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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source analysis of peroxyacetyl nitrate (PAN) in Guangzhou, China: a yearlong observation study" *by* B. G. Wang et al.

Anonymous Referee #2

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The authors present yearlong measurements of PAN and related species in 2012 at a megacity of China – Guangzhou. To my knowledge, there have been some studies of PAN in China in the recent decade, especially in Beijing and Pearl River Delta (where Guangzhou is located in), but most of the measurements are short-term. Although the data is valuable and the manuscript is well organized, there are some fatal problems or weakness in the data analysis and interpretation, and some conclusions are highly doubtful. Therefore, I recommend that this submission is rejected, and the authors are encouraged to improve the data analysis and re-submit the paper.

Major concerns: 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. 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. 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. 4. Section 3.1: the interpretation of seasonal variation is not convincing too. PAN showed the highest concentrations in October and lower values

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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.

General comments: 1. 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. 2. Page 17095, Line 23, “aromatic compounds of relatively low reactivity”: many aromatic compounds are reactive. 3. Page 17098, Section 2.2: I wonder if the authors have any inter-comparison 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? 4. 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. 5. Page 17102, Line 6: “rates” instead of “rate constants” 6. 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. 7. 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. 8. Table 4: how do you get these results? 9. Figure 1: it is better to show the location of the downtown of Guangzhou. 10. Figure 2: it is better to provide the standard deviations of the data. 11. 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

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for the back trajectories?

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