures have been adopted to improve standards and control vehicle VOCs emissions, most of these policies only focus on total VOC emissions (or the mass of total emissions) and do not consider the impacts of individual VOC species. To accelerate the implementation of existing policies and to strengthen collaborative regional prevention and control, priority should be placed on specific high-impact VOC species (i.e., *m,p*-xylene and toluene in the industrial emission and gasoline vehicular emission) by considering both their reactivity and abundance. It is also necessary to consider the reduction ratios of VOC/NO_x when VOCs and NO_x are simultaneously controlled. Finally, long-term monitoring studies are necessary to determine the cost-benefits and performance of each policy.

4. Conclusion

In this study, a one-year field sampling campaign was conducted to investigate the VOCs characteristics at an urban site in Nanjing (the JAES site), Jiangsu province. In total, 56 VOCs including 29 alkanes, 10 alkenes, 16

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aromatics and acetylene were identified and quantified. The composition analysis found that alkanes were the dominant group of VOCs observed at the JAES site (~53%), followed by aromatics, acetylene, and alkenes. This finding is consistent with the VOCs measurements in studies conducted in the North China Plain, Pearl River Delta, and Yangtze River Delta. We observed distinct seasonal patterns of TVOCs, with maximum values in winter and minimum values in summer. Similarly, prominent morning and evening peaks were observed in the diurnal variability of TVOCs, influenced by local emissions and meteorology.

Based on the observed VOCs data, we identified five dominant VOC sources at the JAES site using a PMF model. By considering both the abundance and reactivity of individual VOC species in each source, the OBM-MCM model identified vehicular and industrial emissions, particularly *m,p*-xyleme, toluene and propene, to be the main contributors of O_3 pollution. Our results demonstrate that O_3 formation at the JAES site is VOC-limited and is predominantly controlled by a small number of VOCs species. Local governments have strengthened several measures to minimize VOCs pollution from vehicle and industrial emissions in the Jiangsu province in recent years, though most of these policies focus particularly on lowering the total emissions of VOCs. However, our results highlight the need to consider both the abundance and reactivity of individual VOC species in order to formulate effective control strategies to minimize pollution. Further, despite its low relative contribution to the TVOC, our results identified biogenic emissions to be a stronger source of O_3 formation when considering both VOC species abundance and reactivity. We therefore suggest the implementation of measures to monitor and control both the contributions of biogenic and anthropogenic emissions to effectively minimize O_3 pollution in Nanjing.

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Author Contributions. Qiuyue Zhao and Dr. Liu designed the research and carried them out. Dr. Ling performed the model simulation. Dr. Shen performed the observation data analysis. Qiuyue Zhao prepared the manuscript with contributions from all co-authors.

Competing Interests. The authors declare that they have no conflict of interest.

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Reference

An, J., Zhu, B., Wang, H., Li, Y., Lin, X., and Yang, H.: Characteristics and source apportionment of VOCs measured in an industrial area of Nanjing, Yangtze River Delta, China, Atmospheric Environment, 97, 206-214, 2014

An, J., Zou, J., Wang, J., Lin, X., and Zhu, B.: Differences in ozone photochemical characteristics between the megacity Nanjing and its suburban surroundings, Yangtze River Delta, China, Environmental Science and Pollution Research International, 22(24), 19607, 2015.

Cai, C. J., Geng, F. H., Tie, X.X., and An, J. L.: Characteristic and source apportionment of VOCs measured in Shanghai, China, Atmospheric Environment, 44, 5005-5014, 2010.

Cardelino, C. A., and Chameides W. L.: An observation-based model for analyzing ozone precursor relationships in the urban atmosphere, Air and Waste Management Association, 45, 161–180, 1995.

Carter, W.L., and Atkinson, R.: Computer modeling study of incremental hydrocarbon reactivity, Environmental Science and Technology 23, 864-880, 1989.

