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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 #1

Received and published: 28 June 2015

Review of Wang et al. "Source analysis of peroxyacetyl nitrate in Guangzhou: a yearlong observation study"

Does the paper address relevant scientific questions within the scope of ACP? No - manuscript appears to be of local interest only.

Does the paper present novel concepts, ideas, tools, or data? Yes - new data are presented, but no novel concepts, ideas, or tools

Are substantial conclusions reached? Yes, but they require more convincing (see below)

Are the scientific methods and assumptions valid and clearly outlined? There are some

major issues - see comments below

Are the results sufficient to support the interpretations and conclusions? Not in all cases - see comments below

Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? No - MCM calculations need to be described in more detail.

Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Yes

Does the title clearly reflect the contents of the paper? Yes

Does the abstract provide a concise and complete summary? Yes

Is the overall presentation well structured and clear? Yes

Is the language fluent and precise? Yes

Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Yes

Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? Yes - see comments below

Are the number and quality of references appropriate? Yes

Is the amount and quality of supplementary material appropriate? No - see comment below

âĂČ General comments

Wang et al. present, to my knowledge, not previously reported mixing ratios of PAN, measured by a commercial gas chromatograph, and of O3, NO, NO2*, and non-methane hydrocarbons (measured by two online GC-FID's) at Guangzhou (China) for the year 2012. Averages values are compared to literature values at other locations.

The authors show a calculation of peroxyacetyl radical concentrations, which is incorrect. They then use the MCM (V3.1) to perform a box model simulation and conclude that alkenes accounted for more than 50% of the PAN production, though using Hysplit, the authors conclude that much of the PAN observed was produced upwind of the measurement location. Further, it was found that PAN concentrations poorly correlated with those of O3 (which is not surprising as these molecules have different lifetimes in the troposphere). Descriptive correlations between species are presented.

There have now been several measurements of PAN in China, which all have shown impressive mixing ratios. The main novelty in this work lies in the attempt to link precursors to the observed PAN concentrations and to investigate PAN chemistry over several seasons. Overall, this manuscript draft falls short of a paper suitable for publication in ACP as there are several major issues (see below) and the paper as presented falls outside the scope of ACP - "The journal scope is focused on studies with general implications for atmospheric science rather than investigations that are primarily of local or technical interest." (www.atmospheric-chemistry-and-physics.net/about/aims_and_scope.html).

Major/general issues

1) The data are presented in the form of bar graphs and tables of averages - which is not the best format. I would have liked to see a figure showing the (full) time series of the data, perhaps as a table in the supplemental, and one or two representative shorter periods.

2) Section 3.2 presents an estimate of PA radical concentrations that is almost certainly incorrect (see specific comments below).

3) The authors have used MCM box modeling. (a) I wonder why the PA radical concentration calculation in section 3.2 was conducted in the first place as the MCM would have provided a better estimate. (b) How the MCM box model was set up and run was not described. (c) It is unclear if the box model simulations come close to describ-

ing the real world, as no comparisons of box model output to actual data (O3, NOx, selected NMHCs, etc.) are presented.

4) Hysplit calculations were performed, but I got the impression that they were only run for the first day of each month, and then apparently it was assumed that the back trajectories do not vary over the remainder of each of the months.

5) The authors, correctly, state that a significant fraction of the PAN observed at the measurement location was produced upwind, where VOC mixing ratios were in all likelihood different from those measured. However, this suggests that the MCM box model simulations should not have been initialized with local measurements for those time periods.

6) Why were PPN data not reported?

