Response to Reviewers

We appreciate the two anonymous reviewers for their constructive criticisms and valuable comments, which were of great help in improving the quality of the manuscript. We have revised the manuscript accordingly and our detailed responses are shown below. All the revision is highlighted in the revised manuscript.

Interactive comment on "Sources of volatile organic compounds and policy implications for regional ozone pollution control in an urban location of Nanjing, East China" by Qiuyue Zhao et al.

Anonymous Referee #2

In this study, the authors conducted one-year VOC observation at an urban site in Nanjing. They analyzed the seasonal and diurnal characteristics of 56 VOCs as well as their sources using the PMF model. A box model together with a Master Chemical Mechanism (MCM) was used to identify the relationships between the contributions of VOC sources and the O3 formation. The results were also compared with VOCs data from other Chinese megacities like Beijing, Guangzhou, and Shanghai. VOC have been well recognized to be responsible for the swift development of air pollution events since volatile organic compounds are key precursors of O3 and secondary organic aerosols (SOA). However, the speciation and emission strength of these VOC have been demonstrated to be hard to acquire due to the fact that VOC can be emitted from a diversity of domestic and industrial activities. Therefore, measurements of VOC emissions are critically needed in China. This work can be a significant contribution to the atmospheric research community. Overall, the manuscript is fairly well written and I would recommend the manuscript for publication after minor revisions.

Reply: We highly appreciate the reviewer's positive comments and helpful suggestions. We have addressed all the comments/suggestions in the revised manuscript. Detailed responses to the individual specific comment/suggestion are as follows.

Specific concerns:

1. Line 61: What's "photochemical industry"?

Reply: Sorry for the mistake. It should be "petrochemical industry". For details, please refer to Line 62, page 2 in the revised manuscript.

2. Sample location: there is always an asphalt waterproof layer on the rooftop of an office building. How to avoid the interference of this emissions?

Reply: We thank the reviewer's valuable comment. There is a waterproof layer on the rooftop of the building but there was no guarantee that it was made of asphalt. Furthermore, despite this waterproof layer on the rooftop of the building, the interferences of emissions from this layer were believed to be insignificant because: 1) The waterproof layer was covered by the layer of concrete, which was further covered with a layer of ceramic tile; 2) The building had been built for three years before the sampling campaign was started; 3) It was documented that the VOC emitted from asphalt mainly included benzene, toluene, ethylbenzene and xylene. However, the levels of benzene, toluene, ethylbenzene, m/p-xylene and o-xylene were lower than those observed in other urban, industrial and rural environments in different regions (section 3.1, He et al., 2019; Mo et al., 2015, 2017; An et al., 2014 and 2015; Zhang et al., 2012). 4) The sampling inlet was about 2-3 m above the rooftop of the building. Indeed, there is a waterproof layer on the rooftop of building. Therefore, we believe that though there is a waterproof layer for the rooftop of the building, the interference of its emission on ambient VOCs was insignificant.

The above text has been added in the revised manuscript to highlight the insignificant influence of waterproof layer on the rooftop of the building

For details, please refer to Lines 88-97, Page 3 in the revised manuscript.

Reference:

Gardiner, M.S., Lange, C.R., 2005. Comparison of laboratory generated and field-obtained HMA VOCs with odour potential. The International Journal of Pavement Engineering 6, 257-263.

He Zhuoran, et al., 2019. 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. Atmospheric Chemistry and Physics 19, 8801-8816.

Zhang, Y.L., Wang, X.M., Blake, D.R., Li, L.F., Zhang, Z., Wang, S.Y., Guo, H., Lee, F.S.C., Gao, B., Chan, L.Y., Wu, D., Rowland, F.S., 2012. Aromatic hydrocarbons as ozone precursors before and after outbreak of the 2008 financial crisis in the Pearl River Delta region, south China. Journal of Geophysical Research 117, D15306, doi:10.1029/2011JD017356.

3. Aromatics are important of gasoline. So, source 5 could be identified as gasoline cars. Thus, the identification of source 5 to industrious emissions may be need more relevant tracers.

Reply: The reviewer's valuable comment is highly appreciated. We agreed with the reviewer that aromatic hydrocarbons, especially benzene, toluene, ethylbenzene and xylenes could also emitted from gasoline vehicles. However, in addition to gasoline vehicle emissions, industrial emission could be another important contributor to ambient aromatic hydrocarbons in the Yangtze River Delta, Pearl River Delta and North China Plain (Yuan et al., 2009; He et al., 2019; Zhang et al., 2013, 2014; Mo et al., 2015, 2017; An et al., 2014). The tunnel studies and emission-based measurement results found that aromatic hydrocarbons from gasoline vehicle exhaust were coherently emitted with pentanes, butenes, *n*-hexane, and cyclopentane, which were more consistent with the profile in source 3 mentioned above (Liu et al., 2008; Ho et al., 2009; Yuan et al., 2009; Zhang et al., 2018). Therefore, the absence of above species in source 5 indicated that this source could be related to industrial emission (Zhang et al., 2014). Particularly, the high presence of toluene, ethylbenzene, xylenes, ethyltoluene and trimethylbenzene was consistent with the emission-base measurement results conducted in paint and printing industries (Yuan et al., 2010) and manufacturing facilities (Zheng et al., 2013). On the other hand, the profile of high presence of aromatic hydrocarbons (C_7-C_9 aromatics) and the certain amount of ethene, was also agree with the profiles measured in the areas dominated by industrial emissions in the Yangtze River Delta region (An et al., 2014; Shao et al., 2016; Mo et al., 2017). For example, An et al. (2014) reported that toluene, ethylbenzene, xylenes, and trimethylbenzenes could be emitted from different industrial processes, and identified that the factors with high loadings of these species as industrial production, solvent usage and industrial production volatilization sources by PAC/APCS at the industrial

area in Nanjing. On the other hand, Mo et al. (2017) identified the factors with high concentrations of C_7-C_9 aromatics and ethene as residential solvent usage, chemical and paint industries and petrochemical industry with the PMF model applied to the data collected in an industrialized coastal city of Yangtze River Delta region. To further identify source 3 and source 5, the ratio of toluene/benzene (T/B, ppbv/ppbv) in each profile was compared with those obtained from emission-based measurements and tunnel study results (Zhang et al., 2018 and references therein). The ratios of T/B were ~8.2 and ~1.2 for sources 5 and 3, respectively, and were consistent with those of "industrial processes and solvent application", and "roadside and tunnel study", respectively (Zhang et al., 2018 and references therein). This further confirmed that source 3 was related to gasoline vehicular exhaust, while source 5 was associated with industrial emission.

The above discussion has been provided in the revised manuscript to further clarify source 5 and source 3. For details, please refer to Lines 407-440, Pages 14-15 in the revised manuscript.

References:

Ho, K.F., et al., 2009. Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong. Atmospheric Chemistry and Physics 9, 7491-7504.

Liu, Y., et al., 2008. Source apportionment of ambient volatile organic compounds in the Pearl River Delta, China: Part II. Atmospheric Environment 42, 6261-6274.

Shao, P., An, J.L., Xin, J.Y., Wu, F.K., Wang, J.X., Ji, D.S., Wang, Y.S., 2016. Source apportionment of VOCs and the contribution to photochemical ozone formation during summer in the typical industrial area in the Yangtze River Delta, China. Atmospheric Research 176-177, 64-74.

Yanli Zhang, et al., 2013. Species profiles and normalized reactivity of volatile organic compounds from gasoline evaporation in China. Atmospheric Environment 79, 110-118.

Yuan, B., Shao, M., Lu, S.H., Wang, B., 2010. Source profiles of volatile organic compounds associated with solvent use in Beijing, China. Atmospheric Environment 44, 1919-1926.

Zhang Yanli, et al., 2018. Decadal changes in emissions of volatile organic compounds (VOCs) from on-road vehicles with intensified automobile pollution control: case study in a busy urban tunnel in south China. Environmental Pollution 233, 806-819.

Zheng, J.Y., Yu, Y.F., Mo, Z.W., Zhang, Z., Wang, X.M., Yin, S.S., Peng, K., Yang, Y., Feng, X.Q., Cai, H.H., 2013. Industrial sector-based volatile organic compound (VOC) source profiles measured in manufacturing facilities in the Pearl River Delta, China. Science of the Total Environment 456-457, 127-136.

Zibing Yuan, et al., 2009. Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing. Journal of Geophysical Research 114,

D00G15, doi: 10.1029/2008JD011190.

4. Why the diurnal trend of fuel evaporation showed a decrease at noon time since this source is temperature dependent?

Reply: Thanks a lot for the comment. Apart from emissions, ambient VOC concentrations are largely determined by photochemistry and dilution processes, in particular the variations of mixing height in the course of a day (Gillman et al., 2009; Wang et al., 2013). Though the evaporation of fuel is dependent on temperature, the average temperature in the morning and evening (*i.e,* 0800-1000 and 1700-1900 LT, respectively) when peaks of fuel evaporation were found was only about ~1.2 ºC lower than that observed from noon to afternoon (1100-1600 LT), which may not result in much higher fuel evaporation at noon (the difference between maximum and minimum values for fuel evaporation was found to be ~6 μg/m^3). On the other hand, in addition to evaporation from the gas station, fuel could evaporate from hot engines, fuel tanks and the exhaust system when the car is running. Furthermore, the engine remains hot for a period of time after the car is turned off, and gasoline evaporation continues when the car is parked (Technology center, University of Illionois, https://mste.illinois.edu/tcd/ecology/fuelevap.html, access date: 25 December 2019). The similarity of diurnal variations of fuel evaporation to vehicular emissions suggested that the prominent peak in the morning and evening hours were related to the increased vehicles in the traffic rush hour and emissions accumulated in the relatively low boundary layer.

To provide detailed discussion on the diurnal pattern of fuel evaporation, the above analysis text has been added in the revised manuscript. For details, please refer to Lines 490-501, Page 17 in the revised manuscript.

References

Gilman, J.B., Kuster, W.C., Goldan, P.D., Herndon, S.C., Zahniser, M.S., Tucker, S.C., Brewer, W.A., Lerner, B.M., Williams, E.J., Harley, R.A., Fehsenfeld, F.C., Warneke, C., de Gouw, J.A., 2009. Measurements of volatile organic compounds during the 2006 TexAQS/GoMACCS campaign: industrial influences, regional characteristics, and diurnal of dependencies of the OH reactivity. Journal of Geophysical Research 114, D7, doi: 10.1029/2008JD011525.

Wang, H.L., Chen, C.H., Wang, Q., Huang, C., Su, L.Y., Huang, H.Y., Lou, S.R., Zhou, M., Li, L., Qiao, L.P., Wang, Y.H., 2013. Chemical loss of volatile organic compounds and its impact on source analysis through a two-year continuous measurement. Atmospheric Environment 80, 488-498.

Anonymous Referee #1

Zhao et al. describe VOC measurements conducted at the Jiangsu Academy of Environmental Science (JAES) in Nanjing, China. The authors measure VOCs using a GC system, and interpret the sources of these VOCs using positive matrix factorization. The authors evaluate the environmental impacts of these emissions on ozone formation using an observation-based model (OBM) employing the Master Chemical Mechanism (MCM v3.2), and identify the anthropogenic VOCs likely to be significant ozone precursors. The authors also evaluate ozone sensitivities to VOC and NOx reductions, and conclude that VOC reductions would be the best strategy to reduce ozone in Nanjing.

In general, the manuscript reads very well and is well-organized to tell a coherent message. I appreciate the authors work to carefully measure VOCs and benchmark these measurements against other cities in China. I am generally convinced by the PMF results given that the authors interpretation is reasonable, and the PMF factors are prescribed to obvious sources in the Nanjing area (which are very well described); however, I do have some recommendations that could improve the PMF analysis and strengthen the justification of source apportionment. Finally, I believe the use of the OBM is justified to evaluate VOC RIR, but I am not convinced that the OBM can be used to evaluate the ozone isopleth without further evidence that the model is doing an adequate job to capture ozone formation in the Nanjing region. My comments below primarily address PMF and the OBM.

Reply: Thanks for the reviewer's positive comments and helpful suggestions. We have addressed all the comments/suggestions in the revised manuscript. Detailed responses to the individual specific comment/suggestion are as follows.

Major comments

1. The PMF solution appears to be reasonable; however, I believe the authors need to do more to show that the PMF solution is robust. In Section 2.2, the authors state that comparisons were made to observations, emissions inventories, and previous PMF analyses, but no evidence is shown here or in the supplement to convince the reader

that this is true. Can the authors show the Q/Q_{exp} and explain why they setteled on a 5-factor solution? What was the factor space used? Did the authors vary other parameters (e.g. Fpeak) or conduct a bootstrapping analysis to estimate uncertainty? Can the authors show the comparisons to other factor profiles reported in literature (e.g. the industrial factor compared to An et al., 2014).

