Point-by-point response to comments by Reviewer#1

We thank the reviewer for the detailed and constructive review comments. Below is our point-by-point response to each comment, marked in blue. Changes made to the main text are also marked in blue in the revised manuscript file.

Major Comments:

1. Many important parameters were not measured, including some that the authors themselves indicate as very important: for example, CH_4, HONO, photolysis rates, aerosol surface area. There is no attempt to estimate the uncertainty of the model results derived from these missing constraints. In addition, the instrument used to measure NOx has known interferences, especially when it comes to NO_2. This can affect the results but it is not mentioned at all.

Response: Thanks for raising this issue. It is unfortunate that some important parameters were not measured. We'll detail below the rationality of this study based on sensitivity analysis and discuss associated uncertainties. We have also revised the manuscript text accordingly.

1. Sensitivity analysis for those related parameters that have not been measured.

We agree that it would be much better to involve online measurement of CH_4, HONO, photolysis rates, and aerosol surface area in this study. However, these measurements were not conducted due to the absence of those instruments. To reduce uncertainty, we conducted sensitivity analyses of modelled O_3, HCHO, and OH concentrations at different CH_4 concentrations, $HONO/NO_2$ ratio, photolysis rates, and aerosol surface area (Figure 1 to 4 below). Results show that when $HONO/NO_2$ ratio is 0.005, the daytime OH level could decrease by 15.28%. Vice versa, a higher $HONO/NO_2$ (e.g., 0.04) can promote OH concentration by 14.08%. This result indicates that the photolysis of HONO is essential for the generation of OH, and therefore a simultaneous measurement of HONO is highly recommended for the analysis of local radical recycling in the future. The sensitivity analyses show that the O_3, HCHO and OH concentrations could increase by 51.14%, 34.52%, and 50.38%, respectively, when photolysis rates were increased by 40%. On the contrary, when photolysis rates were decreased by 40%, O_3, HCHO and OH concentration could decrease by 50.59%, 30.84%, and 47.24%, respectively. However, the modelled O_3, HCHO, and OH

concentration did not show obvious changes when CH_4 concentrations and aerosol surface area (SA) changes.

2. Uncertainty regarding NOx measurement

We agree that the instrument (Model 42i, Thermo Fischer Scientific, USA) used to measure NOx has interferences. This instrument is widely used in atmospheric research, and according to the study of Xu et al. (2013), this analyzer could accurately measure the NO concentration, while overestimate the concentration of NO_2 to some extent. However, the overestimation of NO_2 could not be precisely quantified without the observation of the actual NO_2 concentration (usually by photolytic converter). Here, to test the potential overestimates of NO_2 concentrations by our NOx analyzer, we calculated the changes in O_3, OH, and HCHO concentrations when cutting NO_2 concentration by 10% ~ 40% (Figure 5). Results suggest that decreasing NO_2 could lead to increase or decrease of O_3, HCHO and OH concentrations in different cases. Overall, decreasing NO_2 by 40% could cause 6.94%, 12.07%, and 6.29% increase in O_3, HCHO, and OH concentrations, respectively. Therefore, more accurate observation of NO_2 should be considered in future studies. The following figures have been inserted to the supporting material.

