Manuscript Number: acp-2021-359

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."