Answer to Referee #2:

The authors appreciate the time the reviewer have spent in assisting us to produce a high quality, understandable publication. All the requested corrections and suggestions are addressed and introduced to the revised version of the manuscript. In addition, a few comments which are mentioned both in general and in specific issues are combined to reduce confusion.

Major concerns:

Comment 2.1

Section 3.2: the calculation of PA radical and PAN production rate is incorrect. PA radical is highly variable and can be assumed to be always in a chemical equilibrium with same production and loss rates. In addition to the reversible reactions of PAN, PA + NO2, which are considered only in the present study, there are some other important pathways that can produce and consume PA radical. Some examples include photolysis and OH oxidation of some oVOC species (e.g., acetaldehyde, etc.) and reaction of PA with NO. Considering only the reversible reactions between PAN and PA would be certainly wrong for calculating the PA concentrations and in turn the PAN production rate. The authors mentioned the MCM model in Section 3.3. Clearly, the MCM model is a much better tool for calculating both PA concentration and PAN production rate. It is strange why the authors did not use it here.

Reply: Thanks for pointing out this issue. Actually we did not run any MCM box modeling in this study, thus no PA radical concentrations calculated from MCM model are available. MCM was only used as a library to provide the rate constants of the reactions for the production of key PA precursors and PA.

In terms of the calculation of PA and PAN production, we admit there were some related reactions missed in the calculation, but the approach to calculate PA radical concentrations by using the reactions to form key PA precursors (6 oVOCs) is accepted by a number of researchers, such as LaFranchi et al. 2009 and Xu et al. 2015. In the new round of PA calculation, the pathways suggested by the reviewer, as well as other related reactions included in some classical references including Altshuller 1993, Aneja et al. 1999, Fischer et al. 2014, LaFranchi et al. 2009, Zhang et al. 2015, are considered to give a more accurate estimate.

Comment 2.2

Section 3.3.1: the authors used the MCM model to calculate the relative contributions of NMHCs to PAN production, but don't provide any detail about the model configuration. Such technical details are very critical for evaluating the conclusions presented here. To be honest, I personally highly suspect that the conclusion that alkenes dominate PAN production is not true. First, in most previous studies,

aromatics were found to dominate the VOC reactivity and O3 formation in the Pearl River Delta including Guangzhou. Second, aromatics such as toluene, xylenes and trimethylbenzenes are significant PAN precursors as they can be oxidized to form methylglyoxal. Third, the abundances of these reactive aromatic compounds observed in the present study were indeed high as seen from Table 3. It would be much helpful to make a detailed description of the MCM model for convincing the reviewer and readers your modeling results.

Reply: Sorry for making the reviewer confused. In the text, it was stated that "We calculated the relative contributions of these 24 NMHCs to PAN formation using MCM and the results are shown in Table 4". We admit this statement would seriously mislead the readers because we did not conduct any MCM simulation but use it as a library instead. This following description is added into the revised manuscript to make this statement clearer.

"We calculated the relative contributions of these 24 NMHCs to PAN formation using the rate constants of involved reactions, which were acquired from the MCM program (MCMv3.1, Master Chemical Mechanism), and the results are shown in Table 4.Note that no MCM simulations are conducted in this study."

Regarding the conclusion, to be honest, we still do not fully understand why aromatics did not dominate the production of PAN in the Pearl River Delta during the course of this campaign. However, the detection of high levels of alkenes (e.g. isoprene and propylene etc) with high reactivity may partially explain the conclusion in this study. This study sparked an interesting question which is worth more investigation in the future. The use of MCM simulation for some specific conditions would be helpful to address this issue.

Comment 2.3

Section 3.3.2: the interpretation of the modest correlation between ozone and PAN is not convincing. The moderate correlation between PAN and O3 is normal and has been found in many locations. A major cause should be the different lifetimes of PAN and ozone at high temperatures – PAN tends to be thermally decomposed at noon and in the afternoon with higher ambient temperature. So it is not convincing that the authors attribute solely the modest correlation to the impact of distant sources of PAN. Another argument is that ozone can also be transported (and much easier given its longer lifetime) along with PAN. So if regional transport plays a role here, there should be also some correlation between ozone and PAN.

Reply: Thanks for the comment. We only tested the relationship of daily average PAN and O_3 showing a modest correlation. In the new round of analysis, a higher correlation coefficient is observed between the two pollutants while the use of daily maximum data to replace daily average data. Therefore, as the reviewer suggested, regional transport might be at least not a major contribution to PAN in the area studied. The new results and discussion are updated in the revised manuscript. Also

these results are compared with previous studies (e.g. Xu et al., 2015) in the revised text to investigate the relationship of the two pollutants under different pollution conditions.

Comment 2.4

Section 3.1: the interpretation of seasonal variation is not convincing too. PAN showed the highest concentrations in October and lower values in summer. The authors attributed this to the higher temperature in summer, which especially leads to lower PAN levels at nighttime. At least, a major factor affecting such seasonal variation should be the distinct air flows driven by the Asian monsoon. In brief, summer monsoons bring clean maritime air in summer while winter monsoons bring continental air masses with also favorable weather conditions in autumn. The authors need carefully examine the impacts of both weather condition (e.g., temperature and solar radiation) and air flow patterns, and then suggest the major factor.