I ask because PMF is partly subjective, and a more thorough discussion is necessary to justify why the authors settle on the solution presented in the manuscript. A 5-factor solution seems reasonable, and the factors discussed all appear to be consistent with the sources surrounding the sampling site, but this could be shown with more evidence in the main text or supplemental information.

Reply: The reviewer's valuable comment is highly appreciated. To provide more evidence for the selection of the five-factor solution from the PMF mode, the following text has been added in the revised manuscript:

"*The PMF model was tested using a variety of factor numbers, 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 previous studies involving PMF/other receptor model simulations (i.e., HKEPD, 2015; Wang et al., 2014; An et al., 2014; Liu et al., 2008a). For example, different solution with different factor numbers was explored and the source apportionment results from a five-factor resolution that could sufficiently explain the observed levels of VOCs were selected (details in Section 3.3). Compared with five-factor solution, the four-factor solution derived two profiles that attributable to gasoline and diesel vehicular exhaust, while most of the aromatic species in these sources and certain amounts of C_3-C_4 species from fuel evaporation were categorized under industrial emission. On the other hand, the six-factor solution has split a factor with high presence of ethyne and certain amounts of ethane (30% in species total), C_3 species and benzene (~20% in species total), while some alkenes (18-80% in species total) were incorporated into fuel evaporation. Furthermore, the performance of the five-factor solution was evaluated using various checks and sensitivity tests. Suitable correlations between the observed concentrations and those of each species predicted*

by the model were observed, with the correlation coefficients (R^2) ranging from 0.60 - 0.91, indicating that the solution adequately reproduced the observed variations of each species. All the scale residuals were within ± 3σ with normal distributions for all species (Baudic et al., 2016). Moreover, different numbers of start seeds were tested during the simulation and no-multiple solutions were found. The ratio of Q(robust)/Q(true) obtained was ~0.93, close to 1 as suggested by previous studies and the user guide manual (Lau et al., 2010; Ling et al., 2016; Paatero, 2000). In addition, the results from bootstrapping analysis for the five-factor solution with bootstrap random seed found that all the factors were mapped to a basic factor in all the 20 bootstrap runs, while the uncertainties of each species from bootstrapping analysis were within the range of 1~20%. In this study, different F_{peak} values ranging from -5 to 5 was tested in the 5-factor solution for a more realistic profile (Lau et al., 2010; Baudic et al., 2016). The profiles with the nonzero F_{peak} values were consistent with those with zero F_{peak} value, reflecting that there was little rotation for the selected solution, confirming that the profiles were reasonably explained by the five-factor solution (Baudic et al., 2016). The results of F_{peak} value = 0.5 (the base run) was selected for analysis in this study. Overall, the above features demonstrated that the five-factor solution from PMF could provide reasonable and stable apportionment results for the observed VOCs at the JAES site." For details, please refer to Lines 152-179, Pages 5-6 in the revised manuscript.

Furthermore, to justify the source apportionment results, more discussion based on the comparison of modelled profiles with the results from emission-based measurements, and other PMF model simulations were highlighted as follows:

"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. Five VOC sources were resolved by PMF, 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 profiles from gasoline-related emissions (Barletta et al., 2005; Tsai et al., 2006). However, the low contributions of incomplete combustion tracers in this profile suggested that the VOCs were sourced from fuel evaporation. The high presence of pentanes in this profile was consistent with the source profile of gasoline volatilization extracted from principal component analysis/absolute principal component scores (PCA/APCs) based on the observed VOC data collected in an industrial area of Nanjing (An et al., 2014), the source profile of gasoline evaporation from PMF at the suburban site and urban site in Beijing and Hong Kong (Yuan et al., 2009; Lau et al., 2010). Particularly, based on the emission-based measurement, Liu et al. (2008b) conducted source apportionments of VOCs in the Pearl River Delta region by the chemical mass balance (CMB) receptor model, which attributed the source with high loadings of n/i-pentanes, cyclopentane and 2/3-methylpentane as gasoline evaporation. Therefore, Source 2 here 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 (Zhang et al., 2018; Guo et al., 2011a, b). Zhang et al. (2018) compared the VOC composition of vehicular emissions from Zhujiang Tunnel in 2014 and 2004 in the Pearl River Delta region with those from other tunnel measurements. C_2-C_4 alkanes and alkenes were found to made the greatest contributions to the loading of VOCs emitted from vehicles in 2014. The higher proportions of n/i-pentane, n-hexane, and methylcyclopentane in Source 3 relative to Source 4 indicated VOCs sourced from gasoline vehicular exhausts (Zhang et al., 2018; 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; Ho et al., 2009). Source 5 was characterized by high concentrations of aromatics. In addition to gasoline

vehicle emissions, industrial emission could be another important contributor to ambient aromatic hydrocarbons in the Yangtze River Delta, Pearl River Delta and North China Plain (Yuan et al., 2009; He et al., 2019; Zhang et al., 2013, 2014; Mo et al., 2015, 2017; An et al., 2014). The tunnel studies and emission-based measurement results found that aromatic hydrocarbons from gasoline vehicle exhaust were coherently emitted with pentanes, butenes, n-hexane, and cyclopentane, which were more consistent with the profile in source 3 mentioned above (Liu et al., 2008; Ho et al., 2009; Yuan et al., 2009; Zhang et al., 2018). Therefore, the absence of above species in source 5 indicated that this source could be related to industrial emission (Zhang et al., 2014). Particularly, the high presence of toluene, ethylbenzene, xylenes, ethyltoluene and trimethylbenzene was consistent with the emission-base measurement results conducted in paint and printing industries (Yuan et al., 2010) and manufacturing facilities (Zheng et al., 2013). On the other hand, the profile of high presence of aromatic hydrocarbons (C_7-C_9 aromatics) and the certain amount of ethene, was also agree with the profiles measured in the areas dominated by industrial emissions in the Yangtze River Delta region (An et al., 2014; Shao et al., 2016; Mo et al., 2017). For example, An et al. (2014) reported that toluene, ethylbenzene, xylenes, and trimethylbenzenes could be emitted from different industrial processes, and identified that the factors with high loadings of these species as industrial production, solvent usage and industrial production volatilization sources by PAC/APCS at the industrial area in Nanjing. On the other hand, Mo et al. (2017) identified the factors with high concentrations of C_7-C_9 aromatics and ethene as residential solvent usage, chemical and paint industries and petrochemical industry with the PMF model applied to the data collected in an industrialized coastal city of Yangtze River Delta region. To further identify source 3 and source 5, the ratio of toluene/benzene (T/B, ppbv/ppbv) in each profile was compared with those obtained from emission-based measurements and tunnel study results (Zhang et al., 2018 and references therein). The ratios of T/B were ~8.2 and ~1.2 for sources 5 and 3, respectively, and were consistent with those of "industrial processes and solvent application", and "roadside and tunnel study", respectively (Zhang et al., 2018 and references therein). This further confirmed that

source 3 was related to gasoline vehicular exhaust, while source 5 was associated with industrial emission."

For details, please refer to Lines 388-440, Pages 13-15 in the revised manuscript.

References:

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

Barletta, B., Meinardi, S., Rowland, F.S., Chan, C.Y., Wang, X.M., Zou, S.C., Chan, L.Y., Blake, D.R., 2005. Volatile organic compounds in 43 Chinese cities. Atmos. Environ. 39 (32), 5979-5990.

Baudic, A., Gros, V., Sauvage, S., Locoge, N., Olivier, S., Sarda-Esteve, R., Kalogridis, C., Petit, J.-E., Bonnaire, N., Baisnee, D., Favez, O., Albinet, A., Sciare, J., Bonsang, B., 2016. Seasonal variability and source apportionment of volatile organic compounds (VOCs) in the Paris megacity (France). Atmospheric Chemistry and Physics 16, 11961-11989.

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

Ho, K.F., Lee, S.C., Ho, W.K., Blake, D.R., Cheng, Y., Li, Y.S., Ho, S.S.H., Fung, K., Louie, P.K.K., Park, D., 2009. Vehicular emission of volatile organic compounds (VOCs) from a tunnel study in Hong Kong. Atmospheric Chemistry and Physics 9, 7491-7504.

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

Liu, Y., Shao, M., Lu, S.H., Chang, C.C., Wang, J.L., Fu, L.L., 2008. Source apportionment of ambient volatile organic compounds in the Pearl River Delta, China: Part II. Atmospheric Environment 42, 6261-6274.

Mo, Z.W., Shao, M., Lu, S.H., Niu, H., Zhou, M.Y., Sun, J., 2017. 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.

Shao, P., An, J.L., Xin, J.Y., Wu, F.K., Wang, J.X., Ji, D.S., Wang, Y.S., 2016. Source apportionment of VOCs and the contribution to photochemical ozone formation during summer in the typical industrial area in the Yangtze River Delta, China. Atmospheric Research 176-177, 64-74.

Tasi, W.Y., Chan, L.Y., Blake, D.R., Chu, K.W., 2006. Vehicular fuel composition and atmospheric emissions in South China: Hong Kong, Macau, Guangzhou, and Zhuhai. Atmospheric Chemistry and Physics 6, 3281-3288.

Yuan, Z.B., Lau, A.K.H., Shao, M., Louie, P.K.K., Liu, S.C., Zhu, T., 2009. Source analysis of volatile organic compounds by positive matrix factorization in urban and rural environments in Beijing. Journal of Geophysical Research 114, D00G15, doi:10.1029/2008JD011190.

Zhang, Y.L., Wang, X., Barletta, B., Simpson, I.J., Blake, D.R., Fu, X., Zhang, Z., He, Q., Liu, T., Zhao, X., Ding, X., 2013. Source attributions of hazardous aromatic hydrocarbons in urban, suburban and rural areas in the Pearl River Delta (PRD) region. Journal of Hazardous Materials

250, 403-411.
Zhang, Y.L., Yang, W.Q., Simpson, I.J., Huang, X.Y., Yu, J.Z., Huang, Z.H., Wang, Z.Y., Zhang, Z., Liu, D., Huang, Z.Z., Wang, Y.J., Pei, C.L., Shao, M., Blake, D.R., Zheng, J.Y., Huang, Z.J., 2018. Decadal changes in emissions of volatile organic compounds (VOCs) from on-road vehicles with intensified automobile pollution control: case study in a busy urban tunnel in south China. Environmental Pollution 233, 806-819.
Zheng, J.Y., Yu, Y.F., Mo, Z.W., Zhang, Z., Wang, X.M., Yin, S.S., Peng, K., Yang, Y., Feng, X.Q., Cai, H.H., 2013. Industrial sector-based volatile organic compound (VOC) source profiles measured in manufacturing facilities in the Pearl River Delta, China. Science of the Total Environment 456-457, 127-136.

2. The authors employ an OBM to evaluate ozone sensitivity to VOCs and NO_x. OBMs are primarily useful because they allow one to evaluate relative incremental reactivity (as the authors describe in section 2.3). One strength of an OBM is that you do not need all of the measurements that described ozone formation; rather, you calculate source functions that explain residual effects on the time evolution of a measured species (e.g. meteorology, chemistry not accounted for in the mechanism, additional precursors that contribute to ozone formation, etc). From these calculations, you can derive the RIR by conducting a small perturbation on the system (e.g., decreasing or increasing the concentration of a species that is measured and well-represented by the model). The calculation of RIR are good and justified with the use of an OBM.

Reply: The reviewer's positive comment on OBM is highly appreciated. Yes, in this study, RIR which has been adopted in previous studies (i.e., Wang et al., 2017; Lyu et al., 2016; Xue et al., 2014; Cheng et al., 2010) as used to assess the sensitivity of precursors to photochemical O_3 formation by changing the concentrations of precursors (i.e., 10% reduction).

References

Cheng, H.R., Guo, H., Wang, X.M., Saunders, S.M., Lam, S.H.M., Jiang, F., Wang, T., Ding, A., Lee, S., Ho, K.F., 2010. On the relationship between ozone and ite precursors in the Pearl Rive Delta: application of an observation-based model (OBM). Environmental Science and Pollution Research 17, 547-560.
Lyu, X.P., Guo, H., Simpson, I.J., Meinardi, S., Louie, P.K.K., Ling, Z.H., Wang, Y., Liu, M., Luk, C.W.Y., Blake, D.R., 2016. Effectiveness of replacing catalytic converters in LPG-fueled vehicles in Hong Kong. Atmospheric Chemistry and Physics 16, 6609-6626.
Wang, Y., Wang, H., Guo, H., Lyu, X.P., Cheng, H.R., Ling, Z.H., Louie, P.K.K., Simpson, I.J.,

Meinardi, S., Blake, D.R., 2017. Long-term O3-precursor relationships in Hong Kong: field observation and model simulation. Atmospheric Chemistry and Physics 17, 10919-10935.
Xue, L.K., Wang, T., Gao, J., Ding, A.J., Zhou, X.H., Blake, D.R., Wang, X.F., Saunders, S.M., Fan, S.J., Zuo, H.C., Zhang, Q.Z., Wang, W.X., 2014. Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes. Atmospheric Chemistry and Physics 14, 13175-13188.

