Response to Reviewer

We appreciate the reviewer for the constructive 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.

Zhao et al. represent a revised manuscript describing the VOC measurements and ozone formation in Nanjing, China. I appreciate the authors response to my suggestions of how to improve the PMF solution. The additional details describing how the authors validated the PMF solution and the expanded discussion of PMF factor assignments are much improved.

Reply: Many thanks for the reviewer's positive comments on the improvement of PMF simulation and source apportionment results in the manuscript.

However, I do not believe the authors have demonstrated that the OBM is reasonably capturing local ozone formation; therefore, I don't believe it is justifiable to use the model for ozone isopleth calculations. The authors have presented two new figures to compare the OBM with ozone observations (Figs. S3-S4) and text discussing these results (Lines 220-266). The comparison between the OBM and observed ozone concentrations (Fig. S3) is difficult to see, but in general, it seems that the model over or under predicts ozone by a factor of 2 on any given day. The authors acknowledge a number of shortcomings of the model (not capturing meteorological conditions, not capturing transported ozone, missing precursors, etc. line 227), which may explain may of the disagreements. I do not expect the authors to capture all of the ozone features over the entire sampling period (e.g. at night or during weather events); however, the model should capture daytime ozone production, especially during the ozone episodes defined in Fig. S7. The model disgreements average out to diurnal pattern that appears to be successful (Fig. S4), and the authors use this diurnal pattern to argue that the model is successful at recreating ozone production rates. This discussion is misleading given the results from Fig. S3.

As written, I don't believe the OBM should be included in this paper. Significant work would be needed to improve the OBM (see suggestions below). The measurements and PMF results are useful, and I encourage the authors to focus on these. Furthermore, I believe the authors could still address the importance of VOC precursors in ozone formation by evaluating proxies such as OH reactivity or maximum incremental reactivity (MIR).

Reply: The reviewer's suggestion is highly appreciated. We agreed with the reviewer that the OBM model in this study could not present more accurate description on the O_3 variations at the JAES sites as: 1) The vertical transport and horizontal transport

were no considered in the model; 2) Some parameters, i.e., the variations of boundary layers, which were obtained from the reanalysis results in China ($0.75^{o} \times 0.75^{o}$) with limited daytime hours (Guo et al., 2016), which could not represent the real boundary layers at the JAES site. On the other hand, the cloudiness, which could influence the solar radiation and albedo was not measured in this study. Therefore, there were still uncertainties for the simulation of photolysis rates from TUV based on the sampling time, longitude and latitude of the sampling site, and the default configuration of clouds and albedo, though the photolysis rate from the TUV model in the present study could provide reasonable estimation on the photolysis rates compared with observations in other areas (Wang et al., 2019; Li et al., 2011). 3) Some precursors, i.e., carbonyl compounds, were not measured in the present study. 4) Dry deposition, which was not measured in the present study and was configured as previous studies (Xue et al., 2014; Zhang et al., 2003). Therefore, according to the reviewer's suggestion, we deleted the analysis using the OBM model.

In addition, to evaluate the contributions of VOC sources and species in different sources to O_3 pollution, the O_3 formation potential (OFP) of these sources and species were determined by maximum incremental reactivity (MIR) method. The discussion on the OFP of different VOC sources and species were provided in the revised manuscript as follows:

"As important O_3 precursors, information on the contributions of VOCs sources and related species to O_3 formation is necessary for the formulation and implementation of VOC control measures. To achieve this goal, the Maximum Incremental Reactivity (MIR) method, which evaluates the O_3 formation potential (OFP) on the basis of mass concentrations and maximum incremental reactivities of VOCs of the OH radical, were adopted in the present study (Shao et al., 2009b, 2011; Mo et al., 2017). Figure 6 presented the relative contributions of individual VOC sources and related VOC species from PMF to OFP at the JAES site. Industrial emissions was found to have the largest contribution to OFP at JAES due to the high loadings of aromatic VOC species that have relatively high OH reactivities in this source profile (Atkinson and Arey, 2003),

