Response to comments by referee #2

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

Wintertime peroxyacetyl nitrate (PAN) in the megacity Beijing: the role of photochemical and meteorological processes (Zhang et al.)
This paper has improved since the first round of review. I am also happy to see that some analysis was expanded. However, there are a still issues left which the authors need to address:
Page 31872, line 9: what is meant by "average": arithmetic mean or median?
Response: "average" here and elsewhere in the manuscript means arithmetic mean.

- Page 31872, lines 9-10: Why can a "small" diurnal cycle be a " significant" diurnal variation?
We used "small" here to emphasize the relatively small amplitude in diurnal cycle when compared with some other observation results. However, the calculated error is obviously smaller than the diurnal change (Fig. 3), so that the diurnal cycle still can be considered significant. To avoid misunderstanding, we have removed the words 'small but'.

- Page 31873, line 1: the ranges given for PA are obscure. Why are the lowest values 0 ppt, while Fig 14 also shows negative values? What are the uncertainties of these values, also given the fact the analyzer used by the authors did not measure NO2 directly?
Our calculations of the PA concentrations are made using approximated formula and several sources of uncertainties are inevitable as we have discussed in the paper. The omitted phys term may be main factor affecting our results. Besides, the calculated concentration of PA also contains errors related to bias in the NO_2 and PAN measurements. The total error in the estimated PA concentration can be so large that it sometimes shows negative but unrealistic values. Therefore, we took zero as the lowest limit in the given PA ranges. Following your suggestion of using uncertainty bars in Figure 14, we have redrawn it and given the standard errors of hourly mean PA concentrations. In addition, we have discussed the uncertainties of the estimate PA values, including the uncertainty due to interferences in NO_2 measurement.

Page 31876, line 24 and line 26: explain abbreviations HYSPLIT and GDAS
Add the following statements.
The HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model is a complete system designed for computing air parcel trajectories to expanded dispersion and deposition simulation. GDAS (Global Data Assimilation System, meteorological reanalysis data archived at National Cholesterol Education Program, 3 hourly, 1 degree×1 degree lat/lon grid, and 23 pressure levels) dataset was used for the meteorological input. And to use these data we must convert data files to HYSPLIT format over a user chosen regional domain after downloading process.
We have added the explanations to the two abbreviations.

Page 31877, line 2: explain abbreviation WRF
The Weather Research and Forecasting (WRF) Model is a next-generation mesoscale numerical weather prediction system used for both operational forecasting and atmospheric research needs. We have added the explanation to this abbreviation.

Page 31877, lines16-23: there is too much speculation about a trend in the PAN data. The time measurement period is too short to make this a conclusive point. The authors should remove this part.
We have removed this part and re-formulated the text.

Page 31878, lines 16-17: what do the authors mean by "modern techniques"? This wording suggests that the previous PAN measurements were not reliable. Why then report those previous measurements?
The early measurements were done using offline technique and old types of GC and ECD. PAN standards were manually synthesized and stored before use. Air samples were manually taken using syringes and injected into the GC systems. The "modern techniques" for PAN measurements use online systems composed of new generation of GC and ECD, program-controlled online sampling/injection and standard preparation, and software for chromatography. Therefore, measurements done using modern techniques are theoretically more reliable. Nevertheless, previous measurements can give an idea of the range of the PAN level.
Following the suggestion of referee 1, we have removed the whole section 3.2 and made only a brief discussion about the winter-summer difference in Beijing's PAN level in section 3.1.

Page 31880, lines 16 etc.: the authors should also discuss the presence background O3 in the Beijing area.
We have added a paragraph at beginning of this section to discuss the background O_3 in the Beijing during winter.

Page 31881, line 3: remove "significant", as r2=0.4 is not a significant number.

We think the "significant positive correlation" here is an appropriate expression. Although the coefficient of determination (R^2=0.4) is not a large one, the correlation is statistically highly significant at α<<0.01 (n=1241).

- Page 31881, lines 14-22: what are the levels of HNO3 in Beijing? It could make a non-negligible contribution the NO2 signal during the daytime.

According to measurements made by Cao et al. (2013), the HNO_3 concentration in Beijing during 6-15 August 2011 fluctuated from 0 to 2 ppb, mostly under 0.5 ppb. No report of winter level of HNO_3 is available. As a photochemical product, however, HNO_3 in winter is not expected to make larger contribution to NO_y than in summer. Moreover, Cao et al. (2013) also demonstrate that the major NOz species (HNO_3,PAN,PPN,HONO) made totally only 7% overestimation of NO_2 concentration when the same type NO_x monitor was used. Considering the high NO_2 concentration we measured, the interferences from HNO_3 and other species should be either minor or negligible. To address your concern, we have included these discussions in the revision manuscript.