In Section 3.4, the authors extend this analysis to evaluate the ozone isopleth. In this context, I don't believe the use of an OBM is justified. Isopleth calculation are defendable if a large fraction of the local, photochemically produced ozone is explained by the measured precursors. If a significant fraction of this produced ozone is explained by the time-dependent source function (i.e, the "residual" ozone), then the authors may not be measuring (or including in the model) a significant fraction of the VOC precursors needed to derive ozone formation. In that case, how can the authors determine whether Nanjing is VOC or NO_x-sensitive? The isopleth presented in Fig.6 is very NO_x saturated, which the authors say generally agrees with previous literature. But do the measurements really defend this?

Reply: Thanks a lot for the reviewer's comment. We agree with the reviewer that the isopleth calculation could be reasonable when photochemically produced ozone from the measured precursors made a significant contribution to observed O_3. As the O_3 simulated by the OBM was derived based on the observed mixing ratios of precursors and local meteorology, it is more appropriate to refer the simulation of O_3 by the OBM as local produced O_3, though the observed mixing ratios of precursors could be both influenced by local emissions and those transported from upwind areas (Liu et al., 2019). Therefore, before using the isopleth calculation, it is necessary to investigate whether locally produced O_3 from OBM could make a significant portion to the observed O_3 at the JAES site. The investigation on the wind parameters found that the average wind speed was ~1.8 m/s on O_3 episode days, with about ~51% of most wind speed data being $\leq$2 m/s (see Figure S2 in the supplementary), suggesting that regional transport may not have a significant influence on the levels of O_3 and its precursors on episode days at the JAES site (Shao et al., 2016; Wang et al., 2017).

Figure S3 in the supplementary showed the timeseries for the comparison between local

produced O_3 from OBM and the observed O_3 mixing ratios, while Figure S4 in the supplementary presented the comparison between the mean diurnal variations of simulated and observed O_3 mixing ratios for all the O_3 episode days at the JAES site. It was found that the model underestimated or overestimated O_3 on some episode days. The comparison between the mean diurnal variations of simulated and observed O_3 suggested that the model captured the diurnal variations of O_3, and the predicted and observed maximum O_3 values were comparable, though the predicted mixing ratios of O_3 were lower than that observed in the early morning. The above discrepancy between observed and predicted O_3 mixing ratios was mainly due to the failure to consider physical processes (i.e., horizontal and vertical transport) and/or the other O_3 precursors (i.e., carbonyls and other oxygenated VOCs (OVOCs)) (Liu et al., 2019; Cheng et al., 2010; Shao et al., 2009a). However, the simulation indeed provided a reasonable description of the O_3 variations using the observation data. To assess the local photochemically produced O_3 against the measured levels of O_3 during the O_3 episode days, the amount of the locally produced O_3 formed by the photochemistry was compared with the observed O_3 accumulations that were calculated as difference between the peak and early-morning concentrations of O_3. The amount of local photochemically produced O_3 was determined by the net O_3 production rate, which was calculated by the difference between the gross production $G(O_3)$ and destruction rates $D(O_3)$ in the model (Equations 1-3).

$$P(O_3) = G(O_3) - D(O_3) \qquad (1)$$

$$G(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum k_{RO_2i+NO}[RO_{2i}][NO] \qquad (2)$$

$$D(O_3) = k_{HO_2+O_3}[HO_2][O_3] + k_{OH+O_3}[OH][O_3] + k_{O(^1D)+H_2O}[O(^1D)][H_2O] + k_{OH+NO_2}[OH][NO_2] + k_{alkenes+O_3}[alkenes][O_3] \qquad (3)$$

Where the k constant values were the rate coefficients for the subscript reaction. The detailed description for the above calculation was provided by Xue et al. (2013, 2014) and Wang et al. (2017). At JAES, the daytime (07:00–19:00 LT) average net O_3 production rate was estimated to be 6.2 ppbv h^{-1}, corresponding to ~74 ppbv O_3 formed from local photochemistry during daytime hours. The amount was coincident with the average increment of O_3 observed from early morning to late afternoon at JAES (~81

ppbv), suggesting that local photochemically produced O_3 significantly contributed to the O_3 increment at JAES. Indeed, the observed minimum O_3 mixing ratios before accumulation which were considered as the residual O_3 levels (or background O_3, the mean value was 20 ppbv) at the sampling site as suggested by the previous studies (Xue et al., 2013, 2014a,b) only accounted for ~20% of the observed maximum O_3 values (the mean value was 102 ppbv) (data not shown). Furthermore, the difference between observed and simulated minimum O_3 mixing ratios which was considered as the fraction of residual O_3 that could not be explained by the OBM model only contributed ~17% of the observed maximum O_3 mixing ratio. The above analysis on the difference between observed and simulated O_3 levels confirmed that local photochemical produced O_3 made a significant fraction to observed O_3 levels at JAES. However, we admitted that the OBM model could not accurately estimate the contributions of residual O_3 to the increment of O_3 values during daytime, which requires to be studies using a combination of different models and dataset (i.e., the regional air quality model, Lagrangian dispersion model and emission inventory) (Wang et al., 2015; Ding et al., 2013a, b; Jiang et al., 2010).

To further evaluate the model performance, the index of agreement (IOA) that was developed to assess the agreement between modelled and observed results was used in this study (Huang et al., 2005; Wang et al., 2013, 2015; Liu et al., 2019). The calculation of IOA was as follows:

$$IOA = 1 - \frac{\sum_{i=1}^{n}(O_i - S_i)^2}{\sum_{i=1}^{n}(|O_i - \overline{O}| + |S_i - \overline{O}|)^2} \qquad (4)$$

Where S_i and O_i were the simulated and observed O_3, respectively, while $\overline{O}$ was the mean of observed O_3, and n is the number of samples. The IOA values ranged between 0 and 1, and a relatively higher value of IOA indicated relatively greater consistency between simulated results and observation data (Wang et al., 2013, 2015, 2017). In this study, the IOA of O_3 was ~0.85, suggesting consistency of the abundance and variation

of O_3 between the observation and simulation, and demonstrating that locally produced O_3 could be explained by the measured precursors.

In the atmosphere, the sensitivity of photochemical O_3 formation was distributed into three regimes, including the VOC-limited regime, the NO_x-limited regime and the transitional regime. In the VOCs-limited regime (the relative concentration $[NO_x]/[VOC]$ is high and/or NO_x is saturated), photochemical O_3 formation decreases with the decrease in the concentration of VOCs (resulting from the control of VOC emissions), while in the NO_x-limited regime (high $[VOC]/[NO_x]$ ratio and/or VOC is saturated), any reduction in the NO_x concentration would shortens the O_3 formation chain length and reduces the photochemical O_3 formation (Jenkin and Clemitshaw, 2000). The mean mixing ratios of NO_x and TVOCs during daytime hours (0700-1800 LT, local time) on O_3 episode days were 19.2 ± 1.2 ppbv, respectively, with the mean ratio of VOCs/NO_x as (ppbC/ppbv) ~3.4, suggested that the atmosphere in at the JAES site was NO_x saturated and photochemical O_3 formation located in the VOC-regime (Jenkin and Clemitshaw, 2000). However, it should be noted that using the ratios of VOCs/NO_x to determine the O_3 formation regime could be biased in different environments as different VOC species react at different rates and with different reaction mechanisms, thus inducing the nonlinear dependency of O_3 formation on NO_x and VOCs. 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% of observed mixing ratios of VOCs and NO_x, point A in Figure 6), 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. Furthermore, to accurately evaluate the O_3-precursor relationship, the RIR values from the OBM model, which were frequently used to evaluate the O_3 formation sensitivity based on observation data, were further explored. Positive RIR values were found for the VOCs (see Figure 7a), while negative values were found for NO_x (i.e., -0.25 ± 0.02), further confirming that O_3 formation at

the JAES site was VOC-limited (Zhang et al., 2008; Shao et al., 2009b; Cheng et al., 2010).

Overall, the above analysis confirmed that simulation of OBM could be used to conduct O_3 isopleth calculation and investigate the O_3-precursor relationship (Shao et al., 2016; Lyu et al., 2019; He et al., 2019).

The above evaluation on the OBM model performance has been provided in Lines 209-266, Pages 7-9 in the revised manuscript, while the O_3-precursor relationship evaluated by the observed data, O_3 isopleth plot and RIR values from the OBM-MCM model was provided in details in Lines 511-533, Page 18 in the revised manuscript.

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If the authors are to present an ozone isopleth, then I believe there needs to be a much larger discussion describing how well the OBM performs in reproducing observed ozone mixing ratios. Without much discussion, I can only assume that there is residual ozone that is explained by the time-dependent source functions derived through OBM calculations, and not by the precursors measured by the precursors measured by GC. How much of the ozone calculated via OBM is explained by the precursors measured by the GC, and how much of the ozone is unexplained? Can the authors show an

analysis (perhaps just a time series) showing ozone explained by the precursors, and ozone explained by the source function? This helps place into context the extent to which the measured VOCs were the primary contributors to ozone observed at the ground site.

Reply: Thanks for the reviewer's comment. Figure S3 and Figure S4 in the supplementary presented the comparisons between the simulated and observed O_3 during O_3 episode days at the JAES site. From the reply of the above comment, it could be concluded that the simulation of OBM could reproduce the observed variations of O_3 during O_3 episode days at the JAES site and the measured VOCs indeed explained the major fraction of observed O_3 levels, with the IOA index of 0.85 between simulation and observation results. The amount of the unexplained O_3 which could be related to the time-dependent source (*i.e.,* the residual O_3) was estimated roughly to be ~17%. However, we agreed with the reviewer that the OBM model could not accurately estimate the contributions of residual O_3 to the increment of O_3 values during daytime, which requires to be studies using a combination of different models and dataset (i.e., the regional air quality model, Lagrangian dispersion model and emission inventory) (Wang et al., 2015; Ding et al., 2013a, b; Jiang et al., 2010).

The detailed discussion on the performance of model simulation on O_3 formation has been provided in Lines 209-266, Pages 7-9 in the revised manuscript.

Finally, the authors also need to provide more details about the OBM itself. The only description of how the model was tailored the Nanjing observations is provided at lines 135-140. What meteorological conditions were used? If this observation-based, I assume that dilution by PBL expansion and wind speed are lumped into the source functions, but what about incident solar radiation? How do the authors calculate photolysis frequencies? Did the authors use a model, such as TUV, or was there a solar spectrum measurement? Can the author provide a JNO2 frequency to orient the readers? The authors constrain CO, NOx, SO2, and O3. How were these species measured, what instrumentation, and how was this instrumentation calibrated? Finally, when were the O3 episodes? A time series showing ozone over the course of the campaign would be useful?

Reply: Thanks for the reviewer's comment. In this study, the meteorological conditions, including the temperature, relative humidity and pressure were incorporated into the model. These parameters, together with wind speed and direction were monitored by a weather station (Vantage Pro TM & Vantage Pro 2 plus TM Weather Stations, Davis Instruments). In the model, the height of the boundary layer was configured to increase gradually from ~300 m in the morning to ~1500 m in the afternoon and then collapsed back to 300 m at night based on the radiosonde and reanalysis data in China (Guo et al., 2016). On the other hand, as neither the photolysis of O_3 ($J(O^1D)$) nor that of NO_2 ($J(NO_2)$) was measured in this study, the photolysis frequencies, including $j(O^1D)$, $j(NO_2)$ and photolysis rates of other species were calculated using the photon flux determined from the Tropospheric Ultraviolet and Visible Radiation model (TUV, version 5.3, http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/, access date: 03 Jan 2020) based on the actual conditions, such as solar radiation, location and time period of the field campaign in Nanjing. The parameterization for the scheme of the TUV (v5.3) module can be found in the code of MCM (http://mcm.leeds.ac.uk/MCMv3.3.1/home.htt, access date: 07 Jan 2010). Additional information on the model calculation and performance has been reported in the previous studies (Pinho et al., 2009; Lam et al., 2013; Shao et al., 2016; Wang et al., 2017). Figure S1 in the supplementary presented the mean diurnal pattern of $J(NO_2)$ simulated by the OBM model using TUV scheme. A typical solar-driven diurnal cycle with the maximum value ($\sim 11.1 \times 10^{-3}$ s^{-1}) at noon (1100-1200 LT) were observed in the photolysis of $J(NO_2)$, which was consistent with those observed and modelled in China (Wang et al., 2019; Li et al., 2011), suggesting that the simulated photolysis frequencies using the TUV scheme in the model was appropriate in the present study.