3. Uncertainties regarding model results

According to the sensitivity analysis described above, when $HONO/NO_2$ ratio is 0.005, the daytime OH level could decrease by 15.28%. Vice versa, a higher $HONO/NO_2$ (e.g., 0.04) can promote OH concentration by 14.08%. However, the modelled O_3, HCHO, and OH concentration did not show obvious changes when CH_4 and aerosol surface area (SA) input changes. As for photolysis rate, the O_3, HCHO and OH concentration could increase by 51.14%, 34.52%, and 50.38%, respectively, when photolysis rates were increased by 40%. On the contrary, when photolysis rates were decreased by 40%, O_3, HCHO and OH concentration could decrease by 50.59%, 30.84%, and 47.24%, respectively. Furthermore, decreasing NO_2 by 40% could cause 6.94%, 12.07%, and 6.29% increase in O_3, HCHO, and OH concentrations, respectively.
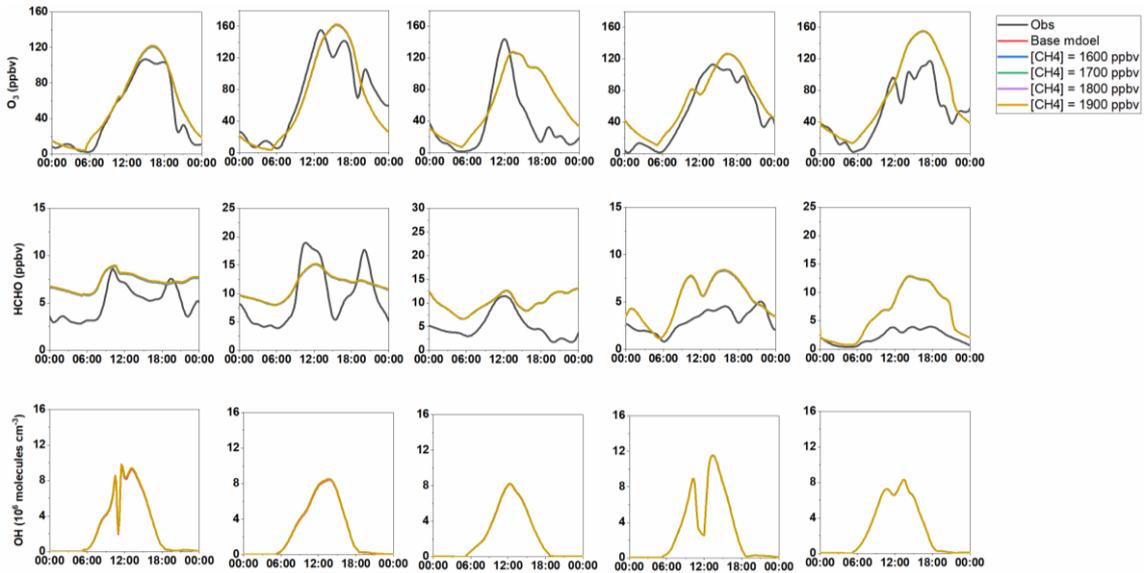
Figure 1. Sensitivity analysis of OBM modelled O_3, HCHO, and OH concentrations with different CH_4 concentrations.
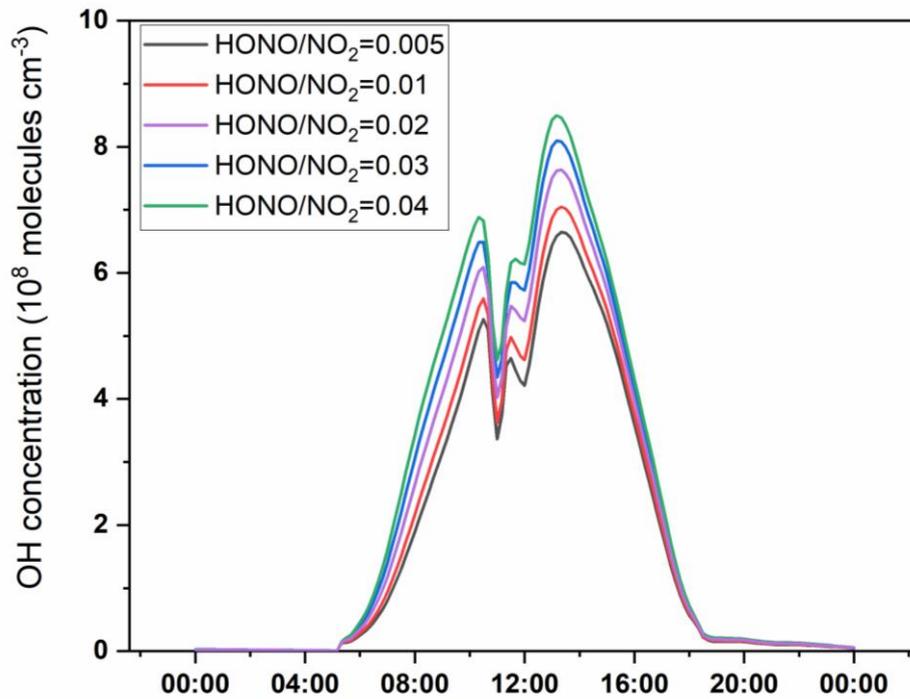
Figure 2. Comparison of OH concentration under different $HONO/NO_2$ ratios.
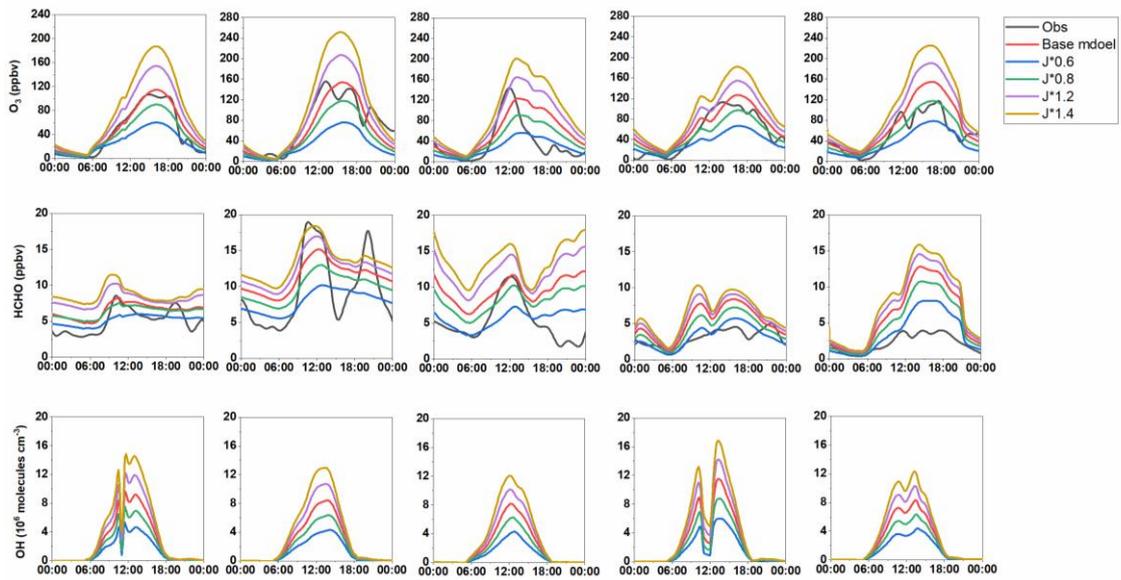
Figure 3. Sensitivity analysis of OBM modelled O₃, HCHO, and OH concentrations with different photolysis rates.
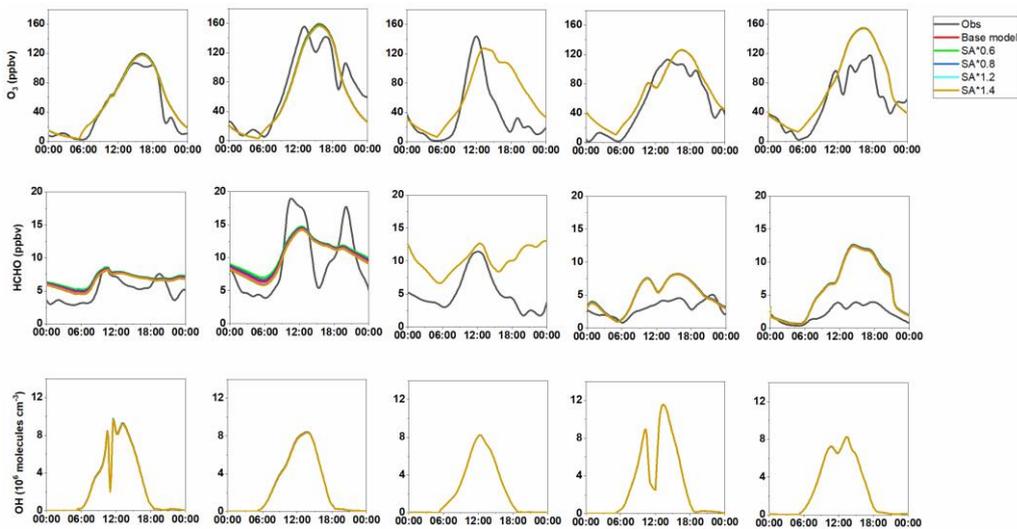
Figure 4. Sensitivity analysis of OBM modelled O₃, HCHO, and OH concentrations with different SA values
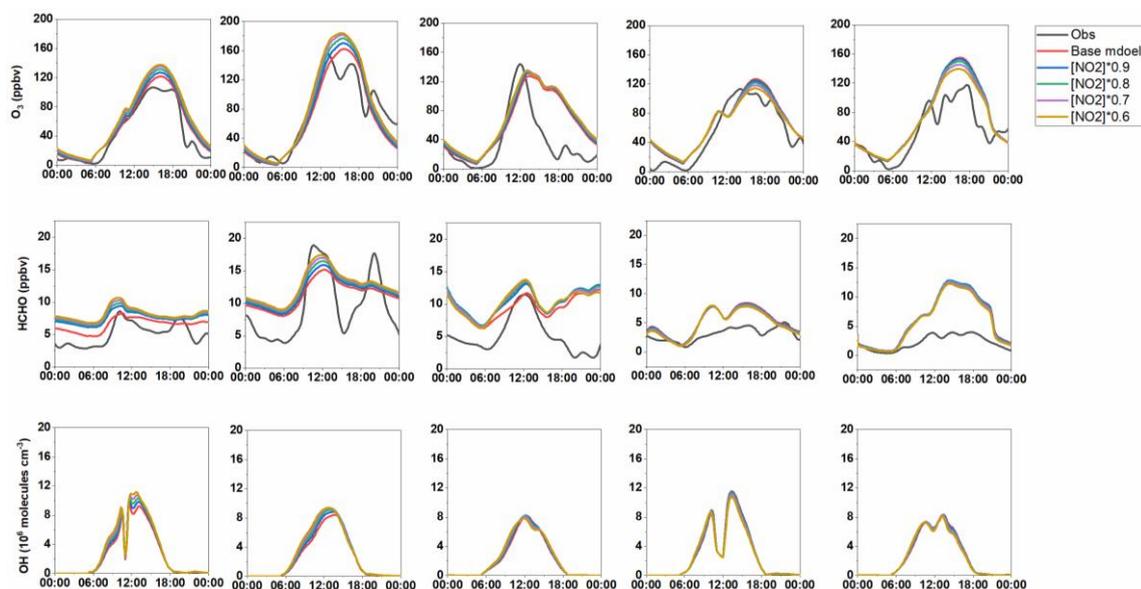
Figure 5. Sensitivity analysis of OBM modelled O_3, HCHO, and OH concentrations with reduced NO_2 concentrations.