Cao, W., Zeng, L., Wu, Y., Hu, M.: An comparative analysis of the accuracy of atmospheric NO_x measurements, Acta Scientiae Circumstantiae, 33,346-355, 2013.

Page 31881, lines 19-20: the statement about the average concentration of NO2 and PAN is not sufficient, as the NO2/PAN ratio can change significantly during the day. The authors should rather estimate the worst case scenario, i.e. during daytime when the NO2/PAN ratio tends to reach a minimum. What would be the contribution of PAN to the NO2 signal?

The PAN/NO_2 ratio reached its maximum at 16:00 (PAN=1.26 ppb, NO_2=25.43 ppb, PAN/NO_2=0.049). Therefore, even in the worst scenario (i.e. at maximum PAN/NO_2 and complete conversion of PAN to NO_2), PAN could cause an overestimation of only 5% of NO_2 concentration. As mentioned above, the total interference from PAN, HNO_3, PPN, and HONO should not be over a few percent. We have added this information to the discussion.

Page 31882, lines 13-22 (and associated Fig 6c): What is the added new information compared to Figures 6a and 6b? I would remove these parts.

This part, including Fig. 6, has been completely removed.

- Page 31883, lines 9-19: this discussion can be shortened significantly, as it is obvious from Fig 7a and 8 that wind speed is the driving force in controlling the concentrations of most pollutants

We have only made a minor revision of this part because we need the information here for the entire section after removing a large part of text directly before this paragraph (as suggested by both referees).

- Page 31884, lines 1-13: Fig 8 shows a combination of Fig 6 and 7. I would strongly

recommend to shorten this lengthy and repetitive.

Fig. 6 and related discussion have been removed. Fig. 8 is needed for showing the contrast of PAN and O_3. The text has been shortened.

Page 31884, lines 10-13: the authors should have Figure 8 split into day vs nighttime data to support their statement and not have speculations,

Splitting Figure 8 into daytime and nighttime does not produce additional information in our context. As can be seen in the following graph (Fig. R1), the only difference between day and night is that there are more data points with low O_3 during nighttime than during daytime. The contrast between PAN and O_3 does change from day to night. Therefore, we decide not to replace the original Figure 8 (now Figure 7) with this graph. To avoid misunderstanding, we have removed this statement.

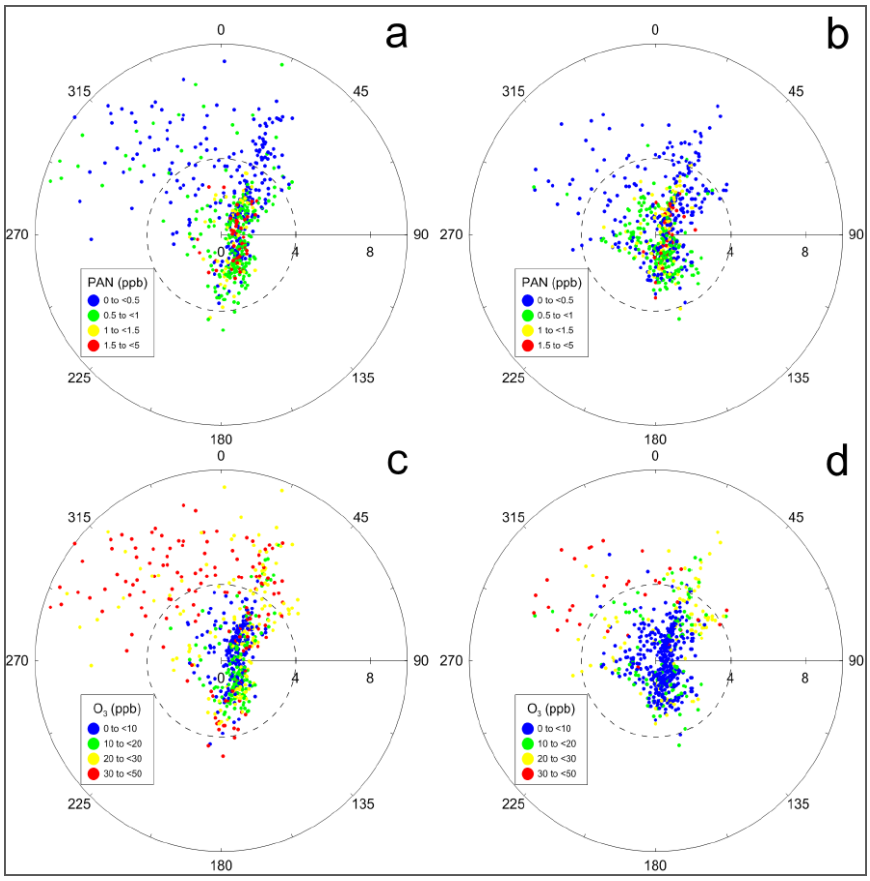

Fig. R1 Scatter plots for the PAN (a,b) and O_3 (c,d) levels observed under different wind directions and speeds during daytime (a,c) and nighttime (b,d).

