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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.

Response to Reviewer #2

This manuscript investigated the occurrence of PAN, typical VOCs, $PM_{2.5}$, HONO and various trace gases during cold season haze events in the North China Plain, to elucidate the cause of rapid increase of PAN. The article was well written with pre-established methodology. The authors provide some useful information about the formation of wintertime PAN. Overall this manuscript should be accepted after the authors address the issues below.

We are grateful for the reviewer’s invaluable comments. We have carefully addressed all the comments. Please see our response below.

Title: I don’t think it is a representative results for cold-season, exactly in autumn, based on the limited observation data.

Following the reviewer’s suggestion, 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”

- Highlight the new findings of this study. The authors should demonstrate the creative results, especially to differentiate those in previous studies. I think, studies on the occurrence of PAN have been widely obtained. The authors should introduce more studies about them, and discuss the formation mechanisms of PAN, especially in autumn.

We have highlighted the new findings of our work in the following:

(1)We have introduced several studies in which formation mechanisms of PAN during cold seasons in China are discussed, as described in Line 79−86 of Section 1 as "For example, Liu et al. (2018) found a positive relationship between HONO and PAN in winter over an urban site of the NCP, thus highlighted the importance of HONO in faster PAN formation during haze episodes. By conducting sensitivity simulations using the WRF-Chem model, Zhang et al. (2020b) reported that HONO photolysis could result in 80%–150% PAN increases in eastern China during pollution days in winter. However, these studies neglect the impact of carbonyl photolysis that allows for fast photochemistry and may play a dominant role in PAN formation over the rural region with low NO_x emissions. The lack of integrated observation of VOCs, HONO and other related chemical species in previous studies hinders the comprehensive understanding of PAN chemistry."

(2) In this study, we find that HCHO photolysis may play a dominant role in HO_x formation over the rural North China Plain with low NO_x emissions, instead of HONO, thus accelerating the chemical formation of PAN. This is a creative finding which has not been reported in previous studies about PAN formation during cold days. We have emphasized this point in Section 4 and added the following sentence in Line 389−391: "Unlike previous studies in which HONO was considered as the key factor of accelerating PAN formation during pollution days (Liu et al., 2018; Zhang et al., 2020b, Hu et al., 2020), our results demonstrate the dominant role of HCHO photolysis in HO_x production and PAN formation during autumn over the rural NCP region."

References:

Hu, B., Liu, T., Hong, Y., Xu, L., Li, M., Wu, X., Wang, H., Chen, J., and Chen, J.: Characteristics of peroxyacetyl nitrate (PAN) in a coastal city of southeastern China: Photochemical mechanism and pollution process, Science of the Total Environment, 719, 10.1016/j.scitotenv.2020.137493, 2020.

Liu, L., Wang, X., Chen, J., Xue, L., Wang, W., Wen, L., Li, D., and Chen, T.: Understanding unusually high levels of peroxyacetyl nitrate (PAN) in winter in Urban Jinan, China, Journal of Environmental Sciences, 71, 249-260, https://doi.org/10.1016/j.jes.2018.05.015, 2018.

Zhang, J., Guo, Y., Qu, Y., Chen, Y., Yu, R., Xue, C., Yang, R., Zhang, Q., Liu, X., Mu, Y., Wang, J., Ye, C., Zhao, H., Sun, Q., Wang, Z., and An, J.: Effect of potential HONO sources on peroxyacetyl nitrate (PAN) formation in eastern China in winter, Journal of Environmental Sciences, 94, 81-87, 10.1016/j.jes.2020.03.039, 2020b.

- Analytical method appeared adequate; however some key procedural and QA/QC details on the observation of PAN, typical VOCs, HONO and various trace gases are missing. Please provide more details in the manuscript.

We have added more detailed information about the measurements and instruments in Section 2.2 (in red), as suggested. Please see in the revised manuscript.

- The authors mentioned that, “Formaldehyde (HCHO) photolysis dominates the daytime HOx production thus contributing to fast photochemistry of PAN”. Limited VOCs species were measured in this study. How about the contributions of other VOCs species? Other studies had found that acetaldehyde was regarded as the most important precursor of PAN during winter in Beijing, could you explain it?

We agree with the reviewer that other processes, such as reactions between alkenes and O_3 could also contribute to HO_x production during the daytime. Because of observation limitation, we could not measure all kinds of VOC species and have difficulty in estimating their contributions. Besides, HO_x production from VOCs oxidation by O_3 is usually supposed to be small during cold days (Tan et al., 2018; Li et al., 2021) owing to rather low O_3 concentrations compared with warm seasons. Therefore, we believe HCHO photolysis dominates the daytime HO_x production in this study based on the current observations.

