Responses to anonymous Referee #1

1. The Lyu et al. manuscript reports on a combined measurement-modeling analysis of a sustained ozone (O_3) pollution event over the North China Plain. Continuous online measurements of O_3, NO, and NO_2 were made in the city of Ji'nan, from the Shandon University campus. For a subset of the measurement period, samples were collected for offline analysis of oxygenated/volatile organic compounds (O/VOCs). Additional chemical and meteorological data were obtained from nearby monitoring stations. Positive matrix factorization (PMF) was used to identify sources of O_3 precursors, using the chemical data as input parameters (VOCs, CO, NO, and NO_2). In addition, the WRF-CMAQ chemical transport model was used to evaluate processes contributing to O_3 formation and depletion, and an MCM-based box model was used to evaluate localized O_3 chemistry. HYSPLIT back trajectory analysis was also performed to identify origins of air masses. Collectively, the research presented represents a significant effort to identify the primary drivers of the sustained O_3 event. No major weaknesses are identified in the approach, the quality of the data, or the simulation results. The major weaknesses are in the presentation of the results and the synthesis of the findings.

We appreciate the referee's time and positive comments. The presentation of the results and the synthesis of the findings in the paper have been improved according to the referee's comments.

2. The introduction starts with a list of publications that have addressed O_3 formation over the North China Plain (NCP). As written, it isn't clear whether there are major discrepancies between studies and/or whether there are gaps in understanding/model representation that are unaddressed by existing studies.

Many thanks for the good comment. The introduction has been reorganized and the knowledge gaps are more clearly presented. In the revised manuscript, the first paragraph in the introduction focuses on the severity and aggravation of O_3 pollution in the NCP. Six publications are cited to illustrate this point, and we summarize the O_3 pollution in the NCP with the sentence "Overall, the NCP suffers from severe O_3 pollution, which is even aggravating." The second and third paragraphs introduce the chemical and meteorological processes influencing O_3 pollution. The knowledge gaps are summarized in the last paragraph as follows.

Despite many previous studies, the evolutions of the synoptic and photochemical processes in O_3 pollution events, and their contributions to the non-attainment of O_3 have been seldom looked into in the NCP. Besides, the local and regional contributions to the elevated O_3 in the NCP are not unambiguously quantified, limited by the deficiencies in model representation of either physical or local chemical processes. The situation was even much worse for Ji'nan, the capital of Shandong province. As early as 2000s, studies (Shan et al., 2008; Yin et al., 2009) reported the maximum hourly O_3 of 143.8 ppbv and 147.8 ppbv in June 2004 and 2005, respectively. Even higher O_3 (198 ppbv) was observed at a rural site downwind of Ji'nan in June 2013 (Zong et al., 2018). However, almost no study was carried out to explore the mechanisms responsible for high O_3 there, though it has been confirmed that air pollution in the NCP cities like Ji'nan influenced air quality in Beijing (Lin et al., 2008; Wang et al., 2010).

For details, please refer to lines 116 – 127, pages 4 – 5.

3. Further, it isn't clear (based on the abstract or implications) how the current work advances the current state of the science (understanding, prediction capabilities, etc.). As written, the implications section highlights that this work confirms O_3 levels are high in the NCP and the NCP may serve as a source region, which do not represent a substantial contribution. However, elucidation of the shifts in regime (from VOC-limited to transition) during the O_3 episodes appears to be a new finding, and therefore should be highlighted and expanded upon.

The valuable comment and suggestion are highly appreciated. Although Ding et al (2009) indicated the transport of O_3 from the NCP to the free troposphere and the downwind areas, their study was based on the aircraft measurement in northeast China and the simulation of the lifting processes of ground-level air masses. To our knowledge, no other study defined the NCP to be a source region of O_3. The present study confirmed that the NCP was an O_3 source, through the ground-level measurement and simulation of in-situ photochemistry. Therefore, we still think that this finding advanced our understanding on the role of the NCP in O_3 pollution in the downwind regions and even whole China. We clarify the differences between this study and Ding et al (2009) in the implications, though the studies corroborated each other in term of the finding that the NCP is a source region of O_3.

