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Interactive comment

Interactive comment on "Decoupling peroxyacetyl nitrate from ozone in Chinese outflows observed at Gosan Climate Observatory" *by* Jihyun Han et al.

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Correspondence to Referee #1

Thank you very much for your constructive comments. The response for each comment is given below and manuscript was revised accordingly.

Major comments The authors highlighted PM10. I wonder why PM10 not PM2.5, as I would expect the same or even better correlation with PM2.5. Is this just because the authors had the PM10 mass concentration data, not PM2.5 mass concentration data? If so, the explicit statement of PM10 might be misleading, as the readers would think that PAN was specifically correlated with larger particles. Otherwise, the authors can

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Discussion paper

simply mention aerosols without size information. The authors need clarifications on this point. The authors finding of good correlation of PAN to aerosols is interesting and this is obvious from the data, but on the other hand the correlation of PAN to O3 is also good. So, I think decoupling of PAN from O3 is a bit too strong statement, and furthermore, PAN as a potential indicator of overall aerosol formation aged air masses impacted by biomass burning (so I guess smaller particles like PM2.5) also sounds too strong, with only the observed good correlative behaviors. The authors would need to put more analysis or interpretation on the underlying mechanisms to make this statement more robust.

1) PM2.5

During the experiment, PM2.5 was measured under guidance of NIER (National Institute of Environmental Research). However, we were not allowed to report PM2.5 measurement results publically because PM2.5 measurement officially began in 2015. That is why we used PM10 instead of PM2.5 in the manuscript, even though PM2.5 measurements were included for data analysis. These days, however, the levels of PM2.5 has become one of the top issues of Korea and accordingly, it gets much easier to get an access to air quality data. Thus, PM10 was replaced with PM2.5 and relevant statements were changed in revised manuscript. .

2) Decoupling

In urban air, PAN is proportionally increased with O3, leading to good correlation between their daily maxima (e.g., Lee et al., 2008; Zhang et al. 2009) as well as their single measurements.

[Zhang et al., 2009] [Lee et al., 2008]

Zhang, J. M., Wang, T., Ding, A. J., Zhou, X. H., Xue, L. K., Poon, C. N., Wu, W. S., Gao, J., Zuo, H. C., Chen, J. M., Zhang, X. C., and Fan, S. J.: Continuous measurement of peroxyacetyl nitrate (PAN) in suburban and remote areas of western China, Atmos.

Environ., 43, 228-237, 2009.

Lee, G., Jang, Y., Lee, H., Han, J.-S., Kim, K.-R., and Lee, M.: Characteristic behavior of peroxyacetyl nitrate (PAN) in Seoul megacity, Korea, Chemosphere, 73, 619-628, 10.1016/j.chemosphere.2008.05.060, 2008.

In this study, there is reasonable correlation between hourly O3 and PAN measurements as shown in Figure 5a. However, daily PAN and O3 maxima were not proportionally increased particularly in noticeable episodes associated with Chinese outflows, which is presented in Figure 3. Thus, this episode-specific phenomenon is referred to as 'decoupling' in the manuscript. It is also specified in the title. Nonetheless, we found some confusing statement and a special care was given to eliminate ambiguity. For example, the sentence in the line 192-194 (submitted manuscript) was rewritten as follows.

Therefore, the nighttime maximum of O3 can be attributed to the export of O3 from megacities in China. It causes PAN to be decoupled from O3 because PAN levels remained low, even though there was good correlation between the two species.

3) PAN as fine aerosol (PM2.5)

In revised manuscript, the last statement of the abstract was reworded as follows:

"This study highlights PAN decoupling with O3 in Chinese outflows and suggests PAN as a useful indicator for diagnosing continental outflows and assessing their perturbation on regional air quality in northeast Asia." "

Specific comments

1. Abstract: PM10 and PM2.5 OC and EC. . . Does it mean PM10 mass concentration, OC and EC in PM2.5? Please clarify.

As mentioned above, PM10 was replaced with PM2.5 and the relevant figures and statements were all changed in the revised manuscript.

2. In Introduction (Page 3) and Results (Page 6), the authors mentioned previous measurements. However, some important references are missing for both urban/suburban and remote sites in East Asia, and I would note below-referenced work made in Japan. As far as I read the papers, Tanimoto et al. JGR (1999) reported PAN measurements in Tokyo to be 0.6 ppb in November, and Tanimoto et al. JGR (2002) reported approx. 0.5 ppb in spring at Rishiri Island in northern Japan.

They are all added to the revised manuscript in introduction (page 3, line 63-65) and results (page 6, line 118-126).

3. Page 6, Line 138-140: what about correlation to PM2.5?

As PM10 was replaced with PM2.5, relevant statements, Table 1, and Figures (1, 2, 4, 5, 6) were all changed in the revised manuscript. The following figure shows the relationship between PM10 and PM2.5 mass concentrations (slope and r2 values inside) that was not included in the manuscript.

4. Page 7, Line 147-149: PAN is not always coupled with O3... Again, the authors used the word "decoupling" and implied PAN and O3 are not correlated at all, but in fact they are reasonably correlated and the PAN-aerosol correlation was just better that PAN-O3. Do you consider to rephrase the statement?

Please see the response for major comments.

5. Page 8, Line 167-168: elevated concentrations of O3 and/or PAN at night. This is a bit ambiguous. From Figure 3, I can see O3 is elevated but PAN is not. Please clarify or justify.

The highest PAN concentrations were observed during the day in haze days, which is shown in Figure 3. While PAN reached the maximum during the day on Oct 20 and Nov 5, their concentrations were increased from the previous day through the night. This sentence was added to the text to make it clear.

6. In Sections 4.2 and 4.3, the authors discuss fast and slow transport, respectively.

I would suggest to put some estimates on time-scales (how fast and how slow these transport episodes were). In Page 8, Line 181-185, the authors mentioned PAN and O3 formation in the outflow during transport. However, Tanimoto et al. SOLA (2008) paper reported negligible O3 enhancement in fast transported plumes from biomass burning in Siberia.

The time scale is given to the text. It would take 2 days at most for air being transported from Beijing area to Gosan. In contrast, it took about 3 days during haze episode due to the stagnant condition. Although Beijing area is farther from Jeju than Jiangsu province, the Beijing plume reached faster than the biomass combustion impacted air coming from Jinangsu Province.

Tanimoto et al. (2008) compared Boreal biomass burning plumes observed in Rishiri Island and reported that O3 production was not substantial in fresh air masses. In this study, the Beijing plume captured in Gosan is thought to be relatively fresh (less than 2 days) and could be no considerable ozone production during transport. In addition, there was the best correlation between O3 and PAN. Thus, the following sentence was removed in the revised manuscript.

"In this episode, PAN and O3 could have been formed in urban areas or produced in the outflow while being transported."

Page 12, Line 266–: The paragraph on CAM-chem can be moved to the Experimental Section.

The paragraph was moved to the experimental section.

7. All figures: I can see the x-axis is local time, but please clarify.

It is clarified in figure captions (Figure 1& 7).

8. Figure 4: What about adding the same figure for PM10?

As suggested, the color coded trajectories by PM2.5 concentrations is added to Figure

4.

9. Figure 6: These figures are highlight of this paper. However, I see sub-figures d and f are somewhat duplicating and I would delete these.

Figure 6f was removed. Figure 6d shows the enhancement of OC against EC (âŰşOC/âŰşEC) for episode 4, indicating the influence of biomass combustion. Therefore, 6c was removed instead of 6d.

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1

Fig. 1.