Reference

Xu, Z., Wang, T., Xue, L. K., Louie, P. K. K., Luk, C. W. Y., Gao, J., Wang, S. L., Chai, F. H., and Wang, W. X.: Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric nitrogen dioxide at four differently polluted sites in China, Atmos. Environ., 76, 221–226, 2013.

Relevant description has been inserted to the manuscript as follows, and the related figures have been inserted to the SI:

Due to limitations in the observations, several issues should be noted in the application of the OBM model to evaluate the local chemistry in the present study. Firstly, methane concentration, which was set to 1850 ppbv based on previous observations, could be an overestimation or underestimation. Thus, we conducted sensitivity analysis of modelled O_3, OH, and HCHO with different methane values (from 1600 ppbv to 1900 ppbv) (Figure S7). The model predicted O_3, HCHO, and OH concentration with negligible change under different CH_4 values. Secondly, the photolysis rates directly influence the key photochemical processes during the day. Since the photolysis rates were not measured during the sampling period, we also conducted sensitivity analysis by increasing or decreasing the photolysis rates by 20% and 40%. Results showed that the O_3, HCHO and OH concentration could increase by 51.14%, 34.52%, and 50.38%, respectively, when photolysis rates were increased by 40% (Figure S8). On the contrary, when photolysis rates were decreased by 40%, O_3, HCHO and OH concentration

decreased by 50.59%, 30.84%, and 47.24%, respectively (Figure S6). According to the study by Xu et al. (2013), NO_2 concentration measured by the molybdenum oxide converter technique can be significantly overestimated in areas far away from fresh NOx emission sources. Therefore, OBM simulations with reduced NO_2 concentrations were conducted. The results suggest that decreasing NO_2 could increase or decrease of O_3, HCHO and OH concentrations under different scenarios (Figure S9). Overall, decreasing NO_2 by 40% could cause 6.94%, 12.07%, and 6.29% increase in O_3, HCHO, and OH concentrations, respectively. Finally, the total surface area of aerosols was obtained from the study of Wang et al. (2014) and the uncertainty of this value could directly influence the heterogeneous reactions in this model. Therefore, we conducted sensitive analysis by using increasing or decreasing SA value by 40% (Figure S10). The results show that O_3, HCHO, and OH concentrations did not exhibit obvious changes when SA changed. Hence, accurate measurement data of photolysis rate and NO_2 concentration is strongly recommended in further OBM analyses.