Another important finding in this study was that the NCP served as an O_3 source. This was ever proposed by Ding et al. (2009), based on the aircraft measurement and simulation of atmospheric dynamics. We confirmed it through the ground-level observation and the simulation of in-situ photochemistry.

For details, please refer to lines 663 – 667, pages 27-28.

In addition, we accept the excellent suggestion on highlighting the change of O_3 formation mechanisms from VOC-limited regime to the transitional regime.

The finding that O_3 formation shifted from VOC-limited regime on relatively low O_3 days to the transitional regime on O_3 non-attainment days may elucidate the cause of the increase in O_3, because O_3 productions in the transitional regime are even higher, despite decreases in NO_x emissions. It is unrealistic to expect a continuously linear reduction in NO_x emissions in the NCP, after the substantial decreases of NO_x emissions from power plants and industries in recent years. In other words, restraining on VOC emissions is urgent for O_3 abatement in the NCP.

For details, please refer to lines 657 – 663, page 27.

Revisions have also been made in the abstract to highlight the two findings.

The NCP has been confirmed as a source region of tropospheric O_3, where the widespread shift of regimes controlling O_3 formation like the case presented in this study can be expected, due to the substantial reductions of NO_x emissions in recent years.

For details, please refer to lines 33 – 35, page 2.

4. Further, though significant effort was clearly made and the quality of the work is high, the results are relatively unorganized and presented as speculative. Regarding the latter, the word “might” is used 30 times in the paper; in many places it seems the authors have sufficient information to make more conclusive statements and the contribution of the work is minimized by presenting it as speculative. Regarding organization, in several places within the results and discussion, individual paragraphs are more than one page long (lines 335-378, 733-762, 795-832).

Thanks for the comments. All the conclusions and inferences have been checked throughout the paper and the wordings have been changed to be more definite wherever it is possible based on our confidence on the conclusions and the inferences. Besides, the whole paper has been reorganized to improve the readability. The long paragraphs pointed out by the referee have been significantly shortened, while the contents are not changed much. For details, please refer to lines 327 – 344, 587 – 605 and 628 – 648.

5. Additionally, there is a lot of repetition in the results and the modeling doesn't clearly build on the measurements (or vice versa). Each section is almost presented as a separate study of processes. Because of these weaknesses, it is difficult to assess the overall importance of the paper and the likely contribution to the field. It is recommended that the paper undergo significant revision before publication in ACP. Specific comments are provided below.

We thank for the comments. The repetitions in the manuscript have been double checked and avoided. For example, the contribution of BVOCs to OH reactivity was discussed in lines 330 – 334 and lines 362 – 367 in the original manuscript, which is now only presented in lines 315 – 318 in the revised manuscript. The low O_3 on July 30 and August 1 were elaborated in the original manuscript in both section 3.1 and section 3.2. However, we only discuss it in section 3.1, with reference to the discussion in section 3.2 – "The low O_3 values on July 30 and August 1 were mainly attributable to the weak solar radiation and low temperature as discussed above." (lines 419-420, page 16). More revisions on the repetition have been made throughout the manuscript.

In fact, the modeling and measurement were built on each other and the results supported each other. In the revised manuscript, the relationships between them are clarified.

The observations indicated the likely different regimes controlling local O_3 formation and the potential impacts of regional transport. To understand the atmospheric chemistry and dynamics, as well as their roles in this O_3 pollution event, the WRF-CMAQ was applied.

For details, please refer to lines 442 – 444, page 18.

The IPR analyses showed that chemical reactions served as an important source of O_3 on episode days in Ji'nan, particularly during 09:00-15:00 LT when O_3 was at high levels. This process was further studied through the simulation of the in-situ photochemistry by PBM-MCM. It should be noted that the simulations were based on the observed concentrations of O_3 precursors, which could be influenced by both local and regional air. It required cautions to extend the results to all the situations in Ji'nan, because the regional effect was not always consistent.