The incorporation of meteorological conditions into the OBM-MCM model, the configuration of planetary boundary layer and the calculation of photolysis frequencies of different species have been provided as above in the revised manuscript. For details, please refer to Lines 190-205, Pages 6-7 in the revised manuscript.

Furthermore, the information for the measurement of trace gases, including O_3, NO_x,

CO and SO_2 was provided as follows:

"*On the other hand, trace gases including CO, NO-NO_2-NO_x, SO_2, and O_3 were measured at 1-min resolution using the commercial instruments of TEI 48i, 42i, 43i and 49i (Thermo Electron Corporation). All these instruments were zero checked daily, span calibrated weekly and multi-point calibrated monthly. Furthermore, meteorological conditions, including the temperature, relative humidity, pressure, wind speed and direction were monitored at 1-min resolution by a weather station (Vantage Pro TM & Vantage Pro 2 plus TM Weather Stations, Davis Instruments).*"

For details, please refer to Lines 133-138, Page 5 in the revised manuscript.

On the other hand, according to the comment, Figure S7 in the supplementary presented the time series of air pollutants for the whole sampling period. In this study, total 88 O_3 episode days (identified as hourly maximum O_3 concentrations > 80 ppbv per day) were selected for further analysis.

Reference

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Other comments

Line 112: PMF can be conducted using many tools. Is this the US EPA model, SoFi, another model, or one that was developed by Yuan et al. or Ling et al.? This should be noted here, with a relevant reference if necessary.

Reply: Thanks for pointing this out. The US EPA PMF model was used in this study. To verify it, the sentence has been revised as follows:

"*In this study, the US EPA PMF (version 4.1) model, which has been widely used to conduct source apportionment of VOCs (He et al., 2019 and references therein; Mo et al., 2017; Zhang et al., 2013), was applied to the observed VOC data to identify potential VOC sources.*"

For details, please refer to Line 140, Page 5 in the revised manuscript.

Line 120: Shao et al. discuss VOC reactivity through analysis of maximum incremental reactivity (MIR) and by calculating propylene-equivalent concentration. Which method are you referring to?

Reply: Thanks for pointing this out. To clarify the method used to investigate total reactivity of NMHCs, the following sentence has been revised as follows:

"…… *of the total measured VOCs through the analysis of maximum incremental reactivity (MIR) (Shao et al., 2009a).*"

For details, please refer to Lines 149-150, Page 5 in the revised manuscript.

Line 130: please provide references for the MCM (see the following website for appropriate references depending on the sub mechanisms used: http://mcm.leeds.ac.uk/MCMv3.2/citation.htt).

Reply: Thanks for the reviewer's comment. References for MCM mechanism have been added as follows:

"*In this study, we applied the observation-based model (OBM) coupled with the MCM (version 3.2) (http://mcm.leeds.ac.uk/MCMv3.2/citation.htt, Lyu et al., 2016; Ho et al.,*

2019)…"

For details, please refer to Lines 181-182, Page 6 in the revised manuscript.

Also, is there a reason that v 3.2 was used, rather than 3.3.1? v3.3.1 has updates to the isoprene mechanism that may (or may not) be relevant here.

Reply: Thank for the reviewer's comment. Compared with version 3.2, MCM version 3.3.1 have the following updates: 1) The updates of HO_x recycling which has a collectively significant impact on OH radical regeneration at lower NO_x levels. 2) The updates of NO_x recycling which include the formation of species that have been reported to play a role in SOA-formation mechanisms, including epoxydiols (initially implemented in MCM v3.2), hydroxymethyl-methyl-a-lactone (HMML) and methacrylic acid epoxide (MAE). These above updates may not be relevant to the present study as the levels of NO_x at the JAES site were not low, with the average mixing ratios of 25 ± 1 (mean ± 95% confidence interval) ppbv in 2016. Furthermore, the present study only focused on the roles of VOCs on O_3 formation through gas-phase mechanisms which may not be influenced by the NO_x recycling updates for SOA formation. However, we did try our best to incorporate the version 3.3.1 MCM into our photochemical box model to evaluate the roles of NMHCs on SOA formation, which is still under construction (Ling et al., "Formation and sink of glyoxal and methylglyoxal in a polluted subtropical environment: observation-based photochemical analysis and impact evaluation", unpublished manuscript).

Line 164: By TVOC, you mean the sum of measured VOCs?

Reply: Yes. It has been revised as follows:

"*The annual average total VOC (TVOC, sum of the measured VOCs)….*"

For details, please refer to Line 292, Page 9 in the revised manuscript.

Line 172: Is this reversed? The first number (referring to weekdays) is lower than the second (referring to weekends).

Reply: Sorry for the mistake. It has been revised accordingly. For details, please refer

to Lines 299-300, Page 10 in the revised manuscript.

Table 1: You only give an average and standard deviation - no mixing ratio ranges are shown. I recommend removing "range".

Reply: Thanks for the reviewer's comment. The "range" has been removed accordingly. For details, please refer to Table 1 in the revised manuscript.

Line 194: Continuous VOC measurements have been available much longer than this in other countries. I would recommend changing this wording to say "online VOC measurements have been available for multiple decades"

Reply: Thanks for the suggestion. The sentence has been revised as "…online VOC measurements have been available for multiple decades…"

For details, please refer to Lines 320-321, Page 11 in the revised manuscript.

Fig.2 This is a nice benchmark of the Nanjing measurements with other cities during a period when developed countries were still reducing mobile emissions (mid 1990s – early 2000s). How does this compare with measurements conducted in developed countries today? It would be nice to see how the mixture in Nanjing compared to London or Los Angeles today, and would also highlight the gap that could be achieved with further VOC reductions.

Reply: Thanks a lot for the reviewer's positive comment. In this study, to highlight the variations of VOCs in different regions, comparison of annual average concentrations of ambient VOCs in different cities based on real-time online continuous measurements of at least one year was present in Figure 2. We do try our best to find as many studies focusing on the long-term (at least one-year) variations of VOCs in developed regions/countries as possible. The results presented in Figure 2 were all the data we can get. It was found that the current ambient VOC concentrations in Chinese megacities are generally comparable to the urban VOC levels in developed countries during the year 2000. However, in developed countries, the mixing ratios of VOCs were observed to decrease in the recent decades following the implementation and formulation of VOC

strategies (Warneke et al., 2012). For example, the mixing ratios of VOCs in Los Angeles have decreased significantly from 1960-2002 at an average annual rate of ~7.5%, while the mixing ratios of VOCs in London presented a higher and faster decreased since 1998 when there were higher VOC mixing ratios than those in Los Angeles, confirming that the earlier implementation of VOC reduction strategies in California had clearly led to the earlier improvement of air quality compared to London (Warneke et al., 2012; von Schneidemesser et al., 2010). Chinese megacities are therefore experiencing significnatly 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 VOC levels in Chinese megacities are known to impact ambient ozone and secondary particle pollution, as well as cause adverse impacts on human health. However, as China has a solid foundation for VOCs monitoring and control, numerous strict, appropriate and targeted reduction strategies for VOCs have been/are being formulated and implemented in Chinese megacities (Guo et al., 2017). It is expected these measures could help China to reduce VOC emissions/mixing ratios and improve air quality in the future.

To highlight the reduction of VOCs in developed regions and the gap that could be achieved with further VOC reductions in China, the above discussion has been added in the revised manuscript. For details, please refer to Lines 333-347, Pages 11-12 in the revised manuscript.

Reference

Guo, H., Ling, Z.H., Cheng, H.R., Simpson, I.J., Lyu, X.P., Wang, X.M., Shao, M., Lu, H.X., Ayoko, G., Zhang, Y.L., Saunders, S.M., Lam, S.H.M., Wang, J.L., Blake, D.R., 2017. Science of the Total Environment 574, 1021-1043.

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Warneke, C., de Gouw, J.A., Holloway, J.S., Peischl, J., Ryerson, T.B., Atlas, E., Blake, D., Trainer, M., Parrish, D.D., 2012. Multiyear trends in volatile organic compounds in Los Angeles, California: Five decades of decreasing emissions. Journal of Geophysical Research 117, D00V17, doi: 10.1029/2012JD017899.

Lines 227-228: Can the authors briefly summarize the conclusions from Wang et al., 2013? Was it due to changes in prevailing winds, or simply due to build up of pollutants during strong inversions?

Reply: Thanks for the reviewer's comment. In Shanghai, relative high levels of VOCs were observed from October to January of the following year and from June to July based on the two-year measurement conducted from 2009 to 2010 (Wang et al., 2013). The inversion layer, the effect of cold front or uniform pressure in winter resulted in high levels of VOCs from October to January of the following year, while the frontal inverted trough or frequently observed stagnant high pressure system with southwest flow that could lead to poor diffusion were unfavorable meteorological conditions for high VOC levels from June to July. In addition, air masses transported from upwind chemical and petrochemical industrial factories located in the southwest and south of the monitoring site was another factor for the high VOC levels in summer (*i.e.,* June and July) and winter.

The above brief summary for the monthly variations of VOC levels in Shanghai have been provided in the revised manuscript. For details, please refer to Lines 363-370, Pages 12-13 in the revised manuscript.

Line 280-281: As the authors note, these differences result, in part, due to the proximity of the different sampling campaigns. However, I think it's also good to note why these differences are important. How much of the population resides in the sampled region? Is the mix measured in a more residential area more important for human exposure? This is certainly a nice motivation to look at the spatial VOC distributions in Nanjing in the future.

Reply: Thanks for the comment. The sampling site (i.e., the JAES site) was located at a more residential and urban area compared to other sites listed in An et al. (2014) and Xia et al. (2014). There are more than 0.22 million people living in the areas surrounding the sampled site (within 3 km of the observation site) which composed of residential communities, schools, government agencies, and business centers.

The above description on the sampling surrounding was added in the Lines 456- 460,

Page 16 in the revised manuscript.

Line 319: Do you mean that you averaged the PMF solutions during the ozone episodes and non-episode days to look at differences?

Reply: Yes. To make it clearer, we have revised as follows:

"*.... we extracted and averaged the contributions of the different sources on these O_3 episode days from the PMF model...*"

For details, please refer to Lines 509-510, Page 17 in the revised manuscript.

Figure 6. The isopleth description is somewhat confusing-is this % change in NOx and VOCs, or % of base-case VOCs.

Reply: Sorry for the mistake and confusion it caused. The horizontal and vertical axes in Figure 6 correspond to the percentage of base-case VOCs and NO_x. It has been revised accordingly in the caption of Figure 6.

Section 3.5. Without more work to convince the reader that the ozone isopleth is reasonable, I believe these statements would need to be amended. First, the authors haven't shown that the ozone precursors measured account for the majority of the ozone modeled in the OBM. Second, the recommendation to prioritize VOC reductions (line 381) is very likely to matter on a local level (as alluded to by the authors), but what about ozone formation on regional scales? In other countries, downwind of major cities, ozone formation transitions to NO_x-sensitive due to the abundance of biogenic sources that can react alongside NOx (e.g. Trainer et al., 1987). I think this should be discussed as well, since NOx reductions matter and are important in the long run.

Reply: We highly appreciated for the reviewer's comment. As discussed previously, the simulation of OBM model could reproduce the observed variations of O_3 and the measured O_3 precursor indeed contributed a major fraction for the model O_3 from OBM and the observed O_3 mixing ratios. On the other hand, we agreed with the reviewer that the results in the present study were based on the local measurement conducted at the urban site of Nanjing city, which likely presented a local perspective. The

recommendation to prioritize VOC reductions was likely matter to the urban area where O_3 formation was VOC-limited. However, O_3 pollution is a regional cross-boundary environmental issue rather than a local pollution problem. Apart from VOCs, NO_x was another important precursor for O_3 formation with its dual roles in O_3 production (enhancing O_3 formation in non NO_x-saturated environment and titrating O_3 in NO_x-saturated environment). In other areas (i.e., the rural environment and/or the downwind areas of urban center in the same region) where the concentrations of NO_x are low and/or there is a non NO_x-saturated environment, the situation may be different and controlling VOCs should be conducted cautiously (Ou, et al., 2016; Yuan et al., 2013; Zheng et al., 2010). Therefore, from a regional perspective, the benefits of VOCs control measures could be further evaluated with those of NO_x (i.e., the appropriate ratios of VOC/NO_x for the reduction of O_3 pollution) as well as the associated O_3-VOCs-NO_x sensitivity. Therefore, one important concern for the policy formulation and implementation system is whether controlling VOCs and NO_x individually or controlling both VOCs and NO_x is more effective and appropriate for alleviating O_3 pollution. It is 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. To provide more accurate discussion on the controlling VOCs and NO_x in a regional/local perspective, the following text has been added:

"*Last but not the least, though the present study suggested that reducing VOC emissions could be more effective in controlling O_3 pollution in the urban area of Nanjing where photochemical O_3 formation was VOC-limited, the results were based on local measurements, which likely presented a local perspective. However, O_3 pollution is a regional cross-boundary environmental issue rather than a local pollution problem. Apart from VOCs, NO_x was another important precursor for O_3 formation with its dual roles in O_3 production (enhancing O_3 formation in non NO_x-saturated environment and titrating O_3 in NO_x-saturated environment). In other areas (i.e., the rural environment and/or the downwind areas of urban center in the same region) where the concentrations of NO_x are low and/or there is a non NO_x-saturated environment, the*

situation may be different and controlling VOCs should be conducted cautiously (Ou, et al., 2016; Yuan et al., 2013; Zheng et al., 2010). Therefore, from a regional perspective, the benefits of VOCs control measures could be further evaluated with those of NO_x (i.e., the appropriate ratios of VOC/NO_x for the reduction of O_3 pollution) as well as the associated O_3-VOCs-NO_x sensitivity. Therefore, one important concern for the policy formulation and implementation system is whether controlling VOCs and NO_x individually or controlling both VOCs and NO_x is more effective and appropriate for alleviating O_3 pollution. It is 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."