2. O_3 and HCHO concentrations are affected by several non-chemical processes, which are difficult to account for with a zero-dimensional model. Although dilution, "aloft exchange" and deposition are mentioned at some point, they are not addressed in the discussion. It is legitimate to use such a model to focus on the in-situ photochemical pathways that form and destroy O_3 and HCHO, but then it should be made very clear that the analysis is limited to those processes and to local conditions.

Response: Thanks for the constructive comment. We agree that the zero-dimension OBM model indeed has limitations. For better clarification, we have addressed that the discussion of model results is limited to local condition in the revised manuscript.

Revised manuscript (Page 10, Line 193-196):
"To investigate the impact of local chemistry on ozone formation and avoid the influence of emission transportation, five days under stagnant condition (with daily average wind speed less than 2m/s and maximum daily 8-h average (MDA8) O_3 concentration >75 ppb) were identified as typical local chemistry cases."
Page 13, Line 251-253:

"It should be noted that, the discussion below is limited to local conditions (cases with average wind speed lower than 2m/s), since transportation of emissions are not considered in the 0-dimensional model."

Page 25, Line 503-505:

"Our observations at a suburban site of the YRD region from April to June in 2018 captured 5 typical local O_3 formation episodes. The detailed atmospheric photochemistry during these episodes were analyzed by a typical 0-D box model on a local scale."

3. It is hard to assess the reliability of the model results without radical measurements, and in the absence of a sensitivity study. As such, the radical budgets (Fig. 5 and 6) are qualitative at best. Previous studies may help with an estimate of the level of agreement between model and measurements, but only to the extent that the models being compared are similar. Moreover, there is some discussion of nocturnal processes, but the results of night-time chemistry are even more uncertain than those of day-time chemistry, because the model is not necessarily good at predicting NO3, as other modelling studies supported by in-situ measurements have shown.

Response: 1. We are grateful for this comment. The observations of radicals are important for assessing the reliability of box model. However, the relevant instruments are quite expensive and most of box model studies were carried out without those observations. To assess the reliability of our model results without radical measurements, we calculated the OH concentrations by using the ratio of two aromatics (ethylbenzene (E) and m,p-xylene (X)) that share common emission sources but with different reactivities with OH radicals as follows:

$$Ethylbenzene + OH \rightarrow products \quad k_{Ethylbenzene,OH} = 7.0 \times 10^{-12}$$

(R1)

$$m,p - Xylene + OH \rightarrow products \quad k_{m,p-Xylene,OH} = 1.89 \times 10^{-11}$$

(R2)
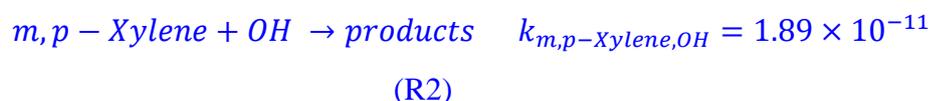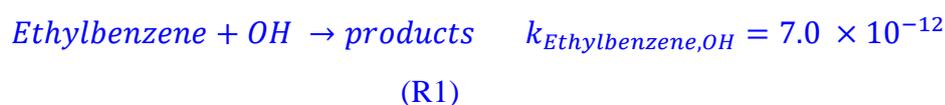
Therefore, mixing ratios of E and X at the sampling time can be expressed as follows:

$$[X]_t = [X]_0 \times e^{-[OH] \times k_{X,OH} \times t} \times f_{d,B}$$

(Eq.1)

where $[X]_0$ and $[X]_t$ are the mixing ratio of X at the initial time and after transport time t. $k_{X,OH}$ represents the temperature dependent reaction rate coefficient of m,p-xylene with OH, which was taken from the IUPAC database (http://iupac.pole-ether.fr/). $f_{d,B}$ represents the dilution factor of m,p-xylene in the atmosphere.