Ding, A.J., Nie, W., Huang, X., Chi, X.G., Xu, Z., et al.: Ozone in the western Yangtze River Delta of China: a synthesis study based on ground, aircraft and sounding measurement 2011-2015, The 6th PEEX meeting, May 2016, 2016

Fu, L., Wan, W., Zhang, W., and Cheng, H.: Air pollution prevention and control progress in Chinese cities, Clean Air Asia, China, available at: http://cleanairasia.org/wp-content/uploads/2016/08/China-Air-2016-Report-Full.pdf., 2016, last access: 16 May 2018.

Guo, H., Cheng, H. R., Ling, Z. H., Louie, P. K. K., and Ayoko, G. A.: Which emission sources are responsible for the volatile organic compounds in the

https://doi.org/10.5194/acp-2019-817
Preprint. Discussion started: 25 October 2019

Atmospheric Chemistry and Physics Discussions

atmosphere of Pearl River Delta?, Journal of Hazardous Materials, 188, 116-124, 2011a.

Guo, H., Zou, S. C., Tsai, W. Y., Chan, L. Y., and Blake, D. R.: Emission characteristics of non-methane hydrocarbons from private cars and taxis at different driving speeds in Hong Kong, Atmos. Environ., 45, 2711–2721, 2011b

Guo, H., Zheng J. Y., Characterisation of VOC sources and integrated photochemical ozone analysis in Hong Kong and the Pearl River Delta region. Report to the Environmental Protection Department of Hong Kong (Tender Reference AS12-02909), Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, 2016.

He, Z., Wang, X., Ling, Z., Zhao, J., Guo, H., Shao, M., and Wang, Z.: Contributions of different anthropogenic volatile organic compound sources to ozone formation at a receptor site in the Pearl River Delta region and its policy implications, Atmos. Chem. Phys., 19, 8801-8816, 2019.

HKEPD (Hong Kong Environmental Protection Department):Characterisation of VOC sources and integrated photochemical ozone analysis in Hong Kong and the Pearl River Delta region. Final report, , Hong Kong, 2015.

Huang, C., Chen, C. H., Li, L., Cheng, Z., Wang, H. L., Huang, H. Y., Streets, D. G., Wang, Y. J., Zhang, G. F., and Chen, Y.R.: Emission inventory of anthropogenic air pollutants and VOC species in the Yangtze River Delta region, China. Atmos. Chem. Phys., 11, 4105-4120, 2011a

Jenkin, M. E. and Clemitshaw, K. C.: Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer, Atmospheric Environment, 34, 2499-2527, 2000.

Kurokawa, J., Ohara, T., Morikawa, T., Hanayama, S., Janssens-Maenhout, G., Fukui, T., Kawashima, K., and Akimoto, H.,: Emissions of air pollutants and greenhouse gases over Asia regions during 2000-2008: Regional Emission inventory in Asia (REAS) version 2, Atmos. Chem. Phys., 13, 11019-11058, 2013.

Lam, S. H. M., Saunders, S. M., Guo, H., Ling, Z. H., Jiang, F., Wang, X. M., and Wang, T. J.: Modelling VOC source impacts on high ozone episode days observed at a mountain summit in Hong Kong under the influence of mountain-valley breezes. Atmos. Environ., 81, 166–176, 2013

Lau, A. K. H., Yuan, Z., Yu, J. Z., and Louie, P. K.: Source apportionment of ambient volatile organic compounds in Hong Kong, Science of the Total Environment, 408, 4138–4149, 2010.

Li, X., Rohrer, F., Brauers, T., Hofzumahaus, A., and Wahner, A.: Modeling of HCHO and CHOCHO at a semi-rural site in southern China during the PRIDE-PRD 2006 campaign, Atmos. Chem. Phys., 14, 33013-33054, 2014.

Ling, Z. H., and Guo, H.: Contribution of VOC sources to photochemical ozone formation and its control policy implication in Hong Kong, Environmental Science and Policy, 38(3), 180-191, 2014.