Page 31887, lines 1-6: the authors should remove this paragraph as the subsequent paragraph discusses the same, but in a more elaborate way.

This paragraph here is introductory and makes not discussion. However, tells the readers that to address the transport process, the MICAPS result (results from observations) and WRF model results (results from simulations) are presented in Figures 12 and 13, respectively. These messages are needed in the next paragraph, which discusses elaborately the transport impact based on Figures 12 and 13.

Therefore, we consider it necessary and have decided to leave it as is. After considering the suggestion of referee 1, we have move section 3.6 to supplementary material.

-Chapter 3.7: this chapter strongly needs an estimate about the uncertainty of the NO2 measurements and its impact on the uncertainty in determination PA.

According to the citation and discussions above, the uncertainty of NO_2 measurements would be 7% in summer and in the worst case, a few percent in winter, due to the interference from PAN and other nitrogen-containing species. If NO_2 were overestimated by 7%, the PA radical would be underestimated by 7.5% according to formula (4). This uncertainty, however, is acceptable for our estimation, which contains even larger uncertainty caused by neglecting physical process. We have included this discussion in the revision.

Page 31889, line 16: what is the estimated contribution of physical processes to PA concentrations? According to Figure 14 it could be significant.

It is difficult to quantify the contribution of physical processes to the PA concentration, not only because we have been using a simplified formula for estimating PA concentration, but also because physical processes can directly and indirectly impact the PA concentration. Assuming that an air-mass containing higher levels of PAN and other pollutants is transported to our site, the rate of change in the PAN concentration can be described as:

$$d[PAN]/dt = k_1[PA][NO_2] - k_2[PAN] + (d[PAN]/dt)_{phys}, \quad (1)$$

where $(d[PAN]/dt)_{phys}$ is the rate of change in PAN related the transport. The PA concentration can be estimated as:

$$[PA] = \{d[PAN]/dt + k_2[PAN] - (d[PAN]/dt)_{phys}\} / k_1[NO_2]. \quad (2)$$

According to the above assumption, $(d[PAN]/dt)_{phys}$ should be a positive value, and both d[PAN]/dt and $k_2[PAN]$ should be larger than those without transport impact. Since we observed a positive PAN-NO_2 correlation (see Fig. 4 in the manuscript), $[NO_2]$ should also be larger than that without transport impact. Therefore, both the numerator and the denominator in (2) become larger if we neglect the transport impact. This means that even if the transport is neglected, its impact to the estimated PA concentration is more or less "buffered" in our case. Nevertheless, such impact may still be significant. Unfortunately, we cannot quantify such impact.

