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Response to Reviewer #1

General Comments:

The authors provided an analysis for the sources of abrupt PAN enhancement at Shangdianzi (SDZ) station on Oct 20 and Oct 25, 2020. The influences from regional transport were evaluated using CO as an inert tracer; the contributions from various precursors are then calculated based on observations. The authors found CH3CHO oxidation by OH is the major pathway of PAN formation at the SDZ site. I recommend the paper for publication after consideration of the points below.

We thank the reviewer's very helpful suggestions which we believe greatly improve our manuscript.

Specific Comments:

1. Improvements in the language are suggested.

We thank the reviewer for pointing this out. We have carefully checked and improved the language throughout the full text.

2. As shown in the title, the scientific importance of this paper relies on the validity of the conclusion to represent rural North China Plain during the cold season haze events. However, it is unclear whether the analysis based on a single station during pollution events (3 days) has enough representation.

We agree with the reviewer that our result may not be a representative result for all cold seasons, but it still provides insights into fast PAN chemical formation in autumn over the rural North China Plain. Thus, we have changed the title as "Measurement report: Fast photochemical production of peroxyacetyl nitrate (PAN) over the rural North China Plain during haze events in autumn". Similar changes related to "cold seasons" have also revised throughout the manuscript.

The observation is conducted at the SDZ site, a WMO Global Atmosphere Watch (GAW) background station in northern China, which has perfect representation of air pollutant in rural North China Plain illustrated in abundant literatures (Meng et al., 2009; Wang et al., 2013; Ma et al., 2016). The pollution episodes discussed in the manuscript reveal useful information about the photochemical production, not reported by previous studies, which could help us understand severe photochemical pollution over the North China Plain. We have added a brief description in Section 2.1 (Line 99−100) as follows: "The SDZ site is a World Meteorological Organization (WMO)/Global Atmosphere Watch (GAW) background station in northern China, which has perfect representation of air pollutants in rural NCP."

References:

Ma, Z., Xu, J., Quan, W., Zhang, Z., Lin, W., and Xu, X.: Significant increase of surface ozone at a rural site, north of eastern China, Atmospheric Chemistry & Physics, 16, 3969-3977, 2016.

Meng, Z. Y., Xu, X. B., Yan, P., Ding, G. A., Tang, J., Lin, W. L., Xu, X. D., and Wang, S. F.: Characteristics of trace gaseous pollutants at a regional background station in Northern China, Atmospheric Chemistry and Physics, 9, 927-936, 10.5194/acp-9-927-2009, 2009.

Wang, Z. B., Hu, M., Sun, J. Y., Wu, Z. J., Yue, D. L., Shen, X. J., Zhang, Y. M., Pei, X. Y., Cheng, Y. F., and Wiedensohler, A.: Characteristics of regional new particle formation in urban and regional background environments in the North China Plain, Atmospheric Chemistry and Physics, 13, 12495-12506, 10.5194/acp-13-12495-2013, 2013.

3. Lines 236-251: More details should be provided for the calculation in this section. The Phys is calculated with dCO/dt * PAN/CO in Eq. 2. However, I assume Eq. 2 should consider PAN and CO along the transport pathway, particularly, the source domain, instead of SDZ site itself.

Thanks the reviewer for pointing this out. In fact, there is no intense anthropogenic source along the transport from downtown Beijing to the SDZ site. In this study, we assume that PAN/CO ratios change little along the transport pathway during four hours (change rates are calculated every 4 hours). This quantitative calculation is a complement to the view that strengthened local photochemical reactions contributed most to PAN enhancement on the mornings of the two pollution days instead of direct transport, which has also been proved by analysis between variations in wind and PAN concentrations.

Following the reviewer's suggestion, we have revised the sentence in Section 3.3 (Line 257−259) as "There are no intense anthropogenic sources along the transport from downtown Beijing to the SDZ site. Thus, we assume that PAN/CO ratios remain constant along the transport pathway, and PAN change ratio at the SDZ site due to direct physical transport is identical with that of CO." Besides, we have added the information in **Method S2** of the supplement: "CO is usually considered as a chemically inert species and also abundant in the urban region. Here, we assume that ratios of PAN/CO keep constant along the transport pathway, because there are no intense anthropogenic sources along the transport from downtown Beijing to the SDZ site. Thus, the PAN change ratios due to physical processes at the SDZ site are assumed to be identical with those of CO (Eq.2)."

4. Section 3.4: The authors indicated that the contribution from CH3CHO oxidation by OH is larger than that from other precursors. I am wondering whether the total contributions from precursors can explain the observed PAN enhancement, quantitatively?

