Response to Referee # *1*

All of the line numbers refer to Manuscript No.: EGUSPHERE-2024-3337.

Title: The Impact of Organic Nitrates on Summer Ozone Formation in Shanghai, China

Journal: Atmospheric Chemistry and Physics

We thank the reviewers' valuable comments and suggestions, we responded to the comments point to point, and revised the manuscript carefully. As detailed below, the referee's comments are shown in italicized font, our response is in orange, and new or modified text is in blue.

Reviewers/Editor comments:

Referee #1:

The study entitled "The Impact of Organic Nitrates on Summer Ozone Formation in Shanghai, China" by Li et al. investigates the role of alkyl nitrates (ANs) and peroxy nitrates (PNs) in ozone (O_3) formation using field measurements and modeling. The authors highlight that PNs suppress O_3 production, and the production yields (α) of ANs significantly influence the sensitivity of O_3 formation to its precursors. These findings are critical for informing future air pollution mitigation policies. While the study is well-conducted and generally well-organized, certain areas require clarification or further analysis before publication.

Major comments:

1. *The abstract mentions that "scenario analyses revealed that production yields (α) of ANs would alter the response of O_3 formation to precursors due to varying compositions of volatile organic compounds." However, the sensitivity tests appear to use a linear relationship between α and VOC concentrations, as indicated in Fig. 8c. It is unclear how this linear relationship was derived. How does α vary with VOC composition in the sensitivity tests? Are there other factors, such as NOx levels, that might influence the variation in α? Adding context in the introduction about the derivation of α and its dependencies would greatly improve clarity.*

Thanks for your suggestion. The branching ratio (α), the reaction ratio $k_b/(k_a+k_b)$, are different for various VOCs. Here, we use the effective α to analyze the effect of ANs chemistry on ozone production, which was calculated by weighted average based on the distribution of VOCs and the corresponding α. Therefore, the change of VOCs composition would change the effective α. As mentioned in our main text, the VOC compositions in polluted areas usually corresponds to high distribution of effective α and clean areas are linked to low distribution of effective α (Rosen et al., 2004;Perring et al., 2010;Perring et al., 2009;Perring et al., 2013;Farmer et al., 2011).Here, for simplicity, α are set to show a linear decrease with the decrease of VOCs to describe the relationship, which has also been used in the previous study (Farmer et al., 2011). To improve clarity, we have added the discussion as below "For simplicity, we use a

linear relationship between α and VOC concentration in the sensitivity analysis, as shown in Fig. 8d. An α value of 0.005 was selected for clean condition with VOC concentration less than 5 ppbv, while 0.12 was selected for polluted condition with VOC concentration larger than 100 ppbv. The lower limit of 0.005 is the average of the α for methane and ethylene. The upper limit of 0.12 is set as the reported value of the α for isoprene and the α for aromatic hydrocarbons are generally distributed around 0.1 (Perring et al., 2013). The assumption of this linear relationship between α and VOC concentration has also been applied in a previous study (Farmer et al., 2011)."

According to current research, there are limited evidences showing the potential influence of NO_x level on α value. The values of α are associated with the carbon chain structure of the VOC molecule, the distribution of functional groups, temperature, and pressure (Reisen et al., 2005;Arey et al., 2001;Wennberg et al., 2018;Russell and Allen, 2005;Butkovskaya et al., 2012;Cassanelli et al., 2007), which varies between 0.1-35% (Table S1).

In addition, the definition of α and its dependencies are added in the introduction as "For ANs formation, the branching ratio (α), the reaction ratio $k_{1b}/(k_{1a}+k_{1b})$, varies between 0.1-35%, which are associated with the carbon chain structure of the molecule, the distribution of functional groups, temperature, and pressure (Reisen et al., 2005;Arey et al., 2001;Wennberg et al., 2018;Russell and Allen, 2005;Butkovskaya et al., 2012;Cassanelli et al., 2007)."

$$RO_2+NO \rightarrow RO+NO_2 \quad (R1a)$$
$$RO_2+NO \rightarrow RONO_2+NO_2 \quad (R1b)$$

2. *The findings on the localized impact of organic nitrates in Shanghai are valuable but would benefit from broader context. For instance, how does the suppression effect of PNs on O_3 in Shanghai compare to other urban or cleaner environments? What factors might explain differences in the impacts across various locations? Expanding the discussion to include comparisons with other field measurements would help strengthen the generalizability of the study's conclusions.*