In Section 3.4, we show that the reaction of acetaldehyde with OH radical is the major source of PA radical, contributing to form PAN. Thus, we consider acetaldehyde as the most important VOC precursor of PAN. Our result is consistent with previous studies in eastern China (Zeng et al., 2019a; Zhang et al., 2020b) and even during winter Beijing (Xu et al., 2021). Using a box model constrained by observed concentrations of precursors, Xu et al. (2021) found that acetaldehyde could be the most important precursor of PAN during winter at an urban site in Beijing. We have added the citation in Section 3.4 and revised the corresponding sentence in Line 297−299 as “Our results are consistent with previous studies, in which they have also confirmed the dominant role of CH_3CHO+OH in PA formation during winter in urban Beijing (Xu et al., 2021), over eastern China (Zeng et al., 2019a; Zhang et al., 2020b) and even on global scale (Fischer, et al., 2014).”

References:

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.

Li, K., Jacob, D. J., Liao, H., Qiu, Y., Shen, L., Zhai, S., Bates, K. H., Sulprizio, M. P., Song, S., Lu, X., Zhang, Q., Zheng, B., Zhang, Y., Zhang, J., Lee, H. C., and Kuk S. K., Ozone pollution in the North China Plain spreading into the late-winter haze season, PNAS, 118, e2015797118, 2021.

Tan, Z., Rohrer, F., Lu, K., Ma, X., and Zhang, Y.: Wintertime photochemistry in Beijing: Observations of ROx radical concentrations in the North China Plain during the BEST-ONE campaign, Atmospheric Chemistry and Physics, 1-33, 2018.

Xu, W., Zhang, G., Wang, Y., Tong, S., Ma, Z., Lin, W., Kuang, Y., and Xu, X.: Aerosol Promotes Peroxyacetyl Nitrate Formation During Winter in the North China Plain, Environmental Science & Technology, 55,6,3568-3581, https://doi.org/10.1021/acs.est.0c08157, 2021.

Zeng, L., Fan, G.-J., Lyu, X., Guo, H., Wang, J.-L., and Yao, D.: Atmospheric fate of peroxyacetyl nitrate in suburban Hong Kong and its impact on local ozone pollution, Environmental Pollution, 252, 1910-1919, https://doi.org/10.1016/j.envpol.2019.06.004, 2019a.

Zhang, J., Guo, Y., Qu, Y., Chen, Y., Yu, R., Xue, C., Yang, R., Zhang, Q., Liu, X., Mu, Y., Wang, J., Ye, C., Zhao, H., Sun, Q., Wang, Z., and An, J.: Effect of potential HONO sources on peroxyacetyl nitrate (PAN) formation in eastern China in winter, Journal of Environmental Sciences, 94, 81-87, 10.1016/j.jes.2020.03.039, 2020b.

- For production rates of HOx and PA under different pollution level, do you compare them with OBM-MCM analysis?

By comparisons, our results about the PA production rates are consistent with previous studies, in which they have also confirmed the dominant role of CH_3CHO+OH in PA formation during winter in urban Beijing (Xu et al., 2021) and over eastern China (Zeng et al., 2019a; Zhang et al., 2020b) using the MCM box model, and even on global scale (Fischer, et al., 2014). These statements have been added in Line 297−300 of Section 3.4 as "Our results are consistent with previous studies, in which they have also confirmed the dominant role of CH_3CHO+OH in PA formation during winter in urban Beijing (Xu et al., 2021) and over eastern China (Zeng et al., 2019a; Zhang et al., 2020b) as indicated by the MCM box model, and even on global scale (Fischer, et al., 2014)."

We have compared the production rates of HO_x with previous OBM-MCM analysis in the 2nd paragraph of Section 3.5. To address it, we have added the sentence in Line 355−356 as "Using the observation-based box models, most of these studies reported the importance of HONO in OH radical and atmospheric oxidation capacity during cold days over the NCP."

Furthermore, we also compared the HO_x production rates due to HCHO photolysis with other studies, as demonstrated in Line 375−378 as: "The HCHO photolysis rate of 3.2×10^6 molec cm^{-3} s^{-1} averaged during daytime of pollution days is higher than pervious results in an industrial zone of southeastern China (1.6×10^6 molec cm^{-3} s^{-1} averaged over 7:00−16:00) (Zheng et al., 2020) and a suburban site of Beijing in 2016 (~0.2 ppb h^{-1} at noon) (Tan et al., 2018), but close to recent modeling result in Beijing during winter 2020 (Li et al., 2021)."

References:

Li, K., Jacob, D. J., Liao, H., Qiu, Y., Shen, L., Zhai, S., Bates, K. H., Sulprizio, M. P., Song, S., Lu, X., Zhang, Q., Zheng, B., Zhang, Y., Zhang, J., Lee, H. C., and Kuk S. K., Ozone pollution in the North China Plain spreading into the late-winter haze season, PNAS, 118, e2015797118, 2021.

Tan, Z., Rohrer, F., Lu, K., Ma, X., and Zhang, Y.: Wintertime photochemistry in Beijing: Observations of ROx radical concentrations in the North China Plain during the BEST-ONE campaign, Atmospheric Chemistry and Physics, 1-33, 2018.