Ling, Z. H., Guo, H., Cheng, H. R., and Yu, Y. F.: Sources of ambient volatile organic compounds and their contributions to photochemical ozone formation

https://doi.org/10.5194/acp-2019-817
Preprint. Discussion started: 25 October 2019

Atmospheric Chemistry and Physics Discussions

at a site in the Pearl River Delta, southern China, Environmental Pollution, 159, 2310-2319, 2011.

Liu, B., Liang, D., Yang, J., Dai, Q., Bi, X., and Feng, Y., Yuan, J., Xiao, Z.M., Zhang, Y.F., Xu, H.: Characterization and source apportionment of volatile organic compounds based on 1-year of observational data in Tianjin, China. Environmental Pollution, 218, 757-769 2015.

Liu, Y., Shao, M., Fu, L. L., Lu, S. H., Zeng, L. M., and Tang, D. G.: Source profiles of volatile organic compounds (VOCs) measured in China: Part I, Atmospheric Environment 42, 6247-6260, 2008a.

Liu, Y., Shao, M., Lu, S., Chang, C. C., Wang, J. L., and Fu, L.: Source apportionment of ambient volatile organic compounds in the Pearl River delta, China: part II, Atmospheric Environment, 42(25), 6261-6274, 2008b.

Liu, Y., Shao, M., Lu, S., Chang, C., Wang, J. L., and Chen, G.: Volatile organic compound (VOC) measurements in the Pearl River delta (PRD) region, China, Atmos. Chem. Phys., 7(5), 1531-1545, 2008c.

Lyu, X., Chen, N., Guo, H., Zhang, W., Wang, N., Wang, Y., and Liu, M.,: Ambient volatile organic compounds and their effect on ozone production in Wuhan, central China, Science of the Total Environment, 548-549(60), 483-483, 2016.

Mo, Z., Shao, M., and Lu, S.: Compilation of a source profile database for hydrocarbon and OVOC emissions in China, Atmospheric Environment, 143, 209-217, 2016.

Mo, Z., Shao, M., Lu, S., Qu, H., Zhou, M., and Gou, B.: Process-specific emission characteristics of volatile organic compounds (VOCs) from petrochemical facilities in the Yangtze River Delta, China, Science of the Total Environment, 533, 422-431, 2015.

Mo, Z., Shao, M., Lu, S. H., Niu, H., Zhou, M. Y., Sun, J.: Characterization of non-methane hydrocarbons and their sources in an industrialized coastal city, Yangtze River Delta, China, Science of the Total Environment, 593-594, 641-653, 2017.

Ou, J., Guo, H., Zheng, J., Cheung, K., Louie, P. K. K., Ling, Z., and Wang D. W.: Concentrations and sources of non-methane hydrocarbons (NMHCs) from 2005 to 2013 in Hong Kong: a multi-year real-time data analysis, Atmospheric Environment, 103(103), 196-206, 2015.

Pan, X., Kanaya, Y., Tanimoto, H., Inomata, S., Wang, Z., Kudo, S., and Uno, I.: Examining the major contributors of ozone pollution in a rural area of the Yangtze River Delta region during harvest season, Atmos. Chem. Phys., 15, 6101-6111, 2015

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of nonaromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161–180, 2003.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: from air pollution to climate change, 2nd edition. Wiley Publisher, New Jersey, USA, 2006.

https://doi.org/10.5194/acp-2019-817
Preprint. Discussion started: 25 October 2019