In this study, we assume that the rates of turbulent mixing and horizontal convection are similar for E and X. Therefore, during the transport time Δt, the dilution factor of E and X are the same. Then rearranging Eq.1 and extend this analysis to E and X will yield the following equation:

$$[OH]_{\frac{E}{X}} = \frac{1}{t \times (k_{E,OH} - k_{X,OH})} \times [ln\left(\frac{[E]}{[X]}\right)_0 - ln(\frac{[E]}{[X]})_t]$$

(Eq. 2)

where $[OH]_{E/X}$ is the estimated regional mixing ratio of OH based on ethylbenzene and m,p-xylene ratio.

The calculated average regional concentrations of OH ($8.39 \pm 5.11 \times 10^6$ molecules cm^{-3}) was in the same magnitude of the OBM-simulated result ($4.59 \pm 5.11 \times 10^6$ molecules cm^{-3}), suggesting that the OBM-simulated radical concentration is reliable.

Relative description has been added in the revised manuscript (Page 8-9, Line 170-185):
"To assess the reliability of model results without OH observation, we compared the OBM-simulated OH concentration with that calculated using the ratio of ethylbenzene (E) and m,p-xylene (X) that share common emission sources but with different reactivity with OH radicals (shown in Equation (5)~(8)):

$$Ethylbenzene + OH \rightarrow products \quad k_{Ethylbenzene,OH} = 7.0 \times 10^{-12} \quad (5)$$

$$m,p-Xylene + OH \rightarrow products \quad k_{m,p-Xylene,OH} = 1.89 \times 10^{-11} \quad (6)$$

$$[X]_t = [X]_0 \times e^{-[OH] \times k_{X,OH} \times t} \times f_{d,B} \quad (7)$$

$$[OH]_{\frac{E}{X}} = \frac{1}{t \times (k_{E,OH} - k_{X,OH})} \times [ln\left(\frac{[E]}{[X]}\right)_0 - ln(\frac{[E]}{[X]})_t] \quad (8)$$

where $[X]_0$ and $[X]_t$ are the mixing ratio of X at the initial time and after transport time t. $k_{X,OH}$ is the temperature dependent reaction rate coefficient of m,p-xylene with OH, which was taken from the IUPAC database (http://iupac.pole-ether.fr/), whereas $f_{d,B}$ is the dilution factor of m,p-xylene in the atmosphere. In this study, we assume that the rates of turbulent mixing and horizontal convection are similar for E and X. Therefore, during the transport time Δt, the dilution factor of E and X are the same. Therefore, rearranging Equation (7) and extending this analysis to E and X will yield Equation (8), where $[OH]_{E/X}$ is the estimated regional mixing ratio of OH by ethylbenzene and m,p-xylene ratio. The calculated average regional concentrations of OH ($8.39 \pm 5.11 \times 10^6$ molecules cm^{-3}) was in the same magnitude of the OBM-simulated result ($4.59 \pm 5.11 \times 10^6$ molecules cm^{-3}), suggesting that the OBM-simulated radical concentration is reliable."

2. We agree that the box model didn't performance well enough to predict nocturnal NO$_3$. Since this paper mainly focuses on daytime photochemical processes, we have removed the discussions about nocturnal chemistry.

4. I don't think the authors have made a compelling case that the chemistry in this area is driven by isoprene, if it is the intention of the paper to demonstrate this. Sure, isoprene is important and affects the formation of ozone and formaldehyde, but does it really dominate over all other VOCs, under these conditions? Before focusing on isoprene, the authors need to show evidence that other VOCs do not contribute as much to the oxidative capacity.

Response: We are grateful for the comment. We agree that isoprene is not the dominate VOCs compared with anthropogenic VOCs. According to observational data, the top 10 abundant VOC species during the observation period are: propane, toluene, ethylene, ethylbenzene, n-butane, ethane, i-butane, acetylene, xylene, i-pentane, and propene. Therefore, anthropogenic VOCs (such as alkanes and benzene series) are more abundant than isoprene. But the aim of this paper is to address the significance of isoprene chemistry in local photochemical processes. Hence, we tested the sensitivity of modelled O$_3$, HCHO, and OH concentrations without EXT (ethylbenzene, xylene, and toluene), alkenes (acetylene, ethylene, and propene), and isoprene. The sensitivity to the presence of alkanes was not conducted since they are relatively inert. Although the averaged isoprene concentration was only 0.37 ± 0.36 ppbv, cutting isoprene input can lead to obvious drop in simulated O$_3$, HCHO, and OH concentration, which was comparable to that of cutting EXT and alkenes, indicating the significant role of isoprene in local photochemical processes.