For details, please refer to Lines 654-669, Page 23 in the revised manuscript.

Minor Comments

Line 19: It would be good to note that the measurements at JAES were conducted using GC.

Reply: Thanks for the reviewer's suggestion. To highlight we use GC for the measurements, it has been revised as:

"*we conducted a one-year sampling exercise using a thermal desorption-GC (gas chromatography) system …..*"

For details, please refer to Lines 18-19, Page 1 in the revised manuscript.

Lines 23-24: Awkward phrasing, recommend saying "We identified VOC sources using positive matrix factorization and assessed their contributions to photochemical O3 formation using an observation-based model employing the MCM".

Reply: Thanks for the comment. The sentence has been revised accordingly. For details, please refer to Lines 23-25, Page 1 in the revised manuscript.

Line 30: "control on" seems strong, given that other factors (e.g. meteorology) play a very important role. May suggest using "precursor to"

Reply: Thanks for the suggestion. We have revised it accordingly. For details, please

refer to Line 30, Page 1 in the revised manuscript.

Line 32-33: Do you mean that the contribution of biogenic emissions to O3 was significantly lower than anthropogenic emissions? It would be useful to make this comparison.

Reply: Yes, by considering both the reactivity and abundance of VOC species, the contribution of biogenic emissions to O_3 pollution was significantly lower than anthropogenic emissions. The text has been revised as follows:

"….. *the contribution of biogenic emissions to O_3 pollution was significantly reduced and lower than vehicular and industrial emissions.*"

For details, please refer to Lines 33-34, Page 1 in the revised manuscript.

Lines 45-48: The word "associated" suggests that rapid economic growth occurred because of increases in pollution. Would recommend replacing associated with "Rapid economic growth has led to ..."

Reply: Thanks for the suggestion. The text has been revised accordingly. Please refer to Lines 46-47, Page 2 in the revised manuscript.

Line 56: "VOCs" should be singular, since it is used as an adjective here. Other instances of this are found sparsely throughout the text.

Reply: Thanks for pointing this out. It has been revised accordingly in the text. Furthermore, other instances have been double-checked and corrected.

Line 62: What do you mean by "industrial structure"? Does you mean that there is a high presence of industry in Ningbo?

Reply: Yes. Ningbo is a coastal city located on the southern wing of the Yangtze River Delta with a high presence of petrochemical industry. Since petrochemical industry is the leading industry in Ningbo, the results of source apportionment show that petrochemical industry is the main source of VOCs in Ningbo (Mo et al., 2015, 2016). The description for industries in Ningbo has been added as followed:

"……*which is a coastal city located on the southern wing of the Yangtze River Delta with petrochemical industry as its lead industry (Mo et al., 2015, 2016).*"

For details, please refer to Lines 63-64, Page 2 in the revised manuscript.

Line 76: You could clarify here that you employ the entire MCM (v 3.2).

Reply: Thanks for pointing this out. It has been revised in the manuscript accordingly (Line 79, Page 3)

Line 78-79: Summarized, proposed, and assessed should be present tense here, since you are recommending these in the present manuscript.

Reply: Yes. It has been revised accordingly (Lines 81-82, Page 3).

Line 100: When you say "the sample was enriched after 600 mL of air sample" do you mean "600 mL of air was sampled"? If so, the latter phrasing may be more clear.

Reply: Thanks a lot for the comment. To clarify the sample collection, the text have been revised as follows:

"*The sampling flow was 15 mL/min. After 600 mL of air was sampled, the cold trap was heated to resolve the compounds adsorbed on to it.*"

For details, please refer to Lines 119-120, Page 4 in the revised manuscript.

Line 101: What is the "Dean's Switch" technology?

Reply: Thanks for the comment. Dean's Switch technology is the technology that transfers the effluent from one column to another column with a different stationary phase. By this technology, all co-eluting impurities in the target analyte and the transferred peak are completely eluted.

To introduce this technology, the following description was added:

"……*By applying the Dean's Switch technology whereby the technology that transfers the effluent from one column to another column with a different stationary phase,*……"

For details, please refer to Lines 120-121, Page 4 in revised manuscript.

Line 107: Was this a custom calibration standard, or a commercially available standard?

If commercially available, it would be good to quote the manufacturer. If prepared in-house, are there uncertainties in the VOC mixture?

Reply: Thanks for pointing this out. The VOC standard was purchased commercially. The following description was added:

"*Seven analyses were performed repeatedly to test the precision of the 56 species. Calibrant concentrations in the gas standard mixture (56 C_2-C_{12} NMHCs, Linde Spectra Environment Gases, Inc, USA) ranged from 20 to 49 ppbC.*"

For details, please refer to Lines 128-129, Page 4 in the revised manuscript.

Line 245: "Identified" is a confusing word choice, since you identified the sources, not the model! I would recommend changing to "Five VOC sources were resolved by PMF".

Reply: Thanks for the reviewer's recommendation. It has been revised as suggested in Line 388, Page 13.

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

Qiuyue Zhao[1,2], Jun Bi[1*], Qian Liu[2], Zhenghao Ling[3*], Guofeng Shen[4], Feng Chen[2], Yuezhen Qiao[2], Chunyan Li[2], Zongwei Ma[1]

[1]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, China
[2]Jiangsu Key Laboratory of Environmental Engineering, Jiangsu Academy of Environmental Sciences, Nanjing 210036, China
[3]School of Atmospheric Sciences, Sun Yat-sen University, Guangzhou 510275, China
[4]College of Urban and Environmental Sciences, Peking University, Beijing 100871, China
Correspondence to: Jun Bi (jbi@nju.edu.cn) and Zhenhao Ling (lingzhh3@mail.sysu.edu.cn)

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 using a thermal desorption-GC (gas chromatography) system 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 VOC sources using positive matrix factorization and assessed their contributions to photochemical O_3 formation using an observation-based model employing the master chemical mechanism (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 precursors to 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 in each source, the contribution of biogenic emissions to O_3 pollution was significantly reduced and lower than vehicular and industrial emissions. 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 has led to 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 (Cai et al., 2010; An et al., 2014; Mo et al., 2015; Pan et al., 2015; 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 VOC 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 petrochemical industry was identified as the highest contributor of ambient VOCs due to the unique industrial structure of Ningbo, which is a coastal city located on the southern wing of the Yangtze River Delta with petrochemical industry as its lead industry (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 demonstrate the contribution 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 (MCM) (version 3.2) 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 summarize and propose control strategies to minimize VOCs pollution and assess 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). There is a waterproof layer on the rooftop of the building but there was no guarantee that it was made of asphalt. Furthermore, despite this waterproof layer on the rooftop of the building, the interferences of emissions from this layer were believed to be insignificant because: 1) The waterproof layer was covered by the layer of concrete, which was further covered with a layer of ceramic tile; 2) The building had been built for three years before the sampling campaign was started; 3) It was documented that the VOC emitted from asphalt mainly included benzene, toluene, ethylbenzene and xylene (Gardiner and Lange, 2005). However, the levels of benzene, toluene, ethylbenzene, m/p-xylene and o-xylene were lower than those observed in other urban, industrial and rural environments in different regions (section 3.1, Zhang et al., 2012; An et al., 2014 and 2015; Mo et al., 2015, 2017; He et al., 2019). 4) The sampling inlet was about 2-3 m above the rooftop of the building. It should be noted that there is a waterproof layer on the rooftop of the building. However, it is not sure that the waterproof layer was made of asphalt. Furthermore, though there is a waterproof layer on the rooftop of the building, the interferences of emissions from the layer were believed to be insignificant because: 1) The waterproof layer was covered by the layer of concrete, which was further covered with a layer of ceramic tile; 2) The building has been built for at least three years when the sampling campaign was started; 3) It was documented that the VOC emitted from asphalt mainly included benzene, toluene, ethylbenzene and xylene (Gardiner and Lange, 2005). However, the levels of benzene, toluene, ethylbenzene, *m/p*-xylene and o-xylene were lower than those observed in other urban and industrial and rural environments in different regions (Zhang et al., 2012; An et al., 2014 and 2015; Mo et al., 2015, 2017; He et al., 2019) (details in section 3.1). 4) The sampling inlet were about 2-3 m

above the rooftop of the building. 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 (Figure 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.

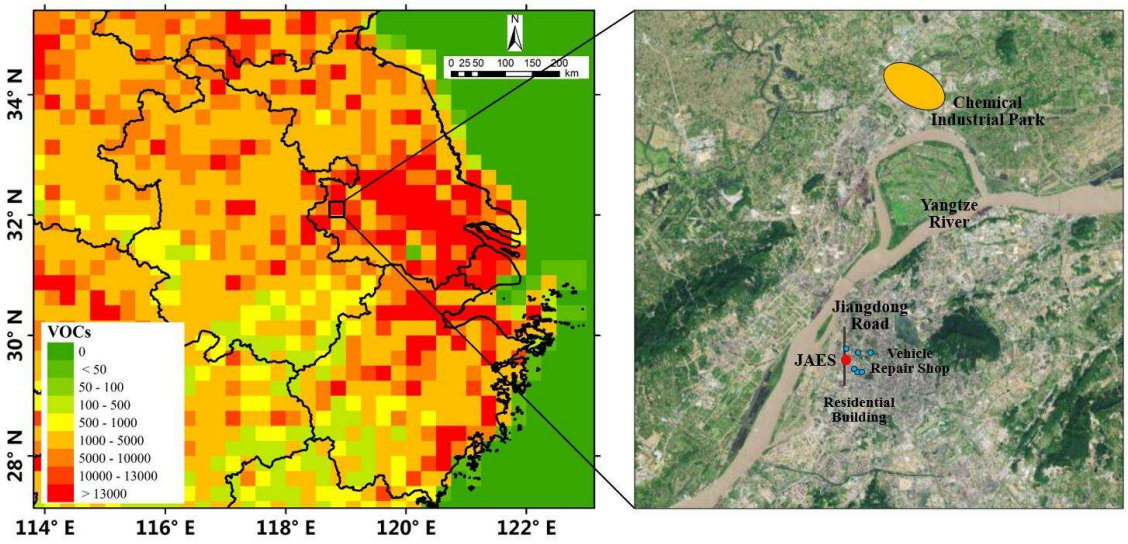

Figure 1. (a) Maps of the study location showing VOCs emission at a resolution of 0.25 degrees (MG/a) (The data were from MEIC emission inventory (www.meicmodel.org, last access date:15 September 2019). (b) The location of the JAES sampling site is indicated by a red circle (The base map was from © Baidu 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 (gas chromatography) 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. After 600 mL of air was sampled, the cold trap was heated to resolve the compounds adsorbed on to it. By applying the Dean's Switch technology whereby the technology that transfers the effluent from one column to another column with a different stationary phase, 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 analyses were performed repeatedly to test the precision of the 56 species. Calibrant concentrations in the gas standard mixture (56 C_2-C_{12} NMHCs, Linde Spectra Environment Gases, Inc, USA) ranged from 20 to 49 ppbC. The relative standard deviations of most of the 56 species were <5%,

representing an error of <0.5 ppb.

On the other hand, trace gases including CO, NO-NO_2-NO_x, SO_2, and O_3 were measured at 1-min resolution using the commercial instruments of TEI 48i, 42i, 43i and 49i (Thermo Electron Corporation). All these instruments were zero checked daily, span calibrated weekly and multi-point calibrated monthly. Furthermore, meteorological conditions, including the temperature, relative humidity, pressure, wind speed and direction were monitored at 1-min resolution by a weather station (Vantage Pro TM & Vantage Pro 2 plus TM Weather Stations, Davis Instruments).