Atmospheric Chemistry and Physics Discussions

574 Shao, M., Lu, S., Liu, Y., Xie, X., Chang, C., Huang, S., and Chen, Z.: Volatile organic compounds measured in summer in Beijing and their role in ground-
575 level ozone formation, Journal of Geophysical Research, 114, D00G06, doi: 10.1029/2008JD010863, 2009.
576
577 Shao, P., An, J. L., Xin, J. Y., Wu, F. K., Wang, J. X., Ji, D. S., and Wang, Y.S.: Source apportionment of VOCs and the contribution to photochemical ozone
578 formation during summer in the typical area in the Yangtze River Delta, China, Atmospheric Research, 176-177, 64-74, 2016.
579
580 Song, Y., Dai, W., Shao, M., Liu, Y., Lu, S. H., Kuster, W, and Goldan, P.: Comparison of receptor models for source apportionment of volatile organic
581 compounds in Beijing, China, Environmental Pollution, 156, 174-183, 2008.
582
583 Statistical yearbook of Nanjing. Nanjing Statistic Bureau: http://221.226.86.104/file/nj2004/2014/jiaotongyunshu/index.htm, last access: 17 May 2018,
584 2014
585
586 Sun, J. J., Li, Z. Y., Xue, L. K., Wang, T., Wang, X. F., Gao, J., Nie, W., Simpson, I.J., Gao, R., Blake, D. R., Chai, F. H., and Wang, W.X.: Summertime
587 C1-C5 alkyl nitrates over Beijing, northern China: spatial distribution, regional transport, and formation mechanisms, Atmospheric Research, 204, 102-
588 109. 2018.
589
590 Volkamer, R., San Martini, F., Molina, L. T., Salcedo, D., Jimenez, J. L., and Molina, M. J.: A missing sink for gas-phase glyoxal in Mexico City: Formation
591 of secondary organic aerosol, Geophysical Research Letters, 34, 255-268, 2007.
592
593 Wang, H., Chen, C., Wang, Q., Huang, C., Su, L., Huang, H., Lou, S., Zhou, M., Li, L., Qiao, L., and Wang, Y.: Chemical loss of volatile organic compounds
594 and its impact on the source analysis through a two-year continuous measurement, Atmospheric Environment, 80, 488-498, 2013.
595
596 Wang, H. L., Lou, S. R., Huang, C., Qiao, L. P., Tang, X. B., Chen, C. H., Zeng, L. M., Wang, Q., Zhou, M., Lu, S. H., and Yu, X.N.: Source profiles of
597 volatile organic compounds from biomass burning in Yangtze River Delta, China, Aerosol and Air Quality Research, 14, 818-828, 2014
598
599 Wang, M., Shao, M., Chen, W., Lu, S., Liu, Y., Yuan, B., and Li, Y.: Trends of non-methane hydrocarbons (NMHCs) emissions in Beijing during 2002-
600 2013, Atmos. Chem. Phys., 15, 1489-1502, 2015.
601
602 Wang, T., Wei, X. L., Ding, A. J., Poon, C. N., Lam, K. S., Li, Y. S., Chan, L. Y., and Anson, M.: Increasing surface ozone concentrations in the background
603 atmosphere of Southern China, 1994–2007, Atmos. Chem. Phys., 9, 6217-6227, 2009.
604
605 Wang, Y., Wang, H., Guo, H., Lyu, X., Cheng, H., Ling, Z.,Louie P., Simpson, I., Meinardi, S., Blake, D., : Long-term O_3-precursor relationships in Hong
606 Kong: field observation and model simulation, Atmos. Chem. Physics., 17(18), 1-29, 2017.
607
608 Xia, L., Cai, C., Zhu, B., An, J., Li, Y., and Li, Y.: Source apportionment of VOCs in a suburb of Nanjing, China, in autumn and winter, Journal of
609 Atmospheric Chemistry, 71(3), 175-193, 2014a.
610
611 Xia, S., Zhao, Q., Li, B., and Shen, G.: Anthropogenic source VOCs emission inventory of Jiangsu Province (In Chinese), Research of Environmental

https://doi.org/10.5194/acp-2019-817
Preprint. Discussion started: 25 October 2019