Relevant description has been added in Page 20, Line 403-410:

"To compare the importance of isoprene and other abundant VOCs in local chemistry at DSL site, sensitivity analysis was conducted for the modelled O$_3$, HCHO, and OH concentrations without the input of active VOCs (toluene, ethylene, ethylbenzene, ethane, acetylene, xylene, propene, and isoprene). Results suggested that, although the average isoprene concentration was only 0.37 ± 0.36 ppbv, cutting isoprene input can lead to obvious drop in simulated O$_3$, HCHO, and OH, which was comparable to that of cutting EXT and alkenes, indicating the significant role of isoprene in local photochemical processes (Figure S6)."
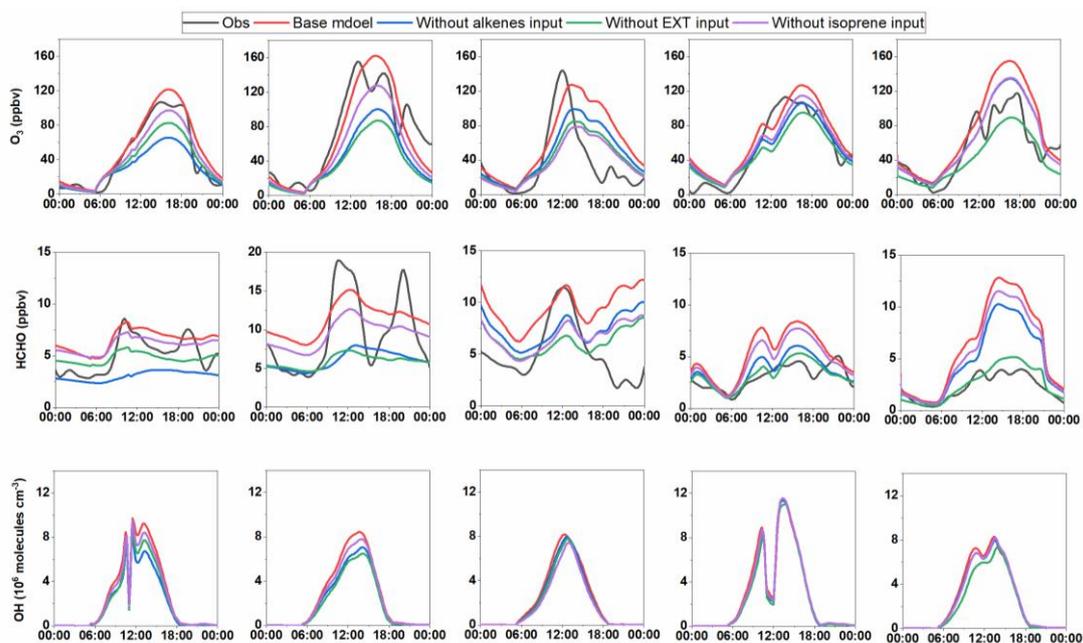
Figure S6. Sensitivity analysis of OBM modelled O₃, HCHO, and OH concentrations without alkenes (including ethylene, propene, and acetylene), isoprene, and EXT (ethylbenzene, xylene, and toluene) input.

Point-by-point response to comments by Reviewer#2

The revised manuscript has addressed most of the comments raised by peer reviewers but a few technical questions remain, as follows:

We thank the reviewer for the detailed and constructive review comments. Below is our point-by-point response to each comment, marked in blue. Changes made to the main text are also marked in blue in the revised manuscript file.

Comment 1: Isoprene measurement should be described or referenced since this species is a key VOC in the manuscript. In addition, other biogenic VOC emissions such as terpenes can be important in terms of contributing to ozone and formaldehyde formation but they are not discussed in the manuscript.

Response: Thank you for raising this issue. We agree that BVOC species like isoprene and terpenes are important precursors of ozone and formaldehyde. Among them, isoprene represents the dominant BVOC specie with highest emissions and is therefore the most commonly used indicator of biogenic emissions in terms of VOCs measurement. Description of the measurement of isoprene has been inserted in the revised manuscript. We also added discussions with respect to other BVOCs species in the revised manuscript.

