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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in urban and suburban atmospheres of Beijing, China" *by* J. B. Zhang et al.

Anonymous Referee #2

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This paper presents measurements of PAN and PPN in Beijing and a southern suburb during the Summer of 2006. The data are sufficiently useful that the paper could be published in some form. However, there are so many problems with the presentation and analysis that this paper will need to be re-worked extensively. Because of that I have to commend rejecting it.

General:

There are so many instances of unclear, or simply wrong language, that I will not take time trying to list all of them. I recommend the authors go through the paper carefully to insure the language is correct and reflects the meaning the authors intended. The

authors seem to be unaware of simple boundary layer meteorology and how it will be reflected in their observations. The nighttime loss of PAN and PPN has a large component that is caused by deposition to surfaces.

Specific Comments

Introduction: The authors missed several studies of PAN compounds in East Asia as noted in the comment by Tanimoto, and also did not note their own study from the Pearl River Delta (Wang et al., 2010). In addition to the papers noted by Tanimoto, the authors would do well to also look at Russo et al., 2003 who reported PAN in air transported from the general region that contains Beijing.

Page 8177, Lines 20-28. The description of how the PAN calibration source works is not correct. The source relies on the photolysis of acetone at 285nm to make an excess of acetyl radicals. Please read the original work of Warneck and Zerbach, 1992, on which the method is based. The authors say PPN was synthesized but not how it, or if, it was used for calibration. It seems that it wasn't since they rely on the Roberts et al., relative response value, which may not be valid for their system.

Page 8178. It is not clear from the language how the ozone monitor worked or how it was calibrated. The NO/NO2/NOx method is similarly unclear. How was NO2 measured? If it was by a heated catalyst, then that measurement is really an NOy measurement. The description of how NO, PAN and PPN were subtracted to get NO2 implies that it was a heated catalyst. In that case the authors attempt to calculate NO2 this way will not work because it ignores the fact that nitric acid will be a large fraction of the "NOx" signal (likely larger than PAN).

Page 8180 Lines 28-29 There are many more compounds that contribute to PAN and PPN formation than the ones listed here. In fact Altshuller 1993, gives a nice summary of the precursor compounds for PANs.

Section 3.2 The authors need to review some basic things about the planetary bound-

ary layer and how it varies diurnally, and modify the discussion in this section accordingly. Much of the increase from sunrise through the early morning is due not to photochemistry, but to the growth and vertical mixing of the boundary layer. Conversely, at night, PANs can deposit on ground surfaces, and will be lost due to thermal decomposition if there are fresh emissions of NO nearby. Since there are NO measurements, they authors should be able to say something about that.

Page 8183, Lines 2-3. The author state that high ratio of PAN/PPN indicate AHC influence. This is the opposite of what is described in the Roberts and Williams et al., papers, since isoprene is a source of PAN but not PPN.

Page 8184. The discussion on this page is incorrect. The correlations between PAN are significant, especially if the authors were to exclude nighttime data and look at individual days. Lines 10-12. These 2 sentences contain several language and chemical structure errors.

It is not clear what the authors are talking about in the section about heterogeneous reactions and the reference, Jia et al., 2006 is not in the reference list, so I couldn't read it to see what it said.

Page 8185 Line 15. CH3C(O)OO is not acetyl-peroxynitrite, it is the peroxyacetyl radical.

Page 8186. Equation 5 is wrong, as noted in a previous comment. The use of pressure dependent forms for the rate constants is completely unnecessary since the reactions are essentially at their high pressure limits under conditions at the surface sites. Contrary to the text, Page 8187, line 14 the results for the 2 sites were not significantly differently if an accurate assessment of the uncertainties in the calculations were done.

The thermal decomposition rate constants in the Kirchner et al., 1999 paper show a slightly higher rate for PAN.

Page 8188, lines 3-4 the author have the effect backwards, if the ratio of the reaction of

PA radical with NO2 to that with NO is smaller for PAN, compared to PP radical, then NO reaction is more important for PAN, not for PPN as stated.

I could not follow the discussion of TDPAN and TDPPN, I have no idea how they were calculated, or what they mean relative to the measured values. There are no equations that show how they were calculated.

Figures. The figures in general need larger print on their labels and the authors need to make sure the captions have a complete explanation of what is in the figures.

References

Altshuller, A.P., (1993) PANs in the atmosphere, J. Air Waste Manag. Assoc., 43, 1221-1230.

Roberts, J.M., C.A. Stroud, B.T. Jobson, M. Trainer, D. Hereid, E.J. Williams, F.C. Fehsenfeld, W. Brune, M. Martinez, and H. Harder, Application of a sequential reaction model to PAN and aldehyde measurements in two urban areas, Geophys. Res. Lett, 28, 4583-4586, 2001.

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