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 #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* $\pm 3\sigma$ *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 152-178, 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 404-456, Pages 14-15 in the revised manuscript.

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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).

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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 ≤ 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 209-265, 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 511-535, Page 18 in the revised manuscript.

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Wang, X.M., Liu, H., Pang, J.M., Carmichael, G., He, K.B., Fan, Q., Zhong, L.J., Wu, Z.Y., Zhang, J.P., 2013. Reductions in sulfur pollution in the Pearl River Delta region, China: assessing the effectiveness of emission controls. Atmospheric Environment 76, 113-124.

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., Guo, H., Blake, D.R., Tang, J., Zhang, X.C., Saunders, S.M., Wang, W.X., 2013. Sources and photochemistry of volatile organic compounds in the remote atmosphere of western China: results from the Mt. Waliguan Observatory. Atmospheric Chemistry and Physics 13, 8551-8567.

Xue, L.K., Wang, T., Wang, X.F., Blake, D.R., Gao, J., Nie, W., Gao, R., Gao, X.M., Xu, Z., Ding, A.J., et al., 2014. On the use of an explicit chemical mechanism to dissect peroxy acetyl nitrate formation. Environmental Pollution 195, 39-47.

Zhang, Y.H., Su, H., Zhong, L.J., Cheng, Y.F., Zeng, L.M., Wang, X.S., Xiang, Y.R., Wang, J.L., Gao, D.F., Shao, M., Fan, S.J., Liu, S.C., 2008. Regional ozone pollution and observation-based approach for analyzing ozone-precursor relationship during the PRIDE-PRD2004 campaign. Atmospheric Environment 42, 6203-6218.

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 209-265, 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 (~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 (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 189-204, 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 132-137, 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

Guo, J.P., Miao, Y.C., Zhang, Y., Liu, H., Li, Z.Q., Zhang, W.C., He, J., Lou, M.Y., Yan, Y., Bian, L.G., Zhai, P.M., 2016. The climatology of planetary boundary layer height in China derived from radiosonde and reanalysis data. Atmospheric Chemistry and Physics 16, 13309-13319.

Lam, S.H.M., Saunders, S.M., Guo, H., Ling, Z.H., Jiang, F., Wang, X.M., Wang, T.J., 2013. Modelling VOC source impacts on high ozone episode days observed at a mountain summit in

Hong Kong under the influence of mountain-valley breezes. Atmospheric Environment 81, 166-176.

Li, J., Wang, Z.F., Wang, X., Yamaji, K., Takigawa, M., Kanaya, Y., Pochanart, P., Liu, Y., Irie, H., Hu, B., Tanimoto, H., Akimoto, H., 2011. Impacts of aerosols on summertime tropospheric photolysis frequencies and photochemistry over Central Eastern China. Atmospheric Environment 45, 1817-1829.

Pinho, P.G., Lemos, L.T., Pio, C.A., Evtyugina, M.G., Nunes, T.V., Jenkin, M.E., 2009. Detailed chemical analysis of region-scale air pollution in western Portugal using an adapted version of MCM v3.1. Science of the Total Environment 407, 2024-2038.

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.

Wang, W.J., Li, X., Shao, M., Hu, M., Zeng, L.M., Wu, Y.S., Tan, T.Y., 2019. The impact of aerosols on photolysis frequencies and ozone production in Beijing during the 4-year period 2012-2015. Atmospheric Chemistry and Physics 19, 9413-9429.

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.

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 139, 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 148-149, 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 180-181, 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 291, 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 298-299, 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 319-320, 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 332-346, 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.

von Schneidemesser, E., Monks, P.S., Plass-Duelmer, C., 2010. Global comparison of VOC and CO observations in urban areas. Atmospheric Environment 44, 5053-5064.

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 362-369, 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 455- 459, 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 O3 episode days from the PMF model...*"

For details, please refer to Lines 508-509, 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 653-668, 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.