Revised manuscript (Page 6, Line 116-120):
A total of 55 VOC species, including 28 alkanes, 10 alkenes (including isoprene), 16 aromatics and acetylene were continuously analyzed at our sampling site by two online gas chromatographs with flame ionization detector (GC-FID) systems (GC-866 airmoVOC C2-C6 #58850712 and airmoVOC C6-C12 #283607112, Agilent., USA) with a time resolution of 1 hour during the study period."
Revised manuscript (Page 26, Line 531-534):
"Furthermore, other biogenic VOCs (BVOCs, such as terpene and sesquiterpene) can also affect local chemistry via photochemical processes, but those BVOCs were not able to be synchronously observed. Therefore, future studies should take into account those BVOCs."

Comment 2: Lines 80-82: Not sure what "trace gases" were collected to understand the impact of isoprene since no key products of isoprene photochemical reaction were observed or measured.

Response: To avoid misunderstanding, we have revised this sentence as following:

In this study, we conducted a comprehensive set of in-situ observations of isoprene, meteorological parameters, and atmospheric pollutants (including O_3, NOx, CO, VOCs, and HCHO) to understand the important impact of isoprene chemistry on atmospheric photochemical processes in suburban YRD region.

Comment 3: Line 153: Figures S1 and S2 do not correspond to the correct graphs, respectively.

Response: Thanks for raising this issue. We have corrected this problem in supporting information and in the revised manuscript. Please refer to Page 8, Line 156-157: " The comparison of simulated and observed O_3 and HCHO concentrations is shown in Figure S1 and Figure S2."

Comment 4: Lines 89-90: It states that DSL has high vegetation coverage, implying more biogenic emissions but that is not the case from Figure 5 of Lin et al (2020).

Response: As suggested by Figure 5 of Lin et al. (2020), the RIR(NHC) is relatively higher than RIR(AHC) at DSL site. Therefore, our previous description "It is located in the west of Shanghai and is close to the Dianshan Lake Scenic area, which has high vegetation coverage" is inappropriate. However, it should be noted that RIR only stands for sensitivity but not the amount of emissions. We have corrected this sentence as "It is located in the west of Shanghai and is close to the Dianshan Lake Scenic area, which has relatively higher vegetation coverage than the urban areas."

Comment 5: Figure S2: The observed and simulated formaldehyde concentrations are less correlated than ozone with the reasons being uncertainties in dry deposition, vertical transport, and so on. Did the authors learn something new or different from these reasons? How did the model treat primary HCHO emissions from secondary? The overall HCHO discussion is useful but diminished due to the inconsistency.

Response: Thanks for this constructive comment. Apart from dry deposition and vertical transportation, primary HCHO emissions can also bring uncertainties in the simulation. Due to

the lack of HCHO sources for areas around DSL, primary HCHO emissions were not included in our model.

Relevant descriptions have been added in Page 8, Line167-170:

"In addition, primary HCHO sources can contributed up to 76% of total HCHO concentration in urban areas (Li et al., 2010). However, due to the lack of primary HCHO sources for areas around DSL, primary HCHO emissions were not included in our model. "

Comment 6: It is not convincing that NO peak occurred in early morning, indicating traffic pattern, while CO was flat. Is this instrument sensitivity issue?

Response: Thanks for the reviewer's careful comment. The sensitivity of CO analyzer was set to 0.1 mg/m^3, which was about 80 ppbv during our observation. This coarse resolution caused the flat CO variations during our observation. The other potential reason is that CO is mainly emitted by gasoline vehicles while NOx are mainly from heavy-duty vehicle exhausts. Since DSL site is far away from urban area, there are rare passenger cars in early morning whereas heavy-duty trucks sometimes pass by, causing NO peaks in early morning.

For better explanation, we have added relevant descriptions in the revised manuscript (Page 10, Line 215-221):

"It should also be noted that, flat CO pattern was found during morning when NOx peaks were observed. This inconformity can be attributed to the coarse resolution of CO analyzer (about 80 ppbv) and CO emission source (mainly gasoline vehicles) while NOx are mainly emitted by heavy-duty vehicle exhausts. Therefore, since DSL site is far from urban area, it is unlikely to have gasoline vehicles in early morning. On the contrary, there are sometimes heavy-duty trucks passing by, causing peaks of NO in early morning."

Besides the above-mentioned revision, we also thoroughly polished the language to improve the quality of the paper.