2.2. The PMF model for VOC source identification

In this study, the US EPA PMF (version 4.1) model, which has been widely used to conduct source apportionment of VOCs (Zhang et al., 2013; Mo et al., 2017; He et al., 2019 and references therein), 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 through the analysis of maximum incremental reactivity (MIR) (Shao et al., 2009a). 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 using a variety of factor numbers, 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 previous studies involving PMF/other receptor model simulations (i.e., HKEPD, 2015; Wang et al., 2014; An et al., 2014; Liu et al., 2008a). For example, different solution with different factor numbers was explored and the source apportionment results from a five-factor resolution that could sufficiently explain the observed levels of VOCs were selected (details in Section 3.3). Compared with five-factor solution, the four-factor solution derived two profiles that attributable to gasoline and diesel vehicular exhaust, while most of the aromatic species in these sources and certain amounts of C_3-C_4 species from fuel evaporation were categorized under industrial emission. On the other hand, the six-factor solution has split a factor with high presence of ethyne and certain amounts of ethane (30% in species total), C_3 species and benzene (~20% in species total), while some alkenes (18-80% in species total) were incorporated into fuel evaporation. Furthermore, the performance of the five-factor solution was evaluated using various checks and sensitivity tests. Suitable correlations between the observed concentrations and those of each species predicted by the model were observed, with the correlation coefficients (R^2) ranging from 0.60 - 0.91, indicating

that the solution adequately reproduced the observed variations of each species. All the scale residuals were within ± 3σ with normal distributions for all species (Baudic et al., 2016). Moreover, different numbers of start seeds were tested during the simulation and no-multiple solutions were found. The ratio of Q(robust)/Q(true) obtained was ~0.93, close to 1 as suggested by previous studies and the user guide manual (Paatero, 2000; Lau et al., 2010; Ling et al., 2016). In addition, the results from bootstrapping analysis for the five-factor solution with bootstrap random seed found that all the factors were mapped to a basic factor in all the 20 bootstrap runs, while the uncertainties of each species from bootstrapping analysis were within the range of 1~20%. In this study, different F_{peak} values ranging from -5 to 5 was tested in the 5-factor solution for a more realistic profile (Lau et al., 2010; Baudic et al., 2016). The profiles with the nonzero F_{peak} values were consistent with those with zero F_{peak} value, reflecting that there was little rotation for the selected solution, confirming that the profiles were reasonably explained by the five-factor solution (Baudic et al., 2016). The results of F_{peak} value = 0.5 (the base run) was selected for analysis in this study. Overall, the above features demonstrated that the five-factor solution from PMF could provide reasonable and stable apportionment results for the observed VOCs at the JAES site.

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) (http://mcm.leeds.ac.uk/MCMv3.2/citation.htt, Lyu et al., 2016; He et al., 2019), 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., 2014a,b,c; 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 (i.e., temperature, relative humidity, pressure and heights of boundary layer) on 88 O_3 episode days (identified as hourly maximum O_3 concentrations > 80 ppbv per day) were used to constrain the model. In the model, the height of the boundary layer was configured to increase gradually from ~300 m in the morning to ~1500 m in the afternoon and then collapsed back to 300 m at night based on the radiosonde and reanalysis data in China (Guo et al., 2016). On the other hand, as neither the photolysis of O_3 ($J(O^1D)$) nor that of NO_2 ($J(NO_2)$) was measured in this study, the photolysis frequencies, including $j(O^1D)$, $j(NO_2)$ and photolysis rates of other species were calculated using the photon flux determined from the Tropospheric Ultraviolet and Visible Radiation model (TUV, version 5.3, http://cprm.acom.ucar.edu/Models/TUV/Interactive_TUV/, access date: 03 Jan 2020) based on the actual conditions, such as solar radiation, location and time period of the field campaign in Nanjing. The parameterization for the scheme of the TUV (v5.3) module can be found in the code of MCM (http://mcm.leeds.ac.uk/MCMv3.3.1/home.htt, access date: 07 Jan 2010). Additional information on the model calculation and performance has been reported in the previous studies (Pinho et al., 2009; Lam et al., 2013; Shao et al., 2016; Wang et al., 2017). Figure S1 in the supplementary presented the mean diurnal pattern of $J(NO_2)$

simulated by the OBM model using TUV scheme. A typical solar-driven diurnal cycle with the maximum value (~11.1 × 10^{-3} s^{-1}) at noon (1100-1200 LT) were observed in the photolysis of $J(NO_2)$, which was consistent with those observed and modelled in China (Li et al., 2011; Wang et al., 2019), suggesting that the simulated photolysis frequencies using the TUV scheme in the model was appropriate in the present study. 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).

As the O_3 simulated by the OBM was derived based on the observed mixing ratios of precursors and local meteorology, it is more appropriate to refer the simulation of O_3 by the OBM as local produced O_3, though the observed mixing ratios of precursors could be both influenced by local emissions and those transported from upwind areas (Liu et al., 2019). Therefore, before using the isopleth calculation, it is necessary to investigate whether locally produced O_3 from OBM could make a significant portion to the observed O_3 at the JAES site. The investigation on the wind parameters found that the average wind speed was ~1.8 m/s on O_3 episode days, with about ~51% of most wind speed data being $\leq$ 2 m/s (see Figure S2 in the supplementary), suggesting that regional transport may not have a significant influence on the levels of O_3 and its precursors on episode days at the JAES site (Shao et al., 2016; Wang et al., 2017).

Figure S3 in the supplementary showed the timeseries for the comparison between local produced O_3 from OBM and the observed O_3 mixing ratios, while Figure S4 in the supplementary presented the comparison between the mean diurnal variations of simulated and observed O_3 mixing ratios for all the O_3 episode days at the JAES site. It was found that the model underestimated or overestimated O_3 on some episode days. The comparison between the mean diurnal variations of simulated and observed O_3 suggested that the model captured the diurnal variations of O_3, and the predicted and observed maximum O_3 values were comparable, though the predicted mixing ratios of O_3 were lower than that observed in the early morning. The above discrepancy between observed and predicted O_3 mixing ratios was mainly due to the failure to consider physical processes (i.e., horizontal and vertical transport) and/or the other O_3 precursors (i.e., carbonyls and other oxygenated VOCs (OVOCs)) (Shao et al., 2009a; Cheng et al., 2010; Liu et al., 2019). However, the simulation indeed provided a reasonable description of the O_3 variations using the observation data. To assess the local photochemically produced O_3 against the measured levels of O_3 during the O_3 episode days, the amount of the locally produced O_3 formed by the photochemistry was compared with the observed O_3 accumulations that were calculated as difference between the peak and early-morning concentrations of O_3. The amount of local photochemically produced O_3 was determined by the net O_3 production rate, which was calculated by the difference between the gross production $G(O_3)$ and destruction rates $D(O_3)$ in the model (Equations 1-3).

$$P(O_3) = G(O_3) - D(O_3) \quad (1)$$

$$G(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum k_{RO_2i+NO}[RO_{2i}][NO] \quad (2)$$

$$D(O_3) = k_{HO_2+O_3}[HO_2][O_3] + k_{OH+O_3}[OH][O_3] + k_{O(^1D)+H_2O}[O(^1D)][H_2O] + k_{OH+NO_2}[OH][NO_2] + k_{alkenes+O_3}[alkenes][O_3] \quad (3)$$

Where the *k* constant values were the rate coefficients for the subscript reaction. The detailed description for the above calculation was provided by Xue et al. (2013, 2014) and Wang et al. (2017). At JAES, the daytime (07:00–19:00 LT) average net O_3 production rate was estimated to be 6.2 ppbv h^{-1}, corresponding to ~74 ppbv O_3 formed from local photochemistry during daytime hours. The amount was coincident with the average increment of O_3 observed from early morning to late afternoon at JAES (~81 ppbv), suggesting that local photochemically produced O_3 significantly contributed to the O_3 increment at JAES. Indeed, the observed minimum O_3 mixing ratios before accumulation which were considered as the residual O_3 levels (or background O_3, the mean value was 20 ppbv) at the sampling site as suggested by the previous studies (Xue et al., 2013, 2014a,b) only accounted for ~20% of the observed maximum O_3 values (the mean value was 102 ppbv) (data not shown). Furthermore, the difference between observed and simulated minimum O_3 mixing ratios which was considered as the fraction of residual O_3 that could not be explained by the OBM model only contributed ~17% of the observed maximum O_3 mixing ratio. The above analysis on the difference between observed and simulated O_3 levels confirmed that local photochemical produced O_3 made a significant fraction to observed O_3 levels at JAES. However, we admitted that the OBM model could not accurately estimate the contributions of residual O_3 to the increment of O_3 values during daytime, which requires to be studies using a combination of different models and dataset (i.e., the regional air quality model, Lagrangian dispersion model and emission inventory) (Jiang et al., 2010; Ding et al., 2013a, b; Wang et al., 2015).

To further evaluate the model performance, the index of agreement (IOA) that was developed to assess the agreement between modelled and observed results was used in this study (Huang et al., 2005; Wang et al., 2013, 2015; Liu et al., 2019). The calculation of IOA was as follows:

$$IOA = 1 - \frac{\sum_{i=1}^{n}(O_i - S_i)^2}{\sum_{i=1}^{n}(|O_i - \overline{O}| + |S_i - \overline{O}|)^2} \quad (4)$$

Where S_i and O_i were the simulated and observed O_3, respectively, while $\overline{O}$ was the mean of observed O_3, and *n* is the number of samples. The IOA values ranged between 0 and 1, and a relatively higher value of IOA indicated relatively greater consistency between simulated results and observation data (Wang et al., 2013, 2015, 2017). In this study, the IOA of O_3 was ~0.85, suggesting consistency of the abundance and variation of O_3 between the observation and simulation, and demonstrating that locally produced O_3 could be explained by the

measured precursors. Overall, the above analysis demonstrated that simulation of OBM could be used to conduct O_3 isopleth calculation and investigate the O_3-precursor relationship (Shao et al., 2016; Lyu et al., 2019; He et al., 2019).

To investigate O_3-precursor relationship, 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. (5), while the average RIR of precursor *X* is calculated as shown in Eq. (6).

$$RIR^S(X) = \frac{\left[P^S_{O_3-NO}(X) - P^S_{O_3-NO}(X-\Delta X)\right]/P^S_{O_3-NO}(X)}{\Delta S(X)/S(X)} \quad (5)$$

$$\overline{RIR} = \frac{\sum_1^N [RIR^S(X) P^S_{O_3-NO}(X)]}{\sum_1^N P^S_{O_3-NO}(X)} \quad (6)$$

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. (7) and Eq. (8), taking into consideration both the reactivity and abundance of VOC species (Ling et al., 2011; Ling and Guo, 2014).

$$RIR\text{-}weighted(X) = \overline{RIR}^X \times conc(X) \quad (7)$$

$$Contribution(X) = \frac{\overline{RIR}^X \times conc(X)}{\sum[\overline{RIR}^X \times conc(X)]} \quad (8)$$

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 VOC observation statistics

Table 1 shows the average concentration and standard deviation of fifty-six VOC species concentrations measured at the JAES site, while Figure S7 in the supplementary presented the time series of all pollution data collected at the JAES site. The annual average total VOC (TVOC, sum of the measured VOCs) 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. The alkenes were found to have higher mixing ratios during weekdays relative to the weekends (3.5 ± 0.2 vs 2.9 ± 0.1 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 mixing ratios 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). 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 for multiple decades. 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 (Huang et al., 2011; Wang et al., 2013). 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 VOC concentrations in Chinese megacities are generally comparable to the urban VOC levels in developed countries during the year 2000. However, in developed countries, the mixing ratios of VOCs were observed to decrease in the recent decades following the implementation and formulation of VOC strategies (Warneke et al., 2012). For example, the mixing ratios of VOCs in Los Angeles have decreased significantly from 1960-2002 at an average annual rate of ~7.5%, while the mixing ratios of VOCs in London presented a higher and faster decreased since 1998 when there were higher VOC mixing ratios than those in Los Angeles, confirming that the earlier implementation of VOC reduction strategies in California had clearly led to the earlier improvement of air quality compared to London (Warneke et al., 2012; von Schneidemesser et al., 2010). Chinese megacities are therefore experiencing significnatly higher ambient VOCs contamination, given the remarkable decrease in VOC emissions in developed countries over the last two decades (Pan et al., 2015; European Environment Agency, 2016; U.S. EPA, 2017;). High VOC levels in Chinese megacities are known to

impact ambient ozone and secondary particle pollution, as well as cause adverse impacts on human health. However, as China has a solid foundation for VOCs monitoring and control, numerous strict, appropriate and targeted reduction strategies for VOCs have been/are being formulated and implemented in Chinese megacities (Guo et al., 2017). It is expected these measures could help China to reduce VOC emissions/mixing ratios and improve air quality in the future.

