

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 88-96, 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 C₇-C₉ 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 432-456, Page 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,

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 °C 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 $\mu\text{g}/\text{m}^3$). 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 Illinois, <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 506-517, Pages 17-18 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 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.