

## Response to comments by referee #1

Dear referee,

Thank you very much for your comments and suggestions. We have revised our paper after considering the comments and suggestions from you and the other referee. Here are our responses (in blue) to your comments and suggestions (in black).

Sincerely,

Xiaobin Xu

On behalf of all author

The authors present two-month wintertime measurements of PAN, O<sub>3</sub> and related species at an urban site in Beijing. They observed decoupling in the variation of ozone and PAN concentrations. The data was analyzed in relation to meteorological transport (using wind and back trajectories and WRF model simulation). Then the wintertime concentrations of PA radical were inferred from the concurrent measurements of PAN and NO<sub>2</sub>, and the formation and thermal decomposition rates were estimated to examine the net contribution of local chemistry to PAN.

There have been very limited measurements of PAN in China. This study reports the first PAN data in cold seasons, which will definitely enrich the literatures. The interpretation of data can be improved by pointing out the significance of PAN measurements in winter and by shortening some general discussions. I suggest publish this manuscript at ACP after the following comments are addressed.

Major comments:

The authors state that previous PAN measurements were all conducted in summer not in winter. Summer time is an obvious season to examine PAN and related pollutants in and around urban areas because of the strongest photochemical activities (producing highest concentrations of PAN and hence the largest impact on human health). The author should elaborate in the introduction the significance of the information on PAN in winter in urban areas, in terms of studies of atmospheric chemistry and/or concern on air quality.

**Yes, we have revised the introduction to make clear the significance of wintertime PAN measurements. Sentences in lines 25-27 on page 31874 have been re-written. And a few sentences have inserted into line 29 to indicate the necessity of the information on PAN in winter.**

The sections on data analysis should focus on some important processes. I found a lot of discussions in the present paper are rather general but have not yielded much new insight on atmospheric processes. I suggest some of these discussions (especially section 3.5) be shortened.

**We have shortened or re-written some parts of the manuscript. See responses to**

## specific comments.

Specific comments:

1. Page 31877, line 17-24: Bernie and Krognes (2000) is cited, but this work is about PAN at a remote site. It is better here to compare the seasonal pattern in the present urban site with other urban sites. In urban areas, PAN should be at highest levels in summer.

**We have removed this part and re-formulated the text, as required by referee 2.**

2. Section 3.2: The author gives a detailed summary of previous measurements in Beijing and other places in China. These results all in summer time, making them different to compare with the present winter data, except pointing out a well-known fact that PAN is higher in summer in urban areas. I suggest removing this section; the authors can briefly compare the results with Beijing summer values in the end of last section.

**We have removed this section and made a brief discussion about the winter-summer difference in Beijing's PAN level at the end of the paragraph of section 3.1.**

3. Figure 3: I suggest showing diurnal profiles of other related species, such as NO, NO<sub>2</sub>, O<sub>x</sub>, T, etc. This will help understand the diurnal variations of PAN and O<sub>3</sub>.

**Yes, this figure has been redrawn and includes now also diurnal profiles of NO<sub>x</sub>, CO, O<sub>x</sub>, and T.**

4. Page 31879, line 25-26: The statement has no supporting data/augment from the authors.

**Indeed, we have no data directly supporting the statement. However, in our previous paper (Lin et al., 2011), we estimated a photochemical O<sub>3</sub> source of 5 ppb/day for the same site and for the winter period. The diurnal O<sub>3</sub> amplitude shown in Fig. 3 is about 14 ppb. These argue for meteorological contribution. We have reworded the text in lines 24-27.**

5. Section 3.4, first paragraph: This part needs to be re-written. When comparing the scatter plot of O<sub>3</sub> and PAN, it is important to keep in mind that the present study is conducted in cold periods and in an urban area. Thus titration of O<sub>3</sub> by NO is important. As a result, the lack of correlation between PAN and O<sub>3</sub> is not surprising. When examining O<sub>3</sub> in urban area where titration is significant, one should use O<sub>3</sub>+NO<sub>2</sub> (O<sub>x</sub>) which takes into account of O<sub>3</sub> titrated by NO. In fact, PAN and O<sub>x</sub> shows a good correction with PAN (Fig 5), as expected. So the discussion of the apparent differences of PAN-O<sub>3</sub> in Beijing and other places do not provide any new information. I suggest re-writing and condensing this and other related parts.

**We have re-written and shortened this paragraph. As suggested by referee 2, we have added before this paragraph another paragraph to discuss the background O<sub>3</sub>. Titration impact on O<sub>3</sub> is mentioned in this added paragraph.**

6. Page 31881, line 13-14: “NO<sub>2</sub> is a better indicator of PAN plume”. I disagree this statement, as Ox should be used for O<sub>3</sub> in this case, and it is a good indicator as well O<sub>3</sub> would be replaced with Ox here.

**This has been removed.**

7. Page 31881, last paragraph: The anti-correlation of O<sub>3</sub> and NO<sub>2</sub>/NO in urban areas is well known, I suggest omit or shorten this part.

**This paragraph has been removed.**

8. Section 3.5, discussions of wind speed and direction: I found this section contains a lot of general and redundant discussions. I suggest the authors significantly shorten this section to clearly indicate the key points they wish to make. When discussing the impacts of wind on the measured pollutants, there is no need to separate the wind speed and direction as they are inherently related with each other. As shown in Figure 8, the westerly winds generally show higher speeds. In the later part of the section on PAN and O<sub>3</sub> lifetimes, it is not surprising to see much shorter lifetime for O<sub>3</sub> due to strong titration of NO, again one should focus on Ox rather than O<sub>3</sub>.

**We have significantly shortened this section. No more separated discussions of impacts of wind speed and direction. Most of the paragraphs 1 and 7, and the whole paragraph 2 are deleted. Some the other text has been re-written. Figure 6 is completely removed. The discussion about the lifetimes is suggested by referee 2 and supports our view about the different behavior of O<sub>3</sub> and PAN. Therefore, we have not changed much in this paragraph, but moved Figure 10 to supplementary material as Fig. S1.**

9. I don't see the need for section 3.6, as the proceeding section has already discussed the impact of air-mass transport (winds and back trajectories) on PAN concentrations. This section can be condensed and combined with section 3.5.

**Following your suggestion, we have removed this section. But we think this case study is not meaningless. Therefore, we have moved this section (text and figures) to supplementary material (S. 2) and added one related sentence at the end of last section.**

10. Section 3.6: It seems that in this section the authors wanted to estimate the rates of formation and decomposition of PAN and then the net chemical formation of PAN. If this is the case, make this purpose clearer in the beginning of the section. I further suggest including the observed rate of change of PAN in Figure 15, this way one can see the relative contributions of local chemistry and dynamic transport. This section can be made more concise.

**We think this comment is made on section 3.7 instead of section 3.6. Following your suggestion, we have re-written this section and redrawn Figure 15 (now Figure 10).**

11. In Fig 2, the unit of CO (ppb) is incorrect, should it be ppm?

**The unit used was wrong. It has been changed to ppm.**