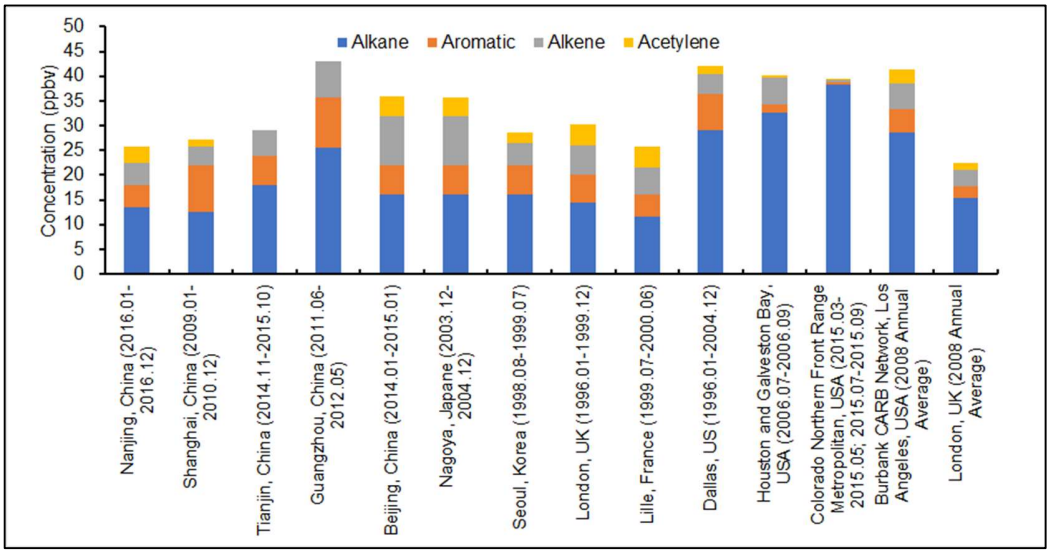

Figure 2. Comparison of annual average concentrations of ambient VOC in different cities based on real-time online continuous measurements of at least one year.

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 (18.5 ± 14.6 ppbv) and autumn (20.1 ± 12.2 ppbv). As shown in Figure S5, 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 VOC variability were also observed. Except for the winter months, similar (and relatively stable) ambient VOC levels in the remaining months were observed for Guangdong (Figure 3). In Shanghai, relative high levels of VOCs were observed from October to January of the following year and from June to July based on the two-year measurement conducted from 2009 to 2010 (Wang et al., 2013). The inversion layer, the effect of cold front or uniform pressure in winter resulted in high levels of VOCs from October to January of the following year, while the frontal inverted trough or frequently observed stagnant high pressure system with southwest flow that could lead to poor diffusion were

unfavorable meteorological conditions for high VOC levels from June to July. In addition, air masses transported from upwind chemical and petrochemical industrial factories located in the southwest and south of the monitoring site was another factor for the high VOC levels in summer (*i.e.,* June and July) and winter. 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.

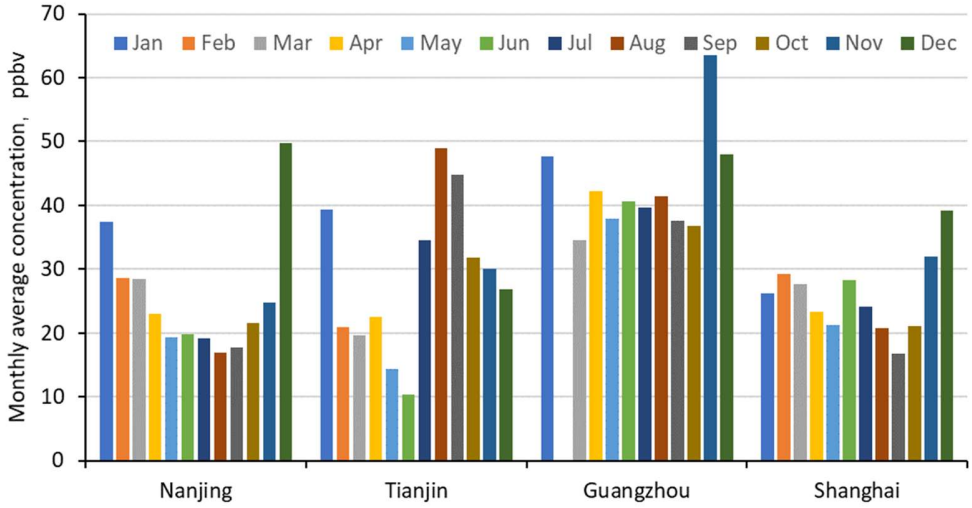

Figure 3. Monthly variability of ambient VOCs at the JAES site and three other Chinese cities, Shanghai (Wang et al., 2013), Guangzhou (Zou et al., 2015), and Tianjin (Liu et al., 2016).

Figure S6 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 VOC 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.

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. Five VOC sources were resolved by PMF, 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 (Lau et al., 2010; Yuan et al., 2012). Source 2 was represented by high proportions of 2-methylpentane, 3-methylpentane, *i*-pentane, and cyclopentane. Pentanes are mainly associated with profiles from gasoline-related emissions (Barletta et al., 2005; Tsai et al., 2006). However, the low contributions of incomplete combustion tracers in this profile suggested that the VOCs were sourced from fuel evaporation. The high presence of pentanes in this profile was consistent with the source profile of gasoline volatilization extracted from principal component analysis/absolute principal component scores (PCA/APCs) based on the observed VOC data collected in an industrial area of Nanjing (An et al., 2014), the source profile of gasoline evaporation from PMF at the suburban site and urban site in Beijing and Hong Kong (Yuan et al., 2009; Lau et al., 2010). Particularly, based on the emission-based measurement, Liu et al. (2008b) conducted source apportionments of VOCs in the Pearl River Delta region by the chemical mass balance (CMB) receptor model, which attributed the source with high loadings of *n*/*i*-pentanes, cyclopentane and 2/3-methylpentane as gasoline evaporation. Therefore, Source 2 here 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; Zhang et al., 2018). Zhang et al. (2018) compared the VOC composition of vehicular emissions from Zhujiang Tunnel in 2014 and 2004 in the Pearl River Delta region with those from other tunnel measurements. C_2-C_4 alkanes and alkenes were found to made the greatest contributions to the loading of VOCs emitted from vehicles in 2014. The higher proportions of *n*/*i*-pentane, *n*-hexane, and methylcyclopentane in Source 3 relative to Source 4 indicated VOCs sourced from gasoline vehicular exhausts (Liu et al., 2008b; Guo et al., 2011b; Zhang et al., 2018). 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 (Ho et al., 2009; Cai et al., 2010; Ou et al., 2015; Liu et al., 2008c). Source 5 was characterized by high concentrations of aromatics. In addition to gasoline vehicle emissions, industrial emission could be another important contributor to ambient aromatic hydrocarbons in the Yangtze River Delta, Pearl River Delta and North China Plain (Yuan et al., 2009; Zhang et al., 2013, 2014; An et al., 2014; Mo et al., 2015, 2017; He et al., 2019). The tunnel studies and emission-based measurement results found that aromatic hydrocarbons from gasoline vehicle exhaust were coherently emitted with pentanes, butenes, *n*-hexane, and cyclopentane, which were more consistent with the profile in source 3 mentioned above (Liu et al., 2008; Ho et al., 2009; Yuan et al., 2009; Zhang et al., 2018). Therefore, the absence of above species in source 5 indicated that this source could be related to industrial emission (Zhang et al., 2014). Particularly, the high presence of toluene, ethylbenzene, xylenes, ethyltoluene and trimethylbenzene was consistent with the emission-base measurement results conducted in paint and printing industries (Yuan et al., 2010) and manufacturing facilities (Zheng et al., 2013). On the other hand, the profile of high presence of aromatic hydrocarbons (C_7-C_9 aromatics) and the certain amount of ethene, was also agree with the profiles measured in the areas dominated by industrial emissions in the Yangtze River Delta region (An et al., 2014; Shao et al., 2016; Mo et al., 2017). For example, An et al. (2014) reported that

toluene, ethylbenzene, xylenes, and trimethylbenzenes could be emitted from different industrial processes, and identified that the factors with high loadings of these species as industrial production, solvent usage and industrial production volatilization sources by PAC/APCS at the industrial area in Nanjing. On the other hand, Mo et al. (2017) identified the factors with high concentrations of C_7-C_9 aromatics and ethene as residential solvent usage, chemical and paint industries and petrochemical industry with the PMF model applied to the data collected in an industrialized coastal city of Yangtze River Delta region. To further identify source 3 and source 5, the ratio of toluene/benzene (T/B, ppbv/ppbv) in each profile was compared with those obtained from emission-based measurements and tunnel study results (Zhang et al., 2018 and references therein). The ratios of T/B were ~8.2 and ~1.2 for sources 5 and 3, respectively, and were consistent with those of "industrial processes and solvent application", and "roadside and tunnel study", respectively (Zhang et al., 2018 and references therein). This further confirmed that source 3 was related to gasoline vehicular exhaust, while source 5 was associated with industrial emission.

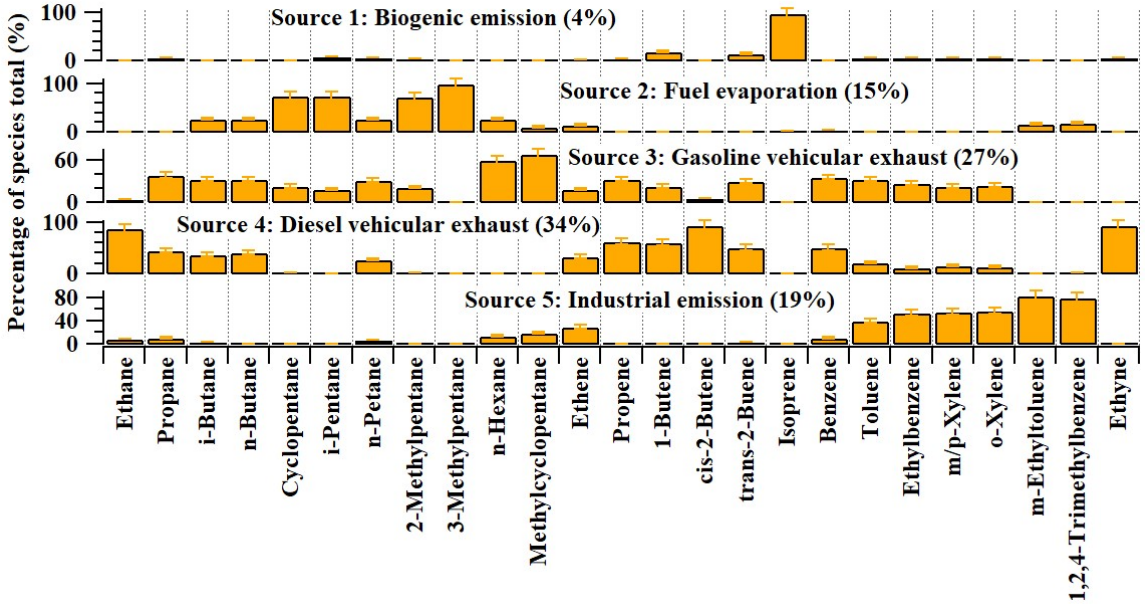

Figure 4. Source profiles of VOCs identified using the PMF model and the relative contributions of the individual VOC species.

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 inconsistent with 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%,

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. For example, the sampling site (i.e., the JAES site) was located at a more residential and urban area compared to other sites listed in An et al. (2014) and Xia et al. (2014). There are more than 0.22 million people living in the areas surrounding the sampled site (within 3 km of the observation site) which composed of residential communities, schools, government agencies, and business centers. 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 (Yuan et al., 2009; Cai et al., 2010; Guo et al., 2011a; Zhang et al., 2013; Wang et al., 2015). 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, an increased mixing height and enhanced photochemical loss (Gillman et al., 2009; Yuan et al., 2009; Wang et al., 2013). A diurnal pattern of fuel evaporation that was similar to that of vehicular emissions. Though the evaporation of fuel is dependent on temperature, the average temperature in the morning and evening (*i.e,* 0800-1000 and 1700-1900 LT, respectively) when peaks of fuel evaporation were found was only about ~1.2 ºC lower than that observed from noon to afternoon (1100-1600 LT), which may not result in much higher fuel evaporation at noon (the difference between maximum and minimum values for fuel evaporation was found to be ~6 μg/m^3). On the other hand, in addition to evaporation from the gas station, fuel could evaporate from hot engines, fuel tanks and the exhaust system when the car is running. Furthermore, the engine remains hot for a period of time after the car is turned off, and gasoline evaporation continues when the car is parked (Technology center, University of Illionois, https://mste.illinois.edu/tcd/ecology/fuelevap.html, access date: 25 December 2019). The similarity of diurnal variations of fuel evaporation to vehicular emissions suggested that the prominent peak in the morning and evening hours were related to the increased vehicles in the traffic rush hour and emissions accumulated in the relatively low boundary layer. Moreover, 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; Leuchner and Rappenglück, 2010).

