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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 #1**

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Review of Zhang – PAN and PPN in Beijing

This paper describes measurements of PAN and PPN, as well as ozone and some hydrocarbons, made at two locations in the Beijing area. As China continues rapid economic growth with consequent changes in emissions, and as PAN is a critical component of reactive nitrogen and has influence on ozone production, such data are of interest to the ACP readership. The measurements are from a photochemically active period and appear to have been carefully made. The paper is readable, but suffers in some parts due to repetition and/or a lack of organization. I also found it difficult to decipher the main scientific message of the paper and find some analyses to be wanting.



That said, I think it may be possible to revise the paper accordingly in order to arrive at a version eventually acceptable for publication in ACP.

It seems that a lack of supporting measurements (NO, NO2, radiation, speciated biogenic VOC, etc) are prohibiting a quantitative analysis of PAN and PPN chemistry in this region to test with the observations. Moreover, some of the analyses that are performed result in conclusions that are not necessarily surprising or the analyses lack sufficient rigor so that the results seem less than robust. I suggest the authors organize the paper to present the observations, and describe the main behaviors, e.g. diel averages, dependence on wind direction, PAN and PPN correlations and ratios, and relationship to ozone. I think the discussions of thermal decomposition and relationships to VOCs are either premature or don't result in a useful conclusion. At present, these analyses are rather distracting from some clear results, e.g. the comparisons that can be drawn in Table 1 (which is by no means complete).

Most of the figures are very difficult to read in the pdf version available on the ACPD website. I found it almost impossible to discern axes labels and often tick labels. Figures should be remade with readability at small sizes being the goal.

Secondary Comments

In the abstract max values of PAN are given for the PKU site, but for PPN at the Yufa site. Why not summarize values of both PAN and PPN at both sites?

In the abstract it is stated that the high correlation between PAN and PPN suggests similar VOC precursors. However, a mix of biogenic and anthropogenic VOC with NOx and oxidants could simultaneously produce (in the same air mass) PAN from biogenic VOC and PPN from anthropogenic VOC, and the PAN and PPN would therefore be correlated.

I suggest removing the thermal decomposition discussion from the abstract – that it is important for the lifetime of these species is well documented and thus not a new result.

I also have questions about the differences in the importance of thermal decomposition of PPN between the two sites (see later).

In the methods, Yufa is described as having high natural vegetation and low local anthropogenic pollutants compared to PKU. Later, it is concluded that anthropogenic VOC dominate the photochemistry at both locations – actually the production of PAN and PPN. That would imply measurements at the Yufa site were dominated by transport in from a site with a more anthropogenic influence because if it were an isolated region, PAN production would more likely be dominated by emissions from the natural vegetation. Are the wind direction and lifetime of PAN consistent with this requirement or is the statement characterizing Yufa not necessarily accurate?

In the equipment section, it is stated that the PPN response was 0.83 compared to that of PAN. The next sentence attributes the 0.83 to an earlier paper by Roberts, et al. Was the relative response independently determined, or do authors assume the same relative response? Is it possible for this relative response to drift or be different for different operating conditions? If so, the PAN vs PPN slopes then have systematic error that might make comparing between different sites difficult.

Also in the equipment section, the uncertainties in PAN and PPN measurements are stated without much illustration of how the values were determined.

The discussion of Figure 4 is rather minimal, and the analysis of the VOC precursors is very cursory – limited only to two plots of a time series. The authors state that these are the dominant VOC precursors but there isn't any support given for that assertion except some references to papers that describe sources of PAN and PPN in other regions. The authors note a negative correlation but no discussion of what that means (if anything). Those VOC could be negatively correlated with PAN and PPN for reasons unrelated to any chemistry that might connect them. For example, emissions into a low mixed layer in the morning and evening with little photochemical processing causes VOC to be elevated during the night, and morning and evening; but boundary layer



ventilation and photochemistry cause the VOC to decrease during the daytime while daytime photochemistry leads to increases of PAN and PPN perhaps from a set of different VOC. My recommendation is to drop the figure and relevant text or greatly enhance the analysis.

In the section on Correlations of PAN, PPN, and O3, the slope of PAN vs PPN at PKU is given as 5.60 while that at Yufa is 5.83. The authors conclude that Yufa has higher biogenic VOC influence. Are these two slopes actually different at the 95% confidence interval? Even so, they seem to be very similar compared to PAN and PPN measurements made in biogenically influenced regions – such as a forest in the southeast U.S.

In section 3.4 it would be helpful to move the rate constant values and expressions to a table if this section stays – an equation like 14 is pretty hard to read. I think the section carries little value and should be cut. For example, one of the conclusions (I think?) is that the PPN thermal decomposition rate is different at Yufa and PKU because the ratio of two rate constants differs by about 15% between the two sites. The ratios are quoted with very good precision (+/- 1%). Is this true? Even if the ratios are known that precisely, are the rate constant expressions and their T-dependencies considered to be that accurate? Related to this topic, it is stated that reaction with NO is more important for loss of PPN than PAN, but in the mechanism presented, NO is required for removal of both PPN and PAN, regardless of the decomposition rate. That is, it can't be more or less important for one them.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8173, 2011.