For details, please refer to lines 493 – 498, page 21.

Despite these discrepancies, overall the observed O_3 at the sampling site was well reproduced. In addition, the spatial distribution of the simulated O_3 was highly consistent with the observed O_3 distribution, as shown in Figure S10.

For details, please refer to Text S1 and Figure S10.

Noticeably, the change of regimes controlling O_3 formation is consistent with that predicted by the $\frac{OH\ reactivity_{VOCs^{\#}}}{OH\ reactivity_{NOx}}$ ratio and the ratio of the reaction rates between "HO_2+RO_2" and "OH+NO_2".

For details, please refer to lines 625 – 627, page 26.

The connections between the sections are also rewritten to make the whole paper more coherent. For details, please refer to lines 368 – 369, lines 442 – 444, lines 493 – 495 and lines 587 – 589.

Specific comments:

1. Technical and Editorial: Abstract, line 23: It would be useful to see the fractional contribution to O_3, as well as the given production rates.

Thanks for the suggestion. The process analysis module in CMAQ did not calculate the contributions of different processes to O_3 (ppbv), but the contributions to the total variation rate of O_3 (ppbv/h). During 9:00 – 15:00 on O_3 episode days, the regional transport and chemical reactions elevated O_3 by 18.7 and 14.0 ppbv/h, respectively, which were most offset by dry deposition (-25.6 ppbv/h) and cloud processes (-0.1 ppbv/h). If the percentage contributions to the total variation rate of O_3 were calculated, they were 268%, 200%, -366% and -1% by regional transport, chemical reactions, dry deposition and cloud processes, respectively. To avoid confusion, we do not provide these seemly strange percentages.

2. Abstract, lines 34-37: On line 34, the use of "great" implies something that is positive; suggestions to replace with "major" or "large" or something similar. On line 23, a local photochemical production rate of 14 ppbv/hr is reported for Aug. 9-10 (I believe that is the associated time period) and on line 32, a simulated local photochemical production rate (maximum) of 21.3 ppbv/hr is reported. With these large production rates, the ~1 ppbv/hr decrease in O_3 formation with a hypothetical 10% decrease in diesel and gasoline exhaust seems

insignificant. Even during non-episode periods, a simulated local maximum production rate of 16.9 ppbv/hr is reported. Thus the suggestion that constraining vehicle emissions is the most effective strategy to control O_3 production is not well supported by the numbers presented, and needs further explanation and/or clarification.

Thanks for the valuable suggestion and comment. The word "great" has been replaced with "large". With regard to the seemingly low sensitivity of O_3 production to gasoline and diesel exhaust, it was because that the gasoline and diesel exhausts were assumed to be reduced by 10%. As shown in Figure S14 (Figure S12 in the original Supplement), the source of gasoline exhaust, diesel exhaust, BVOC, LPG usage, solvent usage and petrochemical industry accounted for 4.7, 5.8, 3.3, 1.4, 2.1 and 2.4 ppbv/hr of the maximum O_3 production, respectively. These O_3 productions added up to 19.6 ppbv/hr, comparable to the 21.3 ppbv/hr during O_3 episodes. The difference was explained by the O_3 production attributable to carbonyls, which were not included in the source apportionment. The statement that constraining vehicle emissions was the most effective strategy to control O_3 was supported by the highest O_3 reduction per 10% decrease in source emission for gasoline exhaust (0.47 ppbv/10% reduction in source emission) and diesel exhaust (0.58 ppbv/10% reduction in source emission). On one hand, we would like to inform the readers that the seemingly insignificant O_3 decrease resulted from 10% emission reduction of gasoline and diesel exhausts was due to the fact that many sources contributed to O_3 production and high reduction percentages were required if actions were only taken against one or two sources. On the other hand, the contributions of vehicle exhausts to O_3 production might be underestimated, without the inclusion of the primarily emitted carbonyls from vehicles. Clarifications have been added in the main text of the revised manuscript as follows, but we do not want to repeat them in the abstract.