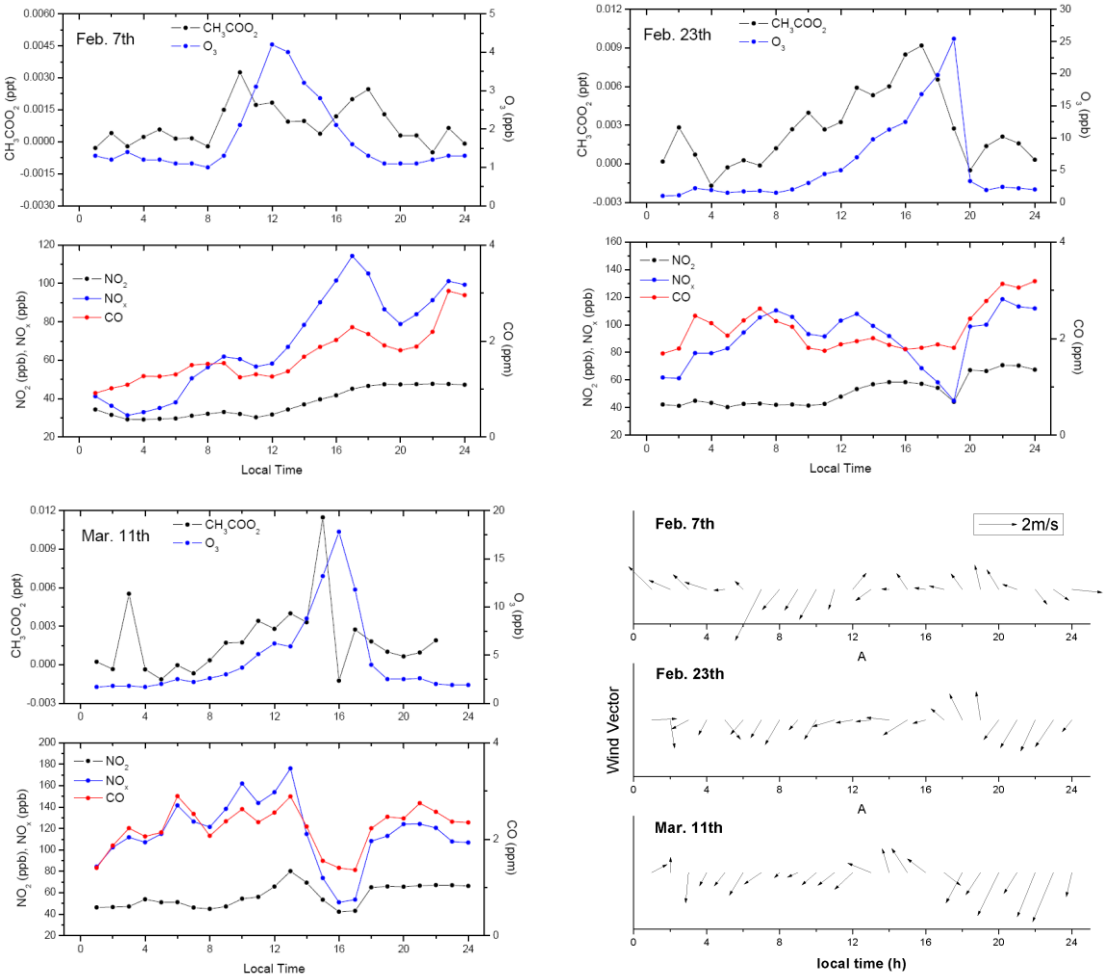

Fig. R2. Diurnal variations of observed O_3, NO_2, NO_x, CO, wind vector, and estimated PA concentrations on 7 February, 23 February, and 11 March, 2010.

Detailed analysis suggests that our estimated PA concentrations for 23 February and 11 March are disturbed for a short time by sudden changes in wind direction and speed. As shown in Fig. R2, the estimated PA concentration drop suddenly around 20:00 LT on 23 February and 16:00 LT on 11 March, respectively. In both case, substantial changes in wind direction and speed occurred, and sudden decrease and rapid recovery of NO_2 and NO_x were observed. In both case, the level of NO_2 was very close to that of NO_x, indicating that polluted urban air over the observation site was replaced for a short period by less-polluted, aged air. Such phenomenon is typically related to physical process (transport). We can see strong disturbance of the estimated PA concentration in Fig. R2. After such disturbance, however, the estimated PA concentration seems to follow the diurnal course.

- Page 31890, line 2-3: Why?

This sentence cannot accurately convey our meaning. Therefore, we have replaced it with "As a photochemical intermediate, PA is highly subject to meteorological conditions and pollutants levels. Therefore, its concentration may vary considerably depending on location and time."

- Page 31890, lines 9-11: units are missing.
For temperature, ℃ is added. For NO_2/NO, ppb/ppb is added.

- Page 31890, line 13: what do the authors mean by "significant"?
We mean that PA was obviously produced during the 09:00–19:00 LT period. We have deleted the word "significant".

- Figure 1: Map of Beijing is way too tiny!
The map has been replaced with a new map clearly showing the topography of Beijing and its surrounding area and the position of the observation site.

- Figure 6c: what is the additional value of this plot compared to 6a and 6b (see also comments above)
We have removed Fig. 6 and related discussions.

- Figure 7: what values are shown: arithmetic mean or median?
All average values shown in our paper are mean values.

- Figure 8: units for windspeed are missing,
The unit is now indicated.

- Figure 11: would suggest to have the yellow background for the daytime period, not for the nighttime period. Is the data for temperature and relative humidity ever discussed in text? Would suggest to remove this plot
Yes, we have changed the background from yellow to grey. Temperature and relative humidity are relevant to our explanation. We have added "Meanwhile, sudden drop of temperature and increase of relative humidity occurred, indicating the air mass had changed (see the grey background area)" in the discussion.

- Figure 12: would suggest to remove the contour lines to enhance clarity of the plot.
The wind contour lines are needed to show the airflow and the convergence zone. To make the plot clearer, we have removed the provincial boundary lines.

- Figure 14: this plot needs uncertainty bars rather than a moving average!
This figure has been modified. Hourly mean values were calculated and plotted on the figure, together with uncertainty bars (standard deviation).

- Figure 15 is still too tiny
The figure has been redrawn, also as required by referee 1.