Reply: Very good comment. The authors are happy to carefully examine the impact from Asian monsoon and include the results and discussion in the revised manuscript.

General comments:

Comment 2.5

Page 17095, Reactions R1-R2: the reactions R1a-c are far from being complete to describe the formation scheme of PA radical, and thus may be misleading here. There are a number of additional reactions that can produce PA, which should be considered by the authors when analyzing their data.

Reply: We agree with the reviewer. More reactions are included in the new round of PA calculation. The text has also been updated accordingly. Please see the answer to *Comment 2.1* for details.

Comment 2.6

Page 17095, Line 23, "aromatic compounds of relatively low reactivity": many aromatic compounds are reactive.

Reply: The comment is accepted and this confusing sentence has been removed from the text.

Comment 2.7

Page 17098, Section 2.2: I wonder if the authors have any intercomparison result for their NMHC measurements. From Table 3, the concentrations of ethene and propene (to some extent) are very high. What's the source of them given the relatively remote location of the study site?

Reply: There are several previous published papers (e.g. Wang et al. 2008 and Luo et al. 2011) reporting the high levels of ethylene and propene in Guangzhou which is consistent with the results in this study. These studies proposed that, in addition to urbane traffic, petrochemical industries in or around Guangzhou may also contribute to the high concentration of ethylene.

Comment 2.8

Page 17101, Lines 8-10, "daily average concentration of PAN exceeded 5 ppbv": I wonder if it is daily average or daily peak concentration. If it is the former, what's the hourly peak value given the 5 ppbv of 24-hour average? It would be also much better if the authors can provide the detailed time series of measurement data, maybe in SI.

Reply: Sorry for this confusing term. Actually it is hourly peak concentration of PAN. The wording has been modified in the revised manuscript. Also, the detailed time series of measurement data are presented in the SI of the revised manuscript.

Comment 2.9

Page 17102, Line 6: "rates" instead of "rate constants"

Reply: This suggestion is accepted and the text has been changed in the revised manuscript accordingly.

Comment 2.10

Page 17108, Lines 7-8: the values of the maximum hourly average concentrations of PAN and O3 in the Conclusion part are inconsistent with those given in the main context.

Reply: Thanks for pointing out this inconsistence. The values in the conclusion were incorrect due to our carelessness. The error has been corrected in the revised manuscript.

Comment 2.11

Table 3: it is not clear why these NMHC species are the precursors of PAN. In addition to acetaldehyde, acetone and methylglyoxal, there are some other PAN precursors such as MACR, MVK, etc.

Reply: The reviewer is right. In terms of chemical reaction mechanisms, in addition to acetaldehyde, acetone and methylglyoxal, the immediate PAN precursors should also include MACR, MVK and biacetaldehyde, etc. All these PAN precursors mainly come from the atmospheric secondary products of anthropogenic and/or natural NMHCs, and also from the primary sources, such as vehicle emissions and use of solvent. In this study, only NMHCs were considered with a purpose to screen the

candidates with high priority for the control of PAN pollution in Guangzhou. We have realized that it would be better to include all the PAN precursors for examining the sources of PAN. Therefore, in the new round of analysis, all related PAN precursors are considered in the calculation. Some data are from previously published studies.

Comment 2.12

Table 4: how do you get these results?

Reply: We first estimated the amount of PAN formed from each single NMHC species by using the reactions acquired from the MCM library and then calculated the relative contribution to PAN production through being divided by the measured PAN concentration. More detailed description is added in the Method section in the revised manuscript.

Comment 2.13

Figure 1: it is better to show the location of the downtown of Guangzhou.

Reply: Thanks for the suggestion. The downtown of Guangzhou is shown in the revised Figure 1.

Comment 2.14

Figure 2: it is better to provide the standard deviations of the data.

Reply: Good point. The standard deviations are added to the figure in the revised manuscript.

Comment 2.15

Figure 7: are these trajectories only calculated for the first day of each month? How can they be representative of the whole month? How many hours are calculated for the back trajectories?

Reply: We did analyze the backward air-mass trajectories using HYSPLT for every single day and also conducted cluster analysis. We calculated 48 hours for the back trajectories. Unfortunately, for some reason, only one day data was presented in the figure. In the revised manuscript, Figure 7 has been updated accordingly. (See more details from the Answer to Comment 1.5)

References

Luo W., Wang B., Liu S., He J., Wang C. (2011) VOC ozone formation potential and emission sources in the atmosphere of Guangzhou, Chinese Journal of Environmental Science and Technology, 34 (5): 80-86.

Wang, B., Zhang Y., Shao, M., Zhou Y., Feng Z. (2008) Sources apportionment of anthropogenic C2-C9 non-methane hydrocarbons in the atmosphere of Guangzhou, China, Acta Scientiae Circumstantiae, 28 (7): 1430-1440.