In fact, the sensitivity of O_3 production rate to the vehicle exhausts might be somewhat underestimated, due to the exclusion of carbonyls in the source apportionment. However, the reductions of O_3 production rate by cutting 10% of vehicle exhausts were still insignificant, compared to the overall maximum O_3 production rate of 21.3 ppbv/hr during O_3 episodes. This indicated that by only restraining emissions from one to two sources, high percentages of emission reductions were required to sufficiently reduce the O_3 production rate. Otherwise, the combined efforts should be made to control the emissions of O_3 precursors from the diverse sources. In particular, it is essential to get rid of the transitional regime featuring high O_3 production rates and low sensitivities of O_3 production to the precursors.

For details, please refer to lines 640 – 648, page 27.

3. Line 45: Suggestion to remove “of researchers”.

Accepted with thanks.

4. Line 52: May to August of which year?

Thanks for the question. The sampling year (2013) is specified (see lines 47-48).

5. Line 80: Can the authors please clarify what is meant by “air profiles”? Chemical composition?

Exactly. To avoid confusion. The term “air profiles” has been changed to “chemical composition of air pollutants”. For details, please refer to line 68, page 3.

6. Lines 92-95: The authors state that sources with a large fraction of alkenes, aromatics and carbonyls are significant contributors to photochemical O_3 production. As an example, they cite a paper by Ling and Guo that shows O_3 was most sensitive to xylenes from solvent usage, but this alone does not require a major contribution of xylenes from solvents.

Thanks for the comment. To better support the statement “Therefore, the sources with a bulk emission of these VOCs generally make considerable contributions to the photochemical production of ground-level O_3”, we cite another study and the sentence has been revised as follows.

For example, Cheng et al. (2010) pointed out that carbonyls increased the peak O_3 production rates at a rural site and a suburban site in South China by 64% and 47%, respectively.

For details, please refer to lines 89 – 91, page 4.

7. Lines 122-123: This sentence starting with “contradictory” is confusing as written. What is contradictory?

Since this paragraph has been revised substantially, the sentence starting with “contradictory” has been deleted.

8. Line 183: Where is the “widely used” weather station in relation to the measurement site?

We thank for the question. The automatic weather station was deployed at the same site where we collected samples. The Model CAWS600-B weather stations produced by China Huayun group are used in ~2/3 of more than 1500 meteorological stations across China. Therefore, we defined it as a "widely used" weather station.

In addition, the meteorological parameters, including wind speed, wind direction, pressure, temperature and relative humidity, were monitored at the sampling site by a widely used weather station (China Huayun group, Model CAWS600-B).

For details, please refer to lines 194 – 196, page 7.

9. Lines 344-346: The authors discuss the potential interferences and overestimation of NO_2, particularly on episode days. Do the authors mean that the OH reactivity during episodes might be overestimated? Or lower than during non-episodes as stated? Is there a way to approximate or bound the potential overestimation?

Thanks for the questions. Yes, the chemiluminescence NO-NO_2-NO_x analyzer generally overestimates NO_2 due to the reason discussed in section 2.2.1.

Studies indicated that NO_2 monitored with chemiluminescence was generally overestimated due to the conversion of the total odd nitrogen (NO_y) to NO by molybdenum oxide catalysts (McClenny et al., 2002; Dunlea et al., 2007; Xu et al., 2013). The positive bias was more significant in more aged air masses, resulting from higher levels of NO_z ($NO_z = NO_y - NO_x$) (Dunlea et al., 2007).

For details, please refer to lines 165 – 169, pages 6-7.

Since OH reacts with NO_2 at a much higher rate than with NO_z, the overestimate of NO_2 leads to overestimate of OH reactivity. NO_z is often expected to be higher on O_3 episode days, because the sources of most NO_z species are dominated by secondary formation. Therefore, we speculated that the OH reactivity was overestimated in this study and more overestimated on O_3 episode days than during non-episodes. Here, we adopted 30% and 10% as the upper limits of NO_2 overestimate during episodes and non-episodes, respectively. The rationality is given in the manuscript as follows.