Specific comments.

pg 17097, lines 3-4. Consider also citing the work by Gao et al. (2014).

pg 17098, line 9 "air samples were first pre-concentrated". Doesn't the Meteorology Consult instrument use a sample loop? Please confirm that the air samples were indeed pre-concentrated, and if so, describe how.

pg 17099, line 7-8 "the CCl4 concentration in the air was very stable". I think I know which peak in their chromatogram the authors are referring to, but can you please provide more information for the uninformed reader (e.g., "retention time of x.y min relative PAN, which eluted at z.x min")? Further, "very stable" is a qualitative statement. Please be quantitative - how stable is "very stable"?

line 9 - "check the stability of PAN signals". Since PAN mixing ratios vary in ambient air and are not expected to be stable between consecutive injections, does this statement refer to the PAN signals during calibrations? If it refers to the calibration, where does the CCl4 would come from, as it is stated that calibrations were carried out in 99.9999% purity N2 balance gas? Or did the authors mean "stability of the air volume injected"?

Please also add a statement as to how much the instrument response drifted/varied over the course of the year.

pg 17101, line 16, and Table 1. Here, the average PAN mixing ratio is compared to averages at other (arbitrarily selected) locations and seasons (most of the other data sets are summertime measurements). As there are many more data sets in the literature, a short statement as to how data sets were selected is needed, or the table needs to be more comprehensive.

My preference here would have been to compare max and median values, to also list the corresponding O3 values, and to compare similar seasons (i.e., for a comparison of summertime data, give the max and median values of your summertime values, as including the other seasons skews the data).

pg 17102 , line 4 - concentration of PA radicals. This entire section is questionable and should be removed. It seems to me that MCM output would have included estimates of PA radicals also that could have been used instead of the questionable steady state expression (2).

line 15 (R3). Please state the values of the rate constants used in the calculation.

Demore et al. 1997 is a very outdated reference, and the expressions for PAN thermal decomposition have been re-measured since. Further, this expression is not valid under conditions when the rate of PAN thermal decomposition is slow (e.g., in winter).

line 20. Eqn (2) is invalid under conditions of high NO concentrations, that also destroy PA radicals. There is also the PA radical reaction with other peroxy radicals to consider.

Table 3. Using only the annual average might lead to misleading results. Consider choosing one or more representative day(s) for each month instead (see comment below)

pg 17105, line 12-14. "We calculate the relative contributions of these 24 NMHCs to PAN formation using MCM". It needs to be described (in detail) how this was done

(preferably in section 2, experimental methods). Also, the results, as presented, sound as if there is only 1 possible scenario, whereas in reality mixing ratios of the precursors, temperatures, and actinic flux have varied considerably throughout the year. Perhaps this calculation should be done for selected days for each of the months sampled. Further, a comparison of MCM output with measurements needs to be presented.

pg 17105, lines 24-25 "the observed PAN concentration is about 1.4 times higher than the calculated value". Considerably uncertainty is introduced by performing a single MCM calculation with annually averaged values. Please comment on the potential role of biogenic compounds such alpha- or beta-pinene (which were not measured).

pg 17106, line 3-4, and Table 5. I would have preferred if the correlations had been calculated for (much) shorter timescales, rather than the for values averaged over 3 month periods, in particular since the back trajectories (pg 17107, and Figure 7) show that air mass origins differed between the months.

Table 5. This table is rather descriptive. Are there any signficant scientific insights?

Figure 3. I am wondering why solar radiation has units of kWh/m2. Shouldn't it be W/m2? Also, consider showing the data in the form of box-and-whisker plots (min, 10th percentile, 25th percentile, median and mean, 75th percentile, 90th percentile, and max) for each month.

Figure 6. It would be informative here to superimpose the thermal lifetime of PAN - to show if it is sufficiently long-lived in the winter months for multi-day transport.

Figure 7 is problematic. It appears that calculations were only carried out for the first of each month, and then the synoptic conditions were assumed to remain constant for the remainder of the month?

References

Gao, T. Y., Han, L., Wang, B., Yang, G., Xu, Z. Q., Zeng, L. M., and Zhang, J. B.: Peroxyacetyl nitrate observed in Beijing in August from 2005 to 2009, J. Environ. Sci.,

26, 2007-2017, 10.1016/j.jes.2014.08.002, 2014.

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