with the OFP value of ~43 μg/m^3 and the contribution percentage of ~32% to the total OFP of all sources, followed by diesel vehicular exhausts (~36 μg/m^3, ~27%), gasoline vehicular exhausts (~32 μg/m^3, ~24%), fuel evaporation (~13 μg/m^3, ~10%) and biogenic emissions (~9 μg/m^3,~7%) though the MIR value of isoprene was much higher than other species. Similarly, using the same method to evaluate OFP of different VOC sources, Mo et al. (2017) found that industrial emissions (including the emissions of petrochemical industry, chemical and paint industries, solvent usage) and vehicular emissions were the dominant VOC sources for the total OFP in an industrialized coastal city (i.e., Ningbo) in the YRD region. Therefore, our results further demonstrated the need to minimize VOC emissions from industrial emissions and vehicle exhausts in order to lower O_3 formation and photochemical pollution in YRD.

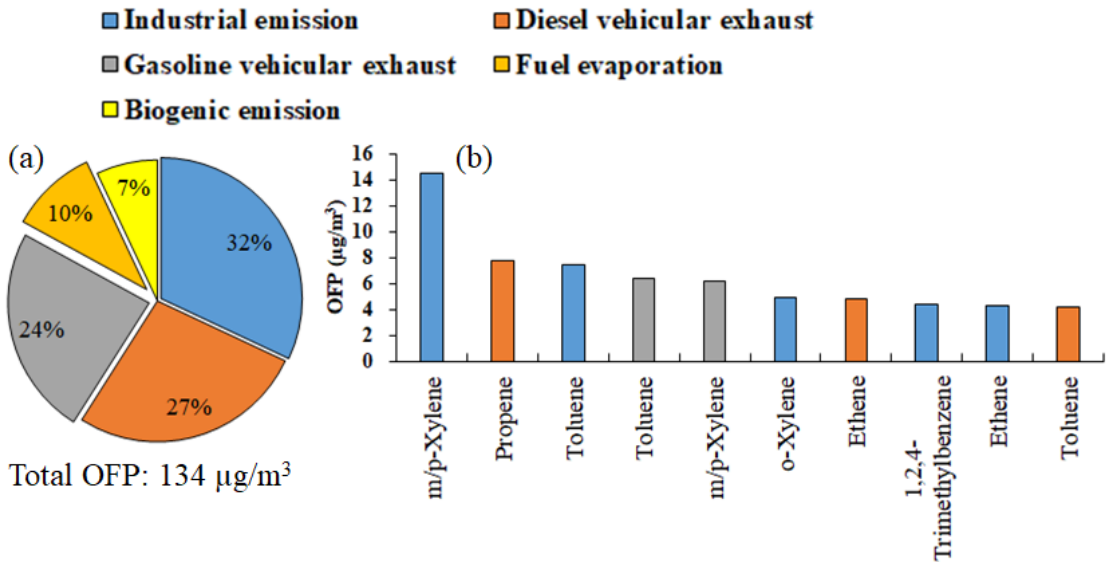

Figure 6. (a) The contribution of individual source to the total OFP of all sources extracted from PMF and (b) OFP values of the top 10 VOC species in the different source categories.

Based on the mass concentrations of individual species in each source, we found that *m,p*-xylene and toluene in industrial emissions and gasoline vehicular emissions, propene, ethene, toluene and *m,p*-xylene in diesel vehicular emissions, and *o*-xylene, 1,2,4-trimethylbenzene and ethene in industrial emissions to be the dominant species from VOC emissions contributing to photochemical O_3 formation. Thus, only a small number of VOC species can be monitored for the effective control of O_3 formation.

For details, please refer to Lines 396-422, Pages 14-15 in the revised manuscript.

(1) The authors define an episode based on periods when ozone exceeds 80 ppb (I assume this is hourly averaged?). Based on Fig S7, this would suggest that the authors are comparing the OBM to data collected between April and October. I would be quite surprised if the boundary layer dynamics used by the authors apply equally to ozone episodes observed in Arpil with those observed in October. Furthermore, it is not clear if adjustments were made to the TUV model to account for photon attenuation (e.g. clouds). Why not focus on a shorter period where the OBM can be tailored to the meteorological conditions measured over a week, as opposed to 5 months?