Atmospheric Chemistry and Physics Discussions

612 Sciences, 27(2), 120-126, 2014b.
613
614 Xu, Z. N., Huang, X., Nie, W., Chi, X. G., Xu, Z., Zheng, L. F., Sun, P., Ding, and A. J.: Influence of synoptic condition and holiday effects on VOCs and
615 ozone production in the Yangtze River Delta region, China, Atmospheric Environment, 168, 112-124, 2017.
616
617 Xue, L., Wang, T., Louie, P. K., Luk, C. W., Blake, D. R., Xu, Z.: Increasing external effects negate local efforts to control ozone air pollution: a case study
618 of Hong Kong and implications for other Chinese cities, Environmental Science and Technology, 48(18), 10769, 2014.
619
620 Yuan, B., Chen, W.T., Shao, M., Wang, M., Lu, S.H., Wang, B., Liu, Y., Chang, C.C., Wang, B: Measurements of ambient hydrocarbons and carbonyls in
621 the Pearl River Delta (PRD), China, Atmos. Res., 116, 93-104, 2012.
622
623 Yuan, Z., Lau, A. K. H., Shao, M., Louie, P. K. K., Liu, S. C., and Zhu, T.: Source analysis of volatile organic compounds by positive matrix factorization
624 in urban and rural environments in Beijing, Journal of Geophysical Research, 114, D00G15, doi:10.1029/2008JD011190, 2009.
625
626 Zhang, J., Wang, Y., Wu, F., Lin, H., and Wang, W.: Nonmethane hydrocarbon measurements at a suburban site in Changsha City, China. Sci. Total Environ.,
627 408 (2), 312-317, 2009.
628
629 Zhang, X., Xue, Z., Li, H., Yan, L., Yang, Y., Wang, Y., Duan, J., Li, L., Chai, F., Cheng, M., Zhang, W.: Ambient volatile organic compounds pollution in
630 China, Journal of Environmental Sciences, 55, 69-75, 2017.
631
632 Zhang, Y. X., An, J. L., Wang, J. X., Shi, Y. Z., Liu, J. D., and Liang, J. S.: Source analysis of volatile organic compounds in the Nanjing industrial area and
633 evaluation of their contribution to ozone, Environmental Science, 39(2), 502-510, 2018.
634
635 Zhang, Y. L., Wang, X. M., Barletta, B., Simpson, I.J., Blake, D.R., Fu, X.X., Zhang, Z., He Q.F., Liu, T.Y., Zhao, X.Y., Ding, X.: Source attributions of
636 hazardous aromatic hydrocarbons in urban, suburban and rural areas in the Pearl River Delta (PRD) region, Journal of Hazardous Materials, 250-251, 403-
637 411, 2013.
638
639 Zhao, Q, Shen, G., Li, L., Chen, F., Qiao, Y.Z., Li C.Y., Liu Q.,and Han, J.Z.: Ambient Particles (PM_{10}, $PM_{2.5}$, and $PM_{1.0}$) and $PM_{2.5}$ chemical components
640 in Western Yangtze River Delta (YRD): An Overview of Data from 1-year Online Continuous Monitoring at Nanjing, Aerosol Science and Engineering, 1,
641 107-118, 2017.
642
643 Zheng, J. Y., Shao, M., Che, W. W., Zhang, L. J., Zhong, L. J., Zhang, Y. H., and Streets, D.: Speciated VOC emission inventory and spatial patterns of
644 ozone formation potential in the Pearl River Delta, China, Environ. Sci. Technol., 43, 8580-8586, 2009.
645
646 Zhou, D., Li, B., Huang X., Virkkula, A., Wu, H.S., Zhao, Q.Y., Zhang, J., Liu, Q., Li, L., Li, C.Y., Chen, F., Yuan, S.Y., Qiao, Y.Z., Shen, G.F., and Ding
647 A.J.: The impacts of emission control and regional transport on $PM_{2.5}$ ions and carbon components in Nanjing during the 2014 Nanjing Youth Olympic
648 Games, Aerosol and Air Quality Research, 17(3), 730-740, 2017.
649

https://doi.org/10.5194/acp-2019-817
Preprint. Discussion started: 25 October 2019

Atmospheric Chemistry and Physics Discussions

650 Zou, Y., Deng, X. J., Zhu, D., Gong, D. C., Wang, H., Li, F., Tan, H. B., Deng, T., Mai, B. R., Liu, X. T., and Wang, B. G.: Characteristics of 1 year of
651 observational data of VOCs, NO_x and O_3 at a suburban site in Guangzhou, China, Atmos. Chem. Phys., 15, 6625–6636, 2015.
652