Thanks for pointing out the issue. We have compared the impact of organic nitrates in SH to that in XJ, which is under a cleaner environment. To better present the generalizability of our study, we further compare our results with previous studies on the effect of PAN chemistry on O_3 production derived from other places. The revised texts and additional comparison are revised as follows. "Here, we compare our observations with the study previously conducted in Xinjin, which is a suburban site, located in basin topography and faces emerging ozone pollution recently, to determine the effect of organic nitrate on O_3 production under different pollution conditions (Li et al., 2023)." The comparison analysis about the effect of PNs on O_3 in section 3.3 is added as below. "The integrated inhibition of PNs photochemistry on O_3 production was 4.5 ppbv in the Shanghai campaign (Fig. 7b), which was less pronounced than the Xinjin campaign (20 ppbv). The reduced inhibition can be attributed to the lower PNs production rate (P(PNs)) observed in the Shanghai campaign (Fig. S3), where the maximum daytime P(PNs) was 0.89 ppbv/h, much lower than that in Xinjin campaign (3.09 ppbv/h). In addition, the two campaigns had similar concentrations of VOCs, but daytime average of NO_x in Shanghai site is 22.0 ppbv, which is much higher than that of Xinjin site (10.2 ppbv). The PNs formation would be reduced under high NO_x condition due to the rapid termination reaction via OH and NO_2, and thus limited the

suppression effect of PNs formation which is the case in Shanghai campaign. Like in Xinjin campaign, PAN chemistry suppressed O_3 formation at a rate of 2.84 ppbv/h at a suburban site in Hong Kong (Zeng et al., 2019). However, it was reported that PAN tended to suppress O_3 production under low-NO_x and low-RO_x conditions but enhanced O_3 production with sufficient NO_x at a rural coastal site in Qingdao, which is consistent with the comparison of Xinjin and Shanghai campaigns (Liu et al., 2021)."

3. *The authors emphasize that organic nitrate chemistry should inform future policy decisions. However, the study indicates that the impact of varying α on O_3 production in Shanghai is insignificant, likely associated with high NOx levels at present. To highlight the increasing importance of organic nitrates in future scenarios, I recommend conducting sensitivity analyses with reductions in NOx (and VOC) emissions. These additional simulations would demonstrate the evolving role of organic nitrates under cleaner air conditions and provide stronger policy-relevant insights.*

Thanks for your suggestion. The related analysis has been provided in section 3.4. To improve the clarity, "Take the cases of the horizontal dashed line as an example, at a fixed NO_x, the $P(O_3)$ start to increase as the VOCs decrease from 100 to about 60 ppbv, and subsequently decrease as VOCs concentrations continue to decrease. Therefore, an increase in α directly correlates with a reduction in the $P(O_3)$ peak." is revised as "Take the cases of the horizontal dashed line as an example, at a fixed NO_x, the $P(O_3)$ increases as the VOCs decrease within the range of about 60 to 100 ppbv, whereas $P(O_3)$ subsequently decrease as VOCs fell below 60 ppbv. Therefore, with the reduction in VOCs emission, an increase in α directly correlates with a reduction in the $P(O_3)$ peak." Cases representing cleaner condition (low NO_x and VOCs) is added in Fig. 8b as suggested by reviewer. The additional sensitivity analyses in section 3.4 are added as follows: "Scenarios with different VOCs reactivity and α are selected for sensitivity tests to further investigate the impact of ANs chemistry on the O_3 pollution control strategy in Shanghai. As illustrated in Fig. 9a, variations of $P(O_3)$ among three scenarios exhibit an initial increase followed by a subsequent decrease with rising NO_x. For the typical VOC reactivity and α obtained from the Shanghai campaign, the turning point from NO_x benefit to NO_x limitation for $P(O_3)$ occurs at NO_x concentration of 1.38 ppbv, when $P(O_3)$ reaches a peak of 33.0 ppbv/h. When VOCs are reduced by 20% without accounting for the reductions in α, the turning point for NO_x decreases to 1.26 ppbv with the $P(O_3)$ peak decreasing to 30.1 ppbv/h. When the reduction of α is considered alongside the decrease in VOCs (α decreases to 0.0265), the peak of $P(O_3)$ remains the same as the initial case. Consequently, neglecting the α changes is likely to overestimate the effectiveness of emission control. Our observations indicated that NO_x in Shanghai was notably high, which accords with the conditions to the right of the turning point in Fig. 9a. In this case, the major chain-termination reaction of the HO_x cycle is the reaction between OH and NO_2 to produce HNO_3, while the share of the reaction that produces ANs through the reaction between RO_2 and NO becomes relatively minor. As illustrated in Fig. 9a, when NO_x changes from 22.0 to 1.0 ppbv, the impact of α change will be larger, as the $P(O_3)$ difference between the two cases ranges from 0.1 to 2.6

