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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.

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Thanks for your suggestive comments. We have reviewed the published papers on PANs. Indeed, most of your comments contribute our improvement of the full-text. Therefore, we have made corresponding revisions and responses as follows. First of all, the reviewer has mentioned that the nighttime loss of PAN and PPN has a large component that is caused by deposition to surface. However, he or she failed to make a link with the full-text about this statement. Namely, we can hardly find out the conflict between the full-text and the reviewer's statement. Secondary, we have updated the literature and related citations have been added in Table 1.

Page 8177, Lines 20-28: For the configuration of PPN's retention time, we used aqueous PPN as a volatile source to make sure its gaseous retention time when it is detected by GC-ECD. , For PPN, the relative response value was used for its quantification. Since the PAN instrument used in this campaign was borrowed from Roberts and his colleagues. The PAN instrument has been used in a number of studies (Roberts et al., 2002; Roberts et al., 2001; Roberts et al., 2007; Roberts et al., 1998). It has been calibrated in lab before and after its running in this campaign. Therefore, the relative response value used in this study is reliable.

Page 8178: Since it is a group campaign, with the consideration about the specific focus on PANs studies, we have briefly introduced the sampling parameters of O3 and other air pollutants. The details can be reviewed in other related studies (Shao et al., 2009; Wang et al., 2010). The mechanism of O3 and NO/NO2/NOx detection are based on ISO10313 chemical luminescence method and ISO7996 chemical luminescence method, respectively. Therefore, the reported NOx by this instrument contains PANs (PAN, PPN, MPAN, etc). During the campaign, there is also a NOy instrument, its value is almost higher than that of NOx instrument. Therefore, the reported NOx by above mentioned instrument was not the value of NOy as the reviewer addressed.

For Page 8180 Lines 28-29: The author addressed there were more compounds that contribute to PAN and PPN formation than the ones listed in the full-text. We agree with the reviewer's comments. A good review on PAN (Altshuller 1993) has provided a comprehensive summary on PAN. However, in this study, we would like to typically focus on PANs atmospheric behavior. Since we have not simultaneously measured their specific VOCs precursors, our present efforts are to investigate their own behaviors and their relationship with total VOCs as a preliminary study. Nonetheless, maybe in the further study, we will try to conduct closure experiment to specifically focus on their VOCs precursors as listed in published review (Altshuller 1993).

Section 3.2 We agree with the reviewer's comments that the planetary boundary layer also plays an important role in the morning's PANs variation. However, it is hard to com-

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pletely conclude the morning rise of PANs just by planetary boundary layer changes. To the best of our knowledge, during the sunrise and increased emission of NOx and VOCs, it should be a major role in contributing the increase of PANs. In addition, there are a number of studies (Ciccioli et al., 1988; Granby et al., 1997; Matsui et al., 2010; Pippin et al., 2001; Shepson et al., 1991; E. J. Williams et al., 1997) have also provided the similar reasons for the increase of secondary photochemical pollutants. Therefore, our statement that the morning rise of PANs concentrations relates to the sunrise and increased emission of primary pollutants cannot be neglected. The reviewer indicated that PANs can deposit on ground surfaces, there is a lack of fraction for this sink. Based on our discussion with the group who is in charge of NOx measurement, the potential of fresh emission at that time can be excluded.

Page 8183, Lines 2-3: The ratio of PAN/PPN is a good indicator to identify anthropogenic control and natural hydrocarbon control. This theory has been well established in a number of studies (Roberts et al., 2001; Roberts et al., 2003; Roberts et al., 2007; J. Williams et al., 2000; J. Williams et al., 1998). Interesting, the reviewer also used Roberts' publication to deny the correctness of the ratio of PAN/PPN as a useful way to preliminary judgment tool. In particular, the reviewer also mentioned that isoprene was a source of PAN but not PPN. It is really the case. However, meanwhile, we also should be neglect that isoprene is also a source of other OVOCs (Duane et al., 2002; Grosjean et al., 1993; Nouaime et al., 1998; Shao 2002; Xie et al., 2008). The fraction of isoprene contributes to PAN formation is complex and problematic. In addition, the source of isoprene is not only just from natural emission.

Page 8184: The reference of Jia et al., 2006 was not cited and will be deleted from the full-text. The discussion about the heterogeneous reactions of PAN and PPN is a preliminary conclusion based on our observation. It has been further investigated in another study (Xu and Zhang 2011).

Page 8185 Line 15: acetyl-perxynitrite will be modified by peroxyacetyl radical.

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Page 8186: The pressure dependent equations listed here is just to provide complete information about PPN's thermal behavior. For further calculation, we also found the pressure variation was not that significantly important in this study. The thermal decomposition rate constants of PAN was depended by local temperature and on the concentration ratio of NO to NO2, therefore, the differences between this study obtained value and the value in (Kirchner et al., 1999) is reasonable. Whatever, there is only slightly different. Page 8188, lines 3-4: the reviewer has neglected the balance of precursor ratio and temperature. Both of them play a role in PAN or PPN formation conversely, namely, with the consideration of the importance of temperature on PAN or PPN formation, NO reaction is more important for PPN. For the part of TDPAN and TDPPN, we have provided detailed steps on its calculation in the section of 3.4. The equations are listed as follows and details about the calculation have been described in the full-text. The main concept for these mathematical calculations has been well established in a number of published references (Grosjean et al., 1994a; Grosjean et al., 1994b; Mineshos and Glavas 1991; Roumelis and Glavas 1992. see Fig PAN generation 1 and 2).