The average overestimation of NO_2 was 22% in Mexico City, which even increased to 50% in the afternoon (Dunlea et al., 2007). Xu et al. (2013) suggested that the chemiluminescence monitors overestimated NO_2 by less than 10% in urban areas with fresh emission of NO_x, but the positive bias went up to 30-50% at the suburban sites. As described in section 2.1, our sampling site was located in the urban area of Ji'nan and was only ~50 m to a main road. Therefore, we infer that NO_2 might not be significantly overestimated in this study. However, the larger overestimations could be expected during O_3 episodes, because the stronger photochemical reactions enhanced the productions of many NO_z species. We adopted 30% (minimum bias in suburban area) and 10% (maximum bias in urban area) as the maximum fraction of NO_2 overestimation during episodes and non-episodes at this urban site, respectively. The influences of the NO_2 measurement interferences on the results were discussed where necessary.

For details, please refer to lines 169 – 180, page 7.

The OH reactivity of NO_x was 4.7 ± 0.8 s^{-1} and 6.9 ± 1.9 s^{-1} during episodes and non-episodes, respectively. Taking 30% and 10% overestimate of NO_2 during episodes and non-episodes into account, we found that the OH reactivity of NO_x during episodes (4.0 ± 0.7 s^{-1}) was indeed lower ($p<0.05$) than during non-episodes (6.6 ± 1.9 s^{-1}). It should be noted that the OH reactivity of VOCs was not influenced by the overestimate of NO_2, which therefore was still comparable between episodes and non-episodes. Since NO accounted for a considerable part of OH reactivity of NO_x, the maximum of 30% and 10% overestimate of NO_2 only led to 17.5 ± 1.1% and 5.4 ± 0.7% overestimate of OH reactivity of NO_x during O_3 episodes and non-episodes, respectively. Discussions are given in the manuscript as follows.

Taking the positive biases of NO_2 measurement into account (section 2.2.1), we found that the OH reactivity of NO_x was overestimated by the maximum of 17.5 ± 1.1% and 5.4 ± 0.7% during O_3 episodes and non-episodes, respectively. In the case of maximum overestimations, the actual OH reactivity of NO_x during episodes (4.0 ± 0.7 s^{-1}) might be lower ($p<0.05$) than that during non-episodes (6.6 ± 1.9 s^{-1}).

For details, please refer to lines 331 – 335, page 12.

10. Line 350: "More importantly" than what? High pressures?

Sorry for the confusion. The sentence has been revised to be more concise, and the term “More importantly” was deleted.

The high OH reactivity during non-episodes mainly occurred on July 30 and August 1, due to the high pressure, weak solar radiation and low temperature.

For details, please refer to lines 335 – 337, page 12.

11. Section 3.3: The authors spend a significant time discussing the quality of the O_3 modeling. Since matching observations is not the primary goal of the modeling component, much of that discussion could be moved to the supplement.

The good suggestion is accepted with thanks.

Discussions on the discrepancies and the detailed model validation are provided in Text S1, Figures S9-S11 and Table S4.

For details, please refer to lines 448-449, page 18, and Text S1, Figures S9-S11 and Table S4.

Responses to anonymous Referee #2

General Comments This paper presented a comprehensive diagnostic study of the Ozone-NO_x-VOCs sensitivity in urban Ji'nan. The analysis is trying to synthesize the analysis tools from both observational constrained box model and regional model. This study is on the good way for the exploration of the ozone chemistry in urban China. Nevertheless, there are still trivial problems on the issues like site representation, measurement quality of key parameters like NO, ways to compare box model and regional model, the use and interpretation of PMF on VOCs source apportionment, etc which I provided detailed comments as follows. I suggest publication after addressing the following comments.

We sincerely thank for the positive and valuable comments. Revisions have been made accordingly, and the responses are given below item by item.

Specific Comments 1. Introduction: the review of the current O_3 studies in the part of the introduction was not as comprehensive as it normally required. Recently, there were several papers about the Ozone-NO_x-VOCs sensitivity issues in Chinese megacities been published. It may be useful to include as a comparison.