ppbv/h. Therefore, the variation of α has a limited impact on O_3 production at high NO_x, whereas it offsets the impact of VOCs reduction as NO_x decrease to around 1.5 ppbv which represents a low-NO_x emission condition. In addition, the sensitivity analyses in a reduced VOC condition show that neglecting the α change still overestimates the impact of VOCs reduction on $P(O_3)$ by around 4 times with NO_x of 1 ppbv (Fig. 9b), which is also more significant than the case in Shanghai campaign."

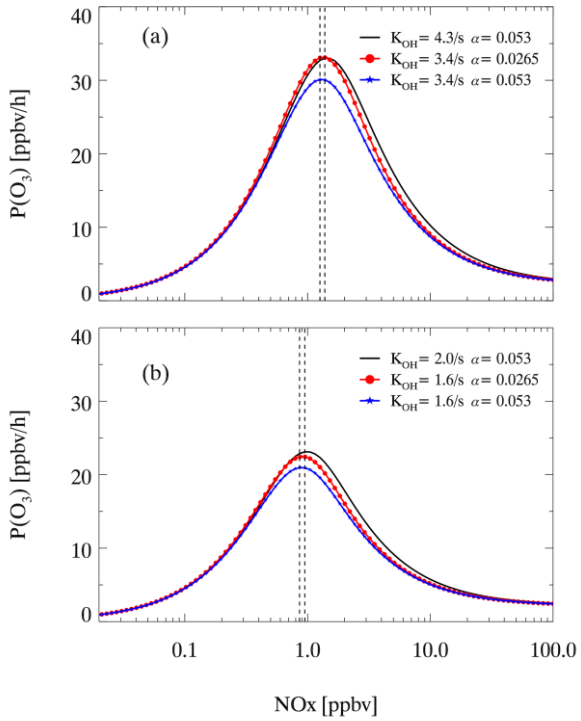

Figure 9. The ozone production rate ($P(O_3)$) varies as a function of NO_x under different VOC-NO_x regimes during Shanghai campaign: (a) under mean measured parameters during the whole campaign (solid line, VOC reactivity (K_{OH}) of 4.3/s, ANs branching ratio (α) of 0.053); a 20% reduction in K_{OH} with a 50% reduction in α (red dot line, 3.4/s, 0.0265); a 20% reduction in K_{OH} with no change in α (blue dot line, 3.4/s, 0.053). (b) under observed parameters during the clean days (solid line, K_{OH} of 2.0/s, α of 0.053); a 20% reduction in K_{OH} with a 50% reduction in α (red dot line, 1.6/s, 0.0265); a 20% reduction in K_{OH} with no change in α (blue dot line, 1.6/s, 0.053). Dash lines show the turning point in different cases.

Minor comments:

1. *Line 54: The statement, "which are produced from RO_2 in the presence of oxidants...", is incorrect.*

Thank you for pointing out the mistake. "which are produced from RO_2 in the presence of oxidants such as OH." is revised as "which produce RO_2 in the presence of oxidants, such as OH.".

2. *Section 2.2: It is unclear how the impact of PNs on $P(O_3)$ was quantified. Please provide a detailed explanation of the methodology.*

Thank you for the suggestion. The methodology related with the impact of PNs on $P(O_3)$ is added in section 2.2 as below "The impact of PNs photochemistry on local ozone is quantified by comparing the difference of the daytime $P(O_3)$ between the scenarios with and without PNs photochemistry via a chemical box model. Here, the PNs photochemistry includes the production and removal of PAN, MPAN and PPN."

3. *Section 3.3: The expression "a/b" is ambiguous, as it could imply either "a or b" or "the ratio of a to b."*

The expression "PAN/PNs" and "PAN/O_3" have been replaced by "PAN or PNs" and "the ratio of PAN to O_3" accordingly.

4. *Figure 8: The caption does not include a description of panel (c). Clarify whether Fig. 8d represents simulations in Shanghai with VOC-dependent α.*

Thanks for pointing the issue. The Figure 8 is revised as below.