I would assume that the best period to choose would be a) when winds are stable, slow, and originating from a single location (b) when skies are clear, and (c) when the boundary layer height can be modeled, measured, or well-represented by the approximation described by the authors.

Reply: Thanks for the reviewer's comment. We agreed with the reviewer that the boundary layer dynamics was different in different months. In the present study, the configuration of boundary layer height was based on the reanalysis data in China with the spatial resolution of $0.75^{o} \times 0.75^{o}$ reported by Guo et al. (2016). According to Guo et al. (2016), the output for the boundary layer height from reanalysis data in China was categorized into spring, summer, autumn and winter. The episode days (i.e., days with maximum hourly average mixing ratio of 80 ppbv during daytime) were selected from April to October because VOCs data were not collected from 03/11/2016 to 20/11/2016 due to the maintenance for the GC system. Therefore, the average conditions of boundary layer height in spring, summer and autumn in Guo et al. (2016) were selected for the episode days in this study. For example, the average boundary layer heights in the morning (0800 LT), in the afternoon (1400 LT) and at night (2000 LT) were within the ranges of 0.25-0.40, 1.2-1.6 and 0.2-0.60 km in spring, summer and autumn,

respectively. Therefore, for the model simulation, the configuration of boundary layer heights from 0.3 km to 1.5 km was reasonable. To investigate the uncertainties for the variation of boundary layer heights, sensitive analysis with variations of boundary layer heights (i.e., from 0.2-1.2 km and 0.3-1.6 km based on the above ranges) were conducted. It was found that the uncertainties for the variations in boundary layer height for the modelled O_3 mixing ratios were < 4% (data not shown). Consistently, the sensitivity analysis on the variations of boundary heights suggested that the variations of boundary layer height on the modelling results was negligible (i.e., < 3% in net O_3 production rates) in four cities (i.e., Beijing, Shanghai, Guangzhou and Lanzhou) in China (Xue et al., 2014). However, uncertainties still existed for the configuration of boundary layer height in this study as 1) the boundary layer heights were not measured in this study; 2) the spatial resolution for the reanalysis data was $0.75^o \times 0.75^o$, which could not represent the real conditions at JEAS site.

On the other hand, according to the reviewer's suggestion, we selected the O_3 episode days when (a) when winds are stable, slow, and originating from a single location (b) when skies are clear and (c) the IOA between the simulation and observation > 0.9 (the IOA ranged within 0.70~0.92 for the whole O_3 episode days). In total, 11 days were selected as the following figure (Figure 1). However, it was found that the model still overpredicted or underpredicted the mixing ratios due to the factors mentioned above, though the O_3-precursor relationship, the contributions of each sources to O_3 formation on these 11 selected days were similar to those on all the O_3 episode days. In addition, a complete picture for all the O_3 episode days could not be provided if only 11 episode days were selected.

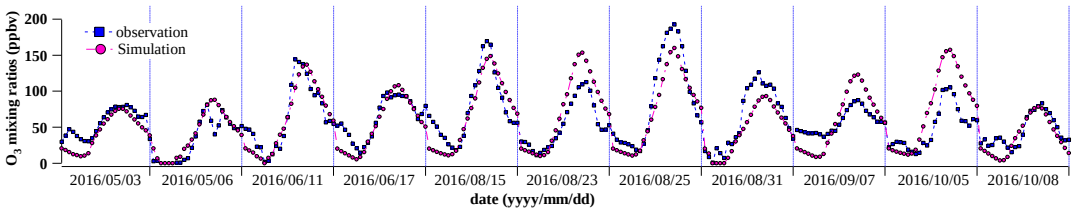

Figure 1 The comparison between observation and simulation results in days with the IOA > 0.90.

Therefore, as suggested by the reviewer above, we deleted the analysis using OBM-

MCM model, and used the MIR method to evaluate the contributions of VOC sources and species in different sources to O_3 pollution.

