Response to Anonymous Referee #1

We have reviewed the published papers on PANs. Indeed, most of your comments do contribute our improvement of the full-text. Therefore, we have thoroughly modified the full-text. Corresponding revisions and responses are provided as follows.

For supporting measurements, it has been stated in the full-text that details can be reviewed in other related studies (Shao et al., 2009; Wang et al., 2010). The mechanism of NO/NO2/NOx detection is based on ISO7996 chemical luminescence method. Unfortunately, during the campaign, the specific VOCs species detection was limited. Maybe in the future study, we will try to conduct VOCs measurement in order to deepen our understanding about PANs pollution.

For Figures, we also agree with the reviewer's suggestions. We would like to enlarge the figures with the help of the publishing staff and workers.

In the abstract, we agreed with the reviewer's suggestion and added related values as follows:

During August 15 to 27 at PKU Site, maximum and average values of PAN were 11.22 ppbv and 1.34 ppbv, maximum and average values of PPN were 1.95 ppbv and 0.15 ppbv. During September 2 to 12 at Yufa, maximum and average values of PAN were 2.51 ppbv and 0.60 ppbv, maximum and average values of PPN were 0.41 ppbv and 0.08 ppbv.

The reviewer didn't agree with the statement that high correlation between PAN and PPN suggested similar VOC precursors. This understanding has been well accepted in a number of

publications (Nowak et al., 2004; Roberts et al., 2002; Roberts et al., 2007; Wang et al., 2010). The reviewer predicated out a situation that PAN was from biogenic VOC and meanwhile PPN was from anthropogenic VOC, it is possible from mathematic calculation. However, there is a lack of evidence. Whether there is available reference to verify this situation? As we know, the VOCs precursors of PAN and PPN have a high component similarity based on previous studies (Nowak et al., 2004; Roberts et al., 2002; Roberts et al., 2007; Wang et al., 2010; Xu and Zhang 2011; J. B. Zhang et al., 2011). Therefore, the supposed situation by the reviewer may be not real.

Based on the reviewer's suggestion about to remove the thermal decomposition discussion form the abstract, we will follow this suggestion after a careful group discussion. However, the reviewer stated that the calculation of thermal decomposition brought no new result. We can hardly agree with it. Since it is a combination work involved couple of pollutants (including PAN, PPN, NO, NO2) and parameters (such as temperature), the obtained thermal decomposition parts of PAN and PPN are good for our understanding about the thermal decomposition degree of PAN and PPN in Beijing and how about its importance.

For the ratio of PAN to PPN in PKU and Yufa, we have statistically examined their difference (p value =. 0023, namely, significant different). The reviewer has mentioned our observed results were similar to the study in a forest in the southeast U.S. However, there is a lack of related reference for our further check. In addition, the statement of similar results cannot directly indicate urban PAN pollution was the same as that in forest area seemingly.

For the methods, we would like to explain that the site of Yufa was carefully chosen and can represent a background site without significant local anthropogenic pollution. Interestingly,

based on our studies of their concentrations and their ratios, it can be concluded that anthropogenic VOC dominate the photochemistry at both locations. One of the most potential reasons for this is regional transportation of NOx, which contributes to the formation of PAN and PPN there away from the emission region. Other studies (Prestbo and Gaffney 1988; Singh and Salas 1989; Watanabe et al., 1998; J. M. Zhang et al., 2009) also provided evidence for this phenomena.

The uncertainties in PAN and PPN measurements, since the PAN instrument was borrowed from Roberts and his colleagues. The uncertainties have been well defined already. 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) have used this instrument to participate atmospheric campaigns.

For the VOCs precursors study, since there were only non-OVOCs being measured during the campaign, we would like to choose the most important species for PAN and PPN analysis based on previous studies (Altshuller 1993; J. B. Zhang and Tang 1994) on the summary of PANs' precursors. The reviewer suggested us to drop the figure and relevant text about PANs and VOCs discussion. We agreed with it and made corresponding revisement.

In the Section 3.4, for the Equation (14):

$$\frac{k_{C2H5C(O)OO-NO}}{k_{C2H5C(O)OO-NO2}} = \frac{6.70\times10^{-12}\times e^{\frac{340}{T}}}{\frac{7.70\times10^{-12}(\frac{300}{T})^{0.2}\times9.00\times10^{-28}(\frac{300}{T})^{8.9}\times6.02\times10^{23}\times(\frac{PV}{RT})}{7.70\times10^{-12}(\frac{300}{T})^{0.2}+9.00\times10^{-28}(\frac{300}{T})^{8.9}\times6.02\times10^{23}\times(\frac{PV}{RT})}\times0.6}^{[1+\left(\lg\frac{9.00\times10^{-28}(\frac{300}{T})^{8.9}\times6.02\times10^{23}\times(\frac{PV}{RT})}{7.70\times10^{-12}(\frac{300}{T})^{0.2}}\right)^2]^{-1}}$$

Based on,

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

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

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

It is not hard to obtained the ratio of $\frac{k_{C2H5C(O)OO-NO}}{k_{C2H5C(O)OO-NO2}}$, which has been calculated in Equation 14.

Due to there have been two reviewers are hard to understand the calculation processes of the thermal decomposition, we finally decided to cut this part in order to prevent misunderstanding about this part. Although thermal decomposition method used in this study has been well established in other studies (Grosjean et al., 1994a; Grosjean et al., 1994b; Mineshos and Glavas 1991; Roumelis and Glavas 1992). .

Thanks for your kind comments for the improvement of our study.

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