Zheng, J., Shi, X., Ma, Y., Ren, X., Jabbour, H., Diao, Y., Wang, W., Ge, Y., Zhang, Y., and Zhu, W.: Contribution of nitrous acid to the atmospheric oxidation capacity in an industrial zone in the

Yangtze River Delta region of China, Atmos. Chem. Phys., 20, 5457-5475, 10.5194/acp-20-5457-2020, 2020.

- The authors are suggested to discuss the impact of environmental factors (including temperature, wind speed and SLP, etc) on the pollution characteristics of PAN.

We agree with the reviewer that environmental factors have great impacts on the pollution characteristics of PAN, which have been discussed in Section 3.2. To clarify it, we have revised the following sentences:

(1) Line 204−206: "As the observation site is located north of the urban region, the prevailing southwesterly winds could promote pollution transport from downtown Beijing to the rural site."

(2) Line 219−222: "Consequently, the meteorological conditions during pollution events are favorable for accumulation and transport of PAN and its precursors, as well as promoting chemical formation due to relatively higher temperature and RH compared with clean days, though reductions of photolysis rates are identified."

Response to Reviewer #3

This paper explored enhancements in PAN over the North China Plain at the Shangdianzi (SDZ) site for two October days. After meteorological analysis, the authors determined that direct PAN transport was impossible given the timing of prevailing southerlies and used CO as a tracer to confirm. Local enhancements in photochemistry were determined to be the source of enhanced PAN. Authors used observations of various precursor species to calculate respective contributions and found that oxidation of acetaldehyde by the hydroxyl radical was the main pathway for PAN formation at the SDZ site.

I recommend this paper for publication given the following minor edits:

We appreciate the positive feedback from the reviewer. All the concerns have been addressed in the following.

Specific comments:

- The title suggests generalizability to all cold-season haze events, though 3 October days were examined. Additional observation/analysis is necessary in order to determine generalizability to all cold-season pollution events with PAN enhancements. Revision to the wording of the title is suggested.

Thank you for the title suggested. The precedent version of the title has been replaced, becoming "Measurement report: Fast photochemical production of peroxyacetyl nitrate (PAN) over the rural North China Plain during haze events in autumn".

- The authors concluded that conditions were anomalously warm and wet for days of study, though title suggests "cold-season". As a reader, I question whether results are generalizable to "cold-season" days when anomalously warm and wet conditions are not present.

As suggested by the reviewer, we have changed “cold-season” in the title as “in autumn”. The meteorological conditions during pollution days are anomalously warm and wet in comparison with clean days. It is not inconsistent with “cold season” or “autumn”.

- Figure 3b -- it is unclear as to what "clean days" refers to.

Thank you for pointing this out. The clean days refer to the days excluding three pollution days during the observation period. The Figure 3 caption now reads: “Wind at 925 hPa and sea level pressure (hPa) derived from ERA5 (a) averaged during 10/13−10/27, (b) clean days (10/13−10/19, 10/21−10/24) and on (c) 10/20 and (d) 10/25. The red asterisk in (a) shows the location of the SDZ site.” Similar changes have been made in captions of Figure 4, Figure 8 and Figure 10.

- Improvements in grammar and language are suggested.

Thanks for the reviewer’s suggestion. We have carefully checked and improved the language throughout the full text.

Technical comments:

- Line 116 - listed chemical species naming is not consistent with respect to chemical formula and English name use.

Following the reviewer’s suggestion, we have revised the sentence as “The proton transfer reaction-time of flight-mass spectrometer (PTR-ToF-MS) is used to measure concentrations of formaldehyde, acetaldehyde, acetone, propene and isoprene etc.”

- Line 185 - lack of consistency in naming wind directions. "Southwesterly" should be used rather than "Northwestern". "Southwesterly" should be followed by "winds" to be complete (i.e. Southwesterly winds)

As suggested by the reviewer, we have changed “southwesterly” to “southwesterly winds” throughout the full text.

- Line 186 - sentence reads “..the SDZ site was **in** the south of a strong” should read “...the SDZ was **to** the south of a strong..”

Corrected. Thanks.

- Line 187 - sentence reads “The southwesterly on 10/25 was caused by a weak high-pressure system with anticyclone in the southeast” should read “the southwesterly ***winds*** on 10/25 ***were*** caused by a weak high-pressure system with **an** anticyclone in the southeast.”

This sentence has been updated as suggested by the reviewer.

- Line 195 - “meridian” should be “meridional”

Corrected. Thanks.

- Line 217 - Wind direction naming consistency -- “southern wind” should be changed to “northerly wind” if this is what is meant.

To keep consistency, we have changed “southern wind” to “southerly wind”.

- Lines 240-245 are not interpretable by the reader because the meaning of (Chem + Phys), (Chem), (Phys), were not clearly defined.

Thanks for your suggestion. We have added the sentence in Line 260 as: “Here, we define PAN change rates induced by chemical processes and physical processes as Chem and Phys, respectively.”

- Line 335 - “while our results *was* based on” should be “while our results ***were*** based on”

Corrected. Thanks.

- Line 358, 395 - wind direction naming consistency needed.

We have changed “southern wind” to “southerly wind” throughout the full text.