We thank for the good comment. The review of the current O_3 studies, particularly on the O_3-VOC-NO_x sensitivity in the introduction has been updated.

Xue et al. (2014) indicated that the summer O_3 formation was limited by NO_x in Lanzhou, consistent with Liu et al. (2010) who identified the NO_x-limited regime in most areas of northwest China. In the southwest, O_3 formation was diagnosed as VOC-limited in Chengdu, but NO_x-limited in Pengzhou due to the large quantities of emissions from petrochemical industry (Tan et al., 2018a). Lyu et al. (2016) reported the VOC-limited regime in Wuhan, central China. The VOC-limited regime has also been repeatedly confirmed for O_3 formation in Shanghai (Xue et al., 2014; Xing et al., 2017) and Nanjing (Ding et al., 2013), eastern China. In the Pearl River Delta of southern China, it was found that O_3 formation was generally limited by VOCs in the southwest, while limited by NO_x in the northeast (Ye et al., 2016). In the NCP, both Han et al. (2018) and Xing et al. (2018) summarized that VOCs limited O_3 formation in most urban areas. However, in the suburban and rural areas, O_3 formation was generally in the transitional regime, *e.g.* Yucheng (Zong et al., 2018), or limited by NO_x, *e.g.* Wangdu (Tan et al., 2018b). From a historical perspective, Jin et al. (2017) pointed out that the sensitivity of O_3 formation to VOCs increased in most Chinese cities, however decreased in some megacities (such as Beijing and Shanghai) due to the stringent control of NO_x emissions in recent years. Different VOCs play non-equivalent roles in O_3 formation.

For details, please refer to lines 70 – 86, page 3.

2. Methodology: as shown by previous studies (e.g. Lu et al., JGR, 2010, 115, D07303; Cardelino and Chameides, AE, 2000, 34, 2325), the measurement quality of NO is of crucial importance for the diagnosis of the Ozone-NOx-VOCs sensitivity, sometimes this may lead to totally different results. The important point is that the detection limit of NO shall be on the level of 100 ppt so that sub-ppb NO can be accurately captured. The use of Mo-converter for the NO_2

measurement is another weakness of the current paper. The interference is really variable case by case.

The excellent and professional comment is highly appreciated. We agree that the accurate diagnosis of O_3-VOC-NO_x sensitivity strongly depends upon the measurement quality of NO and NO_2. In this study, the NO_x analyzer used had the detection limit of 0.4 ppbv for NO, higher than the 50 pptv achievable by Lu et al. (2010) and Cardelino and Chameides (2000). However, the lowest mixing ratio of NO during the sampling period was recorded as 2.4 ppbv, which was also much higher than the lowest mixing ratios (lower than 50 pptv in many afternoons) reported by Lu et al. (2010) and Cardelino and Chameides (2000). Moreover, the lowest value of 2.4 ppbv was 6 times (600% of) the lower detection limit of the instrument. Taking the measurement accuracy of <15% into consideration, we believe that the NO measurement was basically reliable in this study. The reliability of NO measurement is justified in the revised manuscript.

The lowest NO observed during the sampling period was 2.4 ppbv, 6 times (600% of) the lower detection of the NO_x analyzer (0.4 ppbv). Taking the measurement accuracy of <15% into consideration, we believe that the NO measurements were basically reliable.

For details, please refer to lines 160 – 163, page 6.

The potential biases of NO_2 measurements and its influences on the results, including the O_3-VOC-NO_x sensitivity, have been fully discussed in the manuscript.