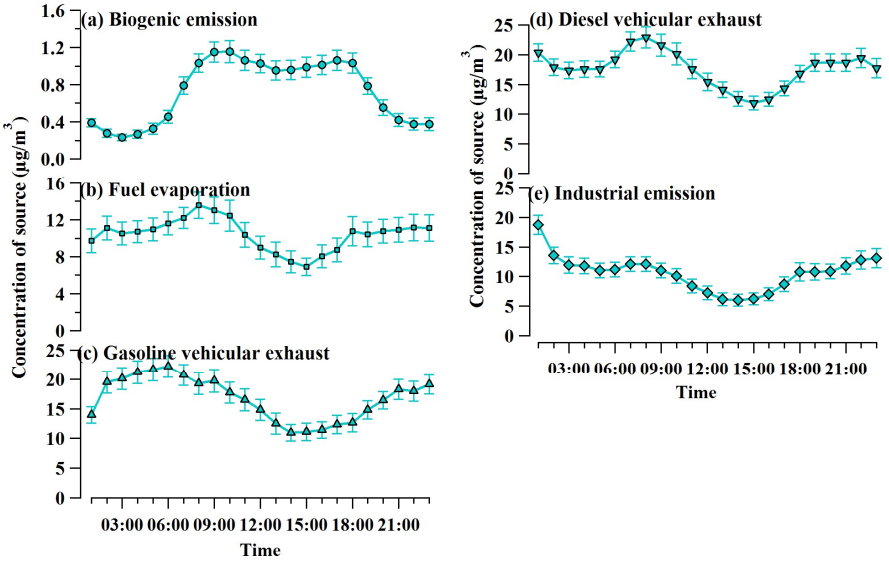

Figure 5. Diurnal patterns in source concentrations of the five identified sources

3.4 Contributions of VOC sources to O_3 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 on these O_3 episode days from the PMF model. It was found that the contributions of gasoline vehicular exhausts had significantly increased during O_3 episode days, with a mean average percentage of 41 ± 5%.

In the atmosphere, the sensitivity of photochemical O_3 formation was distributed into three regimes, including the VOC-limited regime, the NO_x-limited regime and the transitional regime. In the VOCs-limited regime (the relative concentration [NO_x]/[VOC] is high and/or NO_x is saturated), photochemical O_3 formation decreases with the decrease in the concentration of VOCs (resulting from the control of VOC emissions), while in the NO_x-limited regime (high [VOC]/[NO_x] ratio and/or VOC is saturated), any reduction in the NO_x concentration would shortens the O_3 formation chain length and reduces the photochemical O_3 formation (Jenkin and Clemitshaw, 2000). The mean mixing ratios of NO_x and TVOCs during daytime hours (0700-1800 LT, local time) on O_3 episode days were 19.2 ± 1.2 ppbv, respectively, with the mean ratio of VOCs/NO_x as (ppbC/ppbv) ~3.4, suggested that the atmosphere in at the JAES site was NO_x saturated and photochemical O_3 formation located in the VOC-regime (Jenkin and Clemitshaw, 2000). However, it should be noted that using the ratios of VOCs/NO_x to determine the O_3 formation regime could be biased in different environments as different VOC species react at different rates and with different reaction mechanisms, thus inducing the nonlinear dependency of O_3 formation on NO_x and VOCs. 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% of observed mixing ratios of VOCs and NO_x, point A in Figure 6), 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. Furthermore, to accurately evaluate the O_3-precursor relationship, the RIR values from the OBM model, which were frequently used to evaluate the O_3 formation sensitivity based on observation data, were further explored. Positive RIR values were found for the VOCs (see Figure 7a), while negative values were found for NO_x (i.e., -0.25 ± 0.02), further confirming that O_3 formation at the JAES site was VOC-limited (Zhang et al., 2008; Shao et al., 2009b; Cheng et al., 2010). In Figure 6, 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.

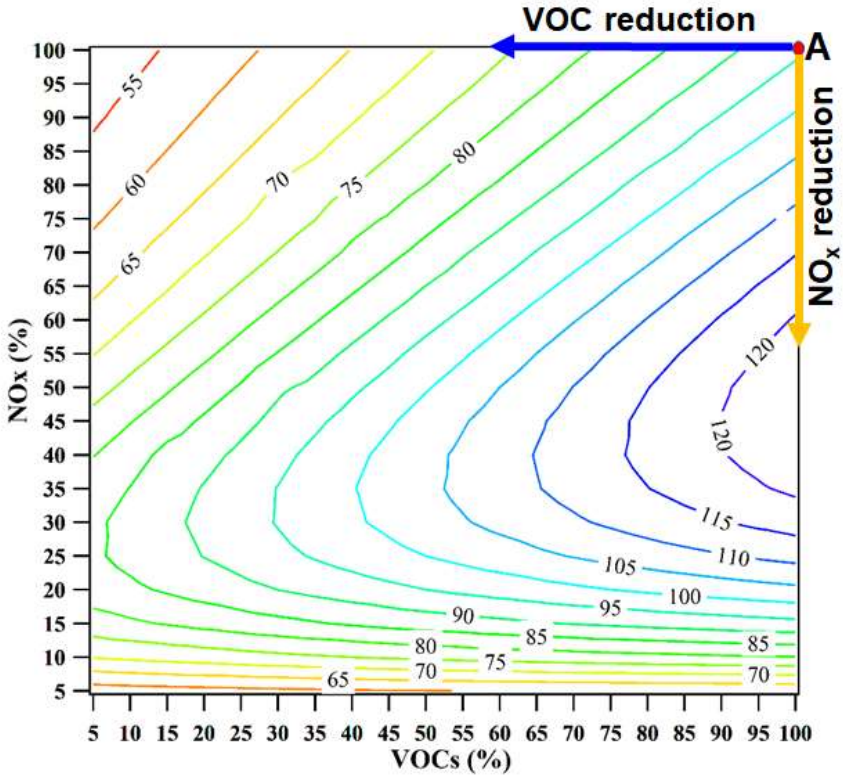

Figure 6. The ozone isopleth in terms of the percentage change of VOCs and NO_x (The horizontal and vertical axes correspond to the percentage of base-case VOCs and NO_x, respectively). The ozone mixing ratios are in ppbv.

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 (Figure 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 (An et al., 2015; Zhang et al., 2018). 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.

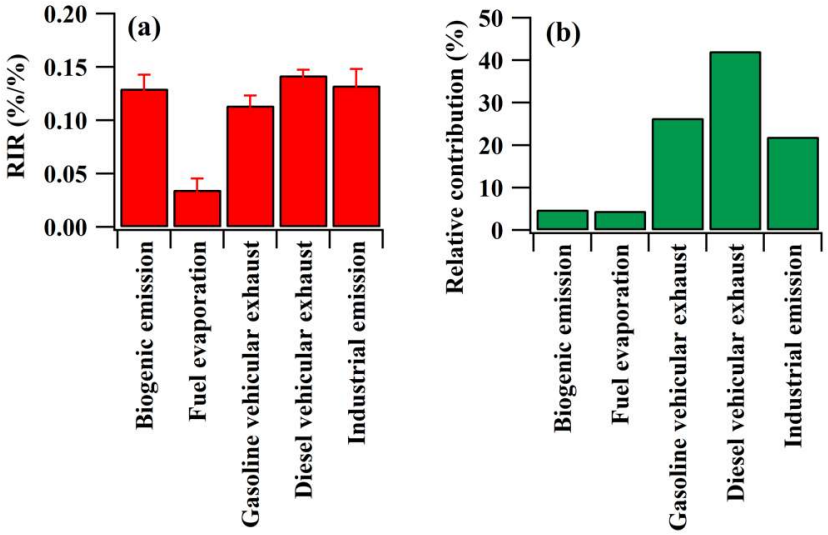

Figure 7a. The average RIR values of VOC sources, and (b) the relative contributions of different VOC sources to photochemical O_3 formation.

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 *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 VOC species can be monitored for effective control of 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 to O_3 formation. This finding further confirms that both VOC reactivity and abundance should be considered for effective control of 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 VOC 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 of O_3 formation.

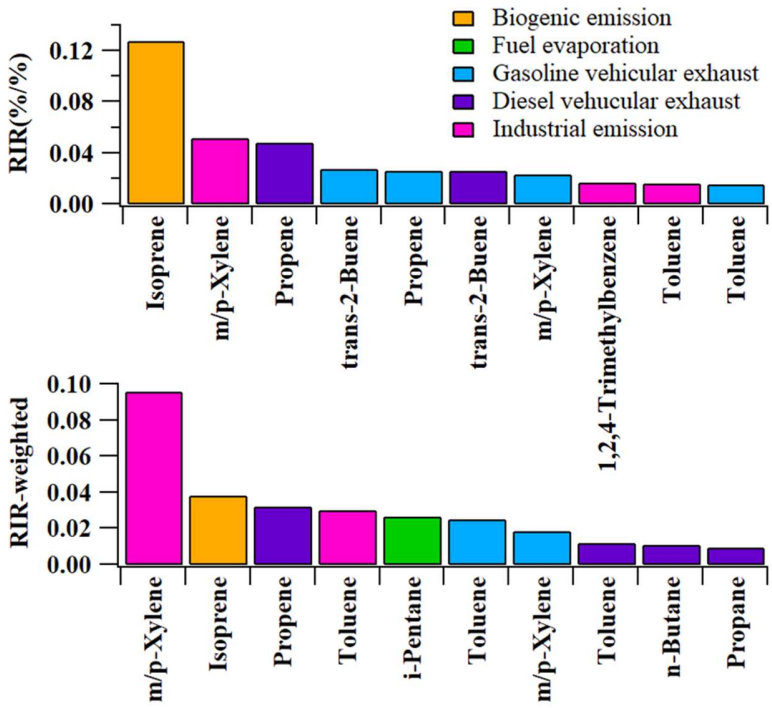

Figure 8. The average RIR values and RIR-weighted values of the top 10 VOC species in the different source categories.

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 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 in urban environments. 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 of controlling 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 VOC 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 regarding 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 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 pertaining to emissions reduction in factories and to control VOC emissions from industrial sources; 7) encouraging the public to live a low-carbon life and supervise and offer 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 as 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 VOC 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. The promotion of intelligent traffic management, implementation of a priority strategy for public transportation, and construction of more efficient traffic systems to promote pedestrian and bicycle use is recommended. Further studies should be conducted to estimate and manage the increasing quantity of vehicles on the road. As of January 1, 2017, regulation stipulate that all new and used vehicles should meet the fifth phase of vehicle emission standards, including vehicle manufacture, sales, registration and importation. For vehicles already in use, an environmental protection examination should be conducted 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 requires 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).

Furthermore, though measures have been adopted to improve standards and control vehicle VOC 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.

Last but not the least, though the present study suggested that reducing VOC emissions could be more effective in controlling O_3 pollution in the urban area of Nanjing where photochemical O_3 formation was VOC-limited, the results were based on local measurements, which likely presented a local perspective. However, O_3 pollution is a regional cross-boundary environmental issue rather than a local pollution problem. Apart from VOCs, NO_x was another important precursor for O_3 formation with its dual roles in O_3 production (enhancing O_3 formation in non NO_x-saturated environment and titrating O_3 in NO_x-saturated environment). In other areas (i.e., the rural environment and/or the downwind areas of urban center in the same region) where the concentrations of NO_x are low and/or there is a non NO_x-saturated environment, the situation may be different and controlling VOCs should be conducted cautiously (Zheng et al., 2010; Yuan et al., 2013; Ou, et al., 2016). Therefore, from a regional perspective, the benefits of VOCs control measures could be further evaluated with those of NO_x (i.e., the appropriate ratios of VOC/NO_x for the reduction of O_3 pollution) as well as the associated O_3-VOCs-NO_x sensitivity. Therefore, one important concern for the policy formulation and implementation system is whether controlling VOCs and NO_x individually or controlling both VOCs and NO_x is more effective and appropriate for alleviating O_3 pollution. It is 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 VOC characteristics at an urban site in Nanjing (the JAES site), Jiangsu province. In total, 56 VOCs including 29 alkanes, 10 alkenes, 16 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 VOC 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 VOC 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, as 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 VOC species. Local governments have strengthened several measures to minimize VOC 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. Furthermore, from a regional perspective, it is suggested that appropriate ratios of VOC/NO_x, their associated sensitivity to O_3 formation and relative benefits/disbenefits of reducing VOCs/NO_x should be investigated and evaluated when control measures of VOCs and NOx were both conducted.

693 **Author Contributions.** Jun Bi, Zhenhao Ling, and Qiuyue Zhao designed the research and carried them out.
694 Zhenhao Ling performed the data simulation. Qiuyue Zhao and Guofeng Shen performed the observation data
695 analysis. Qiuyue Zhao prepared the manuscript with contributions from all co-authors.

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

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