(2) The authors initialized each episode event with a spin-up period of two days that uses the campaign-average diurnal profile of each measurement. There seems to be a lot of variability in the monthly concentrations of VOCs, ozone and NOx (Figs S5-S7). Why not use the hourly data and constrain each event to the measurements conducted each day? Since the analysis is focused on local ozone production, it seems that this would also help to account for ozone transported from upwind sources.

Reply: Thanks for the reviewer's valuable comment and Sorry for the inappropriate description in the manuscript. Indeed, we used observed hourly data as the model input for the spin-up simulation if the observation data on the spin-up days were available. On the other hand, for days that not all the observation data were available, the spin-up simulation was conducted using the monthly averaged diurnal profiles of observation data.

(3) While the focus is on ozone formation, it's also important that the model should reasonably represent NOx and VOC profiles during ozone episodes. This not only affects radical budgets, but is also important in order to differentiate between ozone formed via reactions of NOx alongside biogenic and anthropogenic VOCs. It would be convincing to see how the model performs in reproducing VOC and NOx concentrations.

Reply: Many thanks for the reviewer's comment. As mentioned in the manuscript, though the model simulation was conducted using observation data as input, the evolution of VOCs and NO_x in the model might not be the same as in the real atmosphere. To investigate the model performance in simulating VOCs and NO_x, the correlation and IOA between observed and simulated VOCs or NO_x during daytime hours (0600-1900 LT) were explored. As there were many species of VOCs, here we presented the correlation of total concentrations of VOCs between observation and

simulation. It was found that the simulated mixing ratios of NO, NO_2 and VOCs correlated well with those observed at the JAES site (Figure 2), with the correlation coefficients R^2 (IOA) as 0.65 (0.89), 0.60 (0.74) and 0.86 (0.93), suggesting that the model indeed provide a reasonable description for the simulation of VOCs and NO_x at the JAES site.

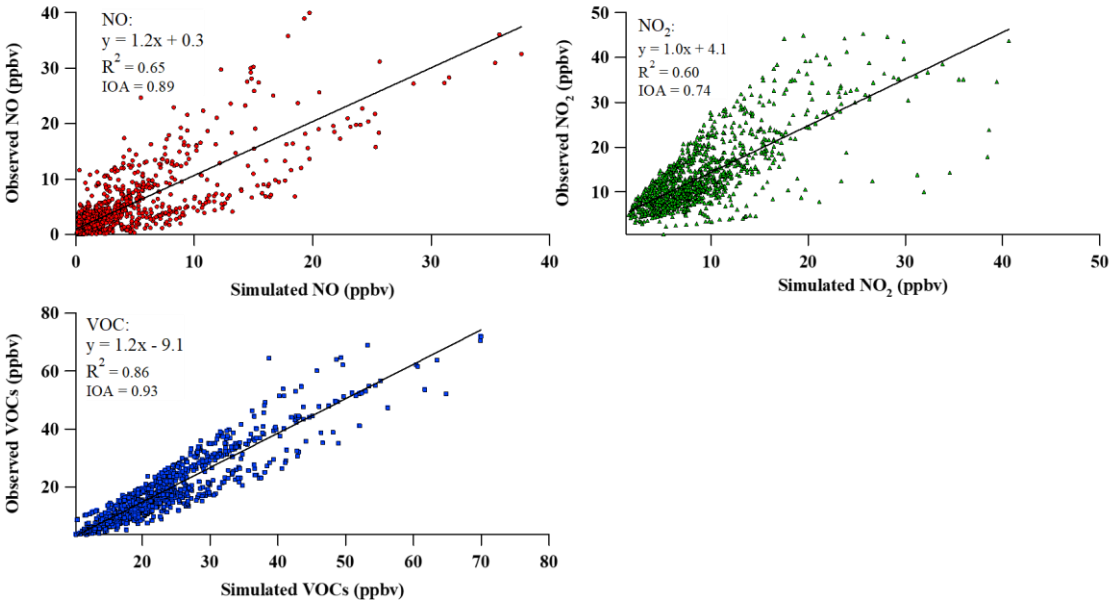

Figure 2 The correlation between observed and simulated mixing ratios of NO, NO_2 and VOCs during daytime hours (0600-1900 LT, local time).