Unlike O_3, precursors of PAN are only a small set of VOCs that can generate peroxyacetyl (PA) radical. PA radical is directly from photolysis and oxidation of oxygenated VOCs (OVOCs) such as acetaldehyde (CH_3CHO), acetone, methacrolein (MACR), methyl vinyl ketone (MVK) and methylglyoxal (MGLY) (Liu et al., 2010; Fischer et al., 2014; Xue et al. 2014). We only consider the impacts of CH_3CHO, acetone, and MGLY, because observed concentrations of MACR and MVK, oxidation products of isoprene and monoterpene, are rather low in autumn (average: 0.12 ppb) during the observation period, resulting in low PA production rate of about 5500 molec cm^{-3} s^{-1} at noon. This value is even lower than the PA production rate from acetone photolysis, and much lower than through CH_3CHO oxidation. To clarify it, we have added the sentence in Section 3.4 (Line 294−297) as "Although methacrolein (MACR) and methyl vinyl ketone (MVK), oxidation products of isoprene and monoterpene, also contribute to PA production through photolysis (Liu et al., 2010; Fischer et al.,

2014), the observed low concentration (average: 0.12 ppb) in autumn resulted in noontime PA production rate of about 5500 molec cm^{-3} s^{-1}. This is even lower than the PA production rate from acetone photolysis." In addition, we also include the impact of MGLY oxidation by OH in Figure 7. Accordingly, the sentence was added in Line 290 as: "Besides, we also calculate the contribution from oxidation of MGLY by OH to PA production using k×[MGLY] ×[OH]."

In Section 4, we claim that the observed PAN increases during pollution days are caused by increased CH_3CHO concentration and HO_x production (P[HO_x]). On the mornings of pollution days, the mean concentration of CH_3CHO was 2.8 times that on clean days, and the corresponding production rate of HO_x on pollution days was about 2 times that during clean days. The increases in CH_3CHO concentration and P[HO_x] on pollution days (5.6 times that on clean days) could almost explain the enhanced net chemical formation rate (6.3 times that on clean days) with nearly constant reaction rate coefficient (k).

References:

Liu, Z., Wang, Y., Gu, D., Zhao, C., Huey, L. G., Stickel, R., Liao, J., Shao, M., Zhu, T., Zeng, L., Liu, S.-C., Chang, C.-C., Amoroso, A., and Costabile, F.: Evidence of Reactive Aromatics As a Major Source of Peroxy Acetyl Nitrate over China, Environmental Science & Technology, 44, 7017-7022, 10.1021/es1007966, 2010.

Xue, L., Wang, T., Wang, X., Blake, D. R., Gao, J., Nie, W., Gao, R., Gao, X., Xu, Z., Ding, A., Huang, Y., Lee, S., Chen, Y., Wang, S., Chai, F., Zhang, Q., and Wang, W.: On the use of an explicit chemical mechanism to dissect peroxy acetyl nitrate formation, Environmental Pollution, 195, 39-47, 10.1016/j.envpol.2014.08.005, 2014.

Fischer, E. V., Jacob, D. J., Yantosca, R. M., Sulprizio, M. P., Millet, D. B., Mao, J., Paulot, F., Singh, H. B., Roiger, A., Ries, L., Talbot, R. W., Dzepina, K., and Deolal, S. P.: Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution, Atmospheric Chemistry and Physics, 14, 2679-2698, 10.5194/acp-14-2679-2014, 2014.

Technical Comments:

1. Line 130-136: improvement in the language is suggested as continuous "In addition" and "Here" are used.

Well taken. We have revised paragraph to avoid continuous using "In addition".

2. Line 146: It seems Zhu et al. 2018 is not southern coast region.

We have corrected the statement as "It is remarkably higher than several observations from the southern China." In Line 163−164.

3. Line 163: which were 10.6 and 7.7 times larger than those during clean days.

Corrected. Thanks.

4. Line 213: the increases of PAN on pollution days are impossibly caused by direct PAN transport.

Added. Thanks.

5. Lines 214-215: rephrase this sentence: “Here, direct transport impact is restricted to PAN that has been formed in other regions, but exclusive of PAN precursors”.

We have rephrased the sentence in Line 232−233 as “Here, direct PAN transport refers to PAN itself, excluding its precursors.”

6. Line 228: what is “urban city”?

We have changed “city” as “site”.

7. Lines 240-241: rephrase this sentence: “It should be noted that the calculation of physical transport impact aims at PAN that has been formed outside of the SDZ site”.

We have rewritten the sentence. Please see the response to the third specific comment above.