Studies indicated that NO_2 monitored with chemiluminescence was generally overestimated due to the conversion of the total odd nitrogen (NO_y) to NO by molybdenum oxide catalysts (McClenny et al., 2002; Dunlea et al., 2007; Xu et al., 2013). The positive bias was more significant in more aged air masses, resulting from higher levels of NO_z (NO_z = NO_y - NO_x) (Dunlea et al., 2007). The average overestimation of NO_2 was 22% in Mexico City, which even increased to 50% in the afternoon (Dunlea et al., 2007). Xu et al. (2013) suggested that the chemiluminescence monitors overestimated NO_2 by less than 10% in urban areas with fresh emission of NO_x, but the positive bias went up to 30-50% at the suburban sites. As described in section 2.1, our sampling site was located in the urban area of Ji'nan and was only ~50 m to a main road. Therefore, we infer that NO_2 might not be significantly overestimated in this study. However, the larger overestimations could be expected during O_3 episodes, because the stronger photochemical reactions enhanced the productions of many NO_z species. We adopted 30% (minimum bias in suburban area) and 10% (maximum bias in urban area) as the maximum fraction of NO_2 overestimation during episodes and non-episodes at this urban site, respectively. The influences of the NO_2 measurement interferences on the results were discussed where necessary.

For details, please refer to lines 165 – 180, pages 6 – 7.

Taking the positive biases of NO_2 measurement into account (section 2.2.1), we found that the OH reactivity of NO_x was overestimated by the maximum of 17.5±1.1% and 5.4±0.7% during O_3 episodes and non-episodes, respectively. In the case of maximum overestimations, the actual OH reactivity of NO_x during episodes (4.0±0.7 s^{-1}) might be lower ($p<0.05$) than that during non-episodes (6.6±1.9 s^{-1}).

For details, please refer to lines 331 – 335, page 12.

In reality, the sensitivity of O_3 formation to NO_x might be underemphasized due to the positive biases of NO_2 measurement (Lu et al., 2010). This effect was expected to be more significant during episodes when the overestimates of NO_2 were higher. However, O_3 formation was not likely only limited by NO_x even during O_3 episodes, which should be still sensitive to VOCs, as NO_2 could not be much overestimated in the urban areas (see section 2.2.1).

For details, please refer to lines 618 – 622, page 26.

3. Methodology: as described the sampling site is very close (~50 m) to a main road which would be a problem for a regional (city scale) perspective.

Thanks for the comment. Though the sampling site was very close to a main road, we still believe that the observations at this site to some extent represented the regional O_3 pollution characteristics, in view of the comparable O_3 at this site to those observed at the air quality monitoring stations in the NCP, and the strong influences of regional transport on O_3 variations at this site. Justifications have been added in the revised manuscript.

The high O_3 at almost all the AQMSs in the NCP (Figure 1 (a)) indicated a regional O_3 pollution event in this period. The regional-wide homogeneity was to some extent represented by the observations at the sampling site, in view of the comparable O_3 levels. This was confirmed by the strong influences of regional transport on O_3 variations at the site, as discussed in section 3.3.

For details, please refer to lines 144 – 148, pages 5-6.

At the same time, O_3 was also elevated by transport at an average rate of 18.7±4.0 ppbv/hr, as a combined effect of vertical transport (-40.8±20.2 ppbv/hr) and horizontal transport (59.5±19.8 ppbv/hr).

For details, please refer to lines 466 – 469, page 19.

4. Section 3.3, Figure 7: it is shown the ozone in Ji'an were actually come from the vertical and horizontal transport processes while removed through chemical reactions for most of time. Even during the O_3 pollution episodes, the chemical production of O_3 were much smaller than that from vertical transport. The diagnosed results again showed that this site is not ideal for the study of the Ozone-NO_x-VOCs sensitivity and significantly reduced the value of current study.

Thanks for the comment. It is true that regional transport made considerable contributions to O_3 variation rate in Ji'nan, though the regional O_3 was still originated from the NCP. However, during 9:00 – 15:00 on O_3 episode days, the contributions of chemical reactions (14.0±2.3 ppbv/hr) and transport (18.7±4.0 ppbv/hr) to O_3 variation rate were comparable.

During O_3 episodes, chemical reactions made positive contributions to O_3 production between 09:00 LT and 15:00 LT, with the average hourly O_3 production rate of 14.0±2.3 ppbv/hr. At the same time, O_3 was also elevated by transport at an average rate of 18.7±4.0 ppbv/hr, as a combined effect of vertical transport (-40.8±20.2 ppbv/hr) and horizontal transport (59.5±19.8 ppbv/hr).