For Figures, we agree with the reviewer's suggestions. We would like to enlarge the figures with the help of the publishing staff and workers. Thanks for your kind comments for the improvement of our study.

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C4335/2011/acpd-11-C4335-2011-supplement.pdf

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

Table 1.

Site	Type	Date	PAN ppbv (max/aver)	PPN ppbv (max/aver)	Reference
Asian continental outflow over the western Pacific (<2 km)	Continental	February-April 2001	4.264/1.225	-/--	(Russo et al., 2003)
Back garden site, Guangzhou, Guangdong Province	Rural	Summer, 2006	3.9/1.24	0.7/0.23	(Wang et al., 2010)

Fig. 1. Table 1

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PAN was generated by acetyl-peroxynitrite ($CH_3C(O)OO\cdot$) and NO_2:

$$CH_3C(O)OO\cdot + NO_2 \rightarrow CH_3C(O)OONO_2 \quad (1)$$

$$CH_3C(O)OO\cdot + NO \rightarrow CH_3C(O)O\cdot + NO_2 \quad (2)$$

$$CH_3C(O)O\cdot \rightarrow CH_3\cdot + CO_2 \quad (3)$$

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO\cdot + NO_2 \quad (4)$$

$$-\frac{d\ln[PAN]}{dt} = \frac{k_2 k_3[NO]}{k_2[NO] + k_1[NO_2]} \quad (5)$$

In which, k_1, k_2, and k_3 are the reaction constants for [PAN], [NO], and [NO_2], respectively. When temperature ranged from 10–40 °C, at standard atmospheric pressure, $k_{6\text{-}PAN}$ = 2.52 × $10^{16}e^{-13573/T}s^{-1}$, $k_{2\text{-}PAN}/k_{1\text{-}PAN}$ = 1.95 ± 0.28 [*Tuazon et al.*, 1991] and $k_{6\text{-}PPN}$ = 7.94 × $10^{16}e^{-13940/T}s^{-1}$ [*Kirchner et al.*, 1999]. Equation (5) can be simplified as

$$-\frac{d\ln[PAN]}{dt} = \frac{k_{6\text{-}PAN}}{1 + \frac{[NO_2]}{1.95[NO]}} \quad (6)$$

$$-\frac{d\ln[PPN]}{dt} = \frac{k_{6\text{-}PPN}}{1 + \frac{k_{1\text{-}PPN}[NO_2]}{k_{2\text{-}PPN}[NO]}} \quad (7)$$

For $C_2H_5C(O)OO$:

$$C_2H_5C(O)OO + NO_2 + M = PPN + M \quad (8)$$

Fig. 2. PAN generation1

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Low pressure limit: 9.00^{E} -28(300/T) ^ 8.9

Hgh pressure limit:7.70^{E} -12(300/T) ^ 0.2

Fc: 0.6, see JPL06 http://jpldataeval.jpl.nasa.gov/download.html) and IUPAC,

http://www.iupac-kinetic.ch.cam.ac.uk/

The equations for the rate constant of reaction (8) are shown as follows:

$$k_r = \frac{k_{\infty,T} k_{0,T}[M]}{k_{\infty,T} + k_{0,T}[M]} F_c^{\left\{1+\left[\lg\frac{k_{0,T}[M]}{k_{\infty,T}}\right]^2\right\}^{-1}} \quad (9)$$

$$[M] = N_a = 6.02E+23\left(\frac{PV}{RT}\right), molec \bullet cm^{-3} \quad (10)$$

PPN thermal decomposition and the reaction between $C_2H_5C(O)OO$ and NO are shown in equations (11) and (12)

PPN = $C_2H_5C(O)OO + NO_2$; 9E-29× exp(14000) (11)

$C_2H_5C(O)OO + NO = NO_2 + CH_3CH_2OO$; 6.70E-12×exp(340/T) (12)

Therefore, $k_{C2H5C(O)OO-NO} = 6.70\times10^{-12}\times e^{\frac{340}{T}}$ (13)

Namely,

$$\frac{k_{C2H5C(O)OO-NO}}{k_{C2H5C(O)OO-NO2}} = \frac{6.70\times10^{-12}\times e^{\frac{340}{T}}}{\frac{7.70\times10^{-12}\left(\frac{300}{T}\right)^{0.2}\times 9.00\times10^{-29}\left(\frac{300}{T}\right)^{8.9}\times 6.02\times10^{23}\times\left(\frac{PV}{RT}\right)}{7.70\times10^{-12}\left(\frac{300}{T}\right)^{0.2}+9.00\times10^{-29}\left(\frac{300}{T}\right)^{8.9}\times 6.02\times10^{23}\times\left(\frac{PV}{RT}\right)}\times 0.6^{\left\{1+\left[\lg\frac{9.00\times10^{-29}\left(\frac{300}{T}\right)^{8.9}\times 6.02\times10^{23}\times\left(\frac{PV}{RT}\right)}{7.70\times10^{-12}\left(\frac{300}{T}\right)^{0.2}}\right]^2\right\}^{-1}}}$$

Fig. 3. PAN generation 2

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