For details, please refer to lines 465 – 469, page 19.

Besides, the O_3-NO_x-VOC sensitivity identified in this study was not necessary to represent the completely local or completely regional photochemistry. In fact, the observation based model simulated the in-situ photochemistry, where the observed concentrations of O_3 precursors could be influenced by both local and regional air. It requires caution to extend the results to all the situations, but it is also hard to negate the possible representativeness of the results. Therefore, we emphasize the in-situ photochemical modeling and acknowledge the limitation of the results in the revised manuscript as follows.

This process was further studied through the simulation of the in-situ photochemistry by PBM-MCM. It should be noted that the simulations were based on the observed concentrations of O_3 precursors, which could be influenced by both local and regional air. It required cautions to extend the results to all the situations in Ji'nan, because the regional effect was not always consistent.

For details, please refer to lines 494 – 498, page 21.

5. Figure 8 and Figure 9, et al.: there is a general problem related to the PMF analysis of the observed VOCs samples. As the observed VOCs concentration were quite different from the emitted values, the PMF analysis is not applicable for the observed VOCs concentrations. To consider the VOCs consumption after emission through an estimation of the photochemical age is also not very helpful. The photochemical ages from different sources would be quite different for this site and also for different compounds. I suggest to remove this part and the following related discussions.

Many thanks for the comment. We agree that the ambient concentrations of VOCs were most likely different from those immediately emitted from the sources, because the VOCs were subject to complicated atmospheric processes (such as dispersion, deposition and chemical reactions). Also due to this, the source apportionment of VOCs using PMF sometimes did not represent the real source emission characteristics and contributions to VOCs. However, as one of the most commonly used receptor models, PMF has been extensively employed to resolve the sources of VOCs with the ambient concentrations as input. We think that this application had some rationalities, if the source apportionment results were explained with caution. What we would like to emphasize is that PMF identified the source contributions to the steady – state concentrations of VOCs in the atmosphere. In fact, the observation – based model to simulate O_3 was also constrained by the steady – state concentrations of VOCs and the other O_3 precursors. That was why PMF was applied in combination with the PBM-MCM model (an observation – based model) in this study. Explanations to the source apportionment results are added as follows.

Since the source apportionment was performed for the ambient O_3 precursors which were already subject to atmospheric processes, such as dispersion, deposition and chemical reactions, the results represented the source contributions to the steady – state concentrations of O_3 precursors and the corresponding O_3 productions.

For details, please refer to lines 552 – 555, page 23.

On one hand, the source apportionment of VOCs was not the main objective of this study. On the other hand, we agree that uncertainties existed in the results due to the reasons raised by the referee and the limited number of samples. Therefore, the source apportionment has been moved to the Supplement. For details, please refer to Text S2.

6. Figure 9: the ozone production rates from the box model and that from the regional model are not directly comparable. The box model results assumed a well-mixed condition of the PBL. And it is better compared with the PBL averaged value of the ozone production rates from the regional model.

Thanks for the comment. It is true that the box model simulations assumed the well-mix of air pollutants within the boundary layer. However, the model was constrained by the concentrations of O_3 precursors near the surface (~ 22 m a.g.l.) in this study. Therefore, we believe that the results from the box model should be compared with those simulated on the ground-level layer by the regional model. The justifications are provided in the revised manuscript.

Since the field observations were conducted near the surface (~ 22 m a.g.l.), and the box model introduced below was constrained by the observations, the modeling results on the ground-level layer were extracted from WRF-CMAQ for analyses in this study.

For details, please refer to lines 260 – 263, page 10.

7. Figure 10: the solid lines #1 - #6 from different retrieved sources were not so meaningful as discussed above.

Thanks for the comment. We keep the solid lines #1 - #6 in Figure 8 (Figure 10 in the original manuscript) and the corresponding discussions in the main text due to the reasons illustrated in the response to comment #5.

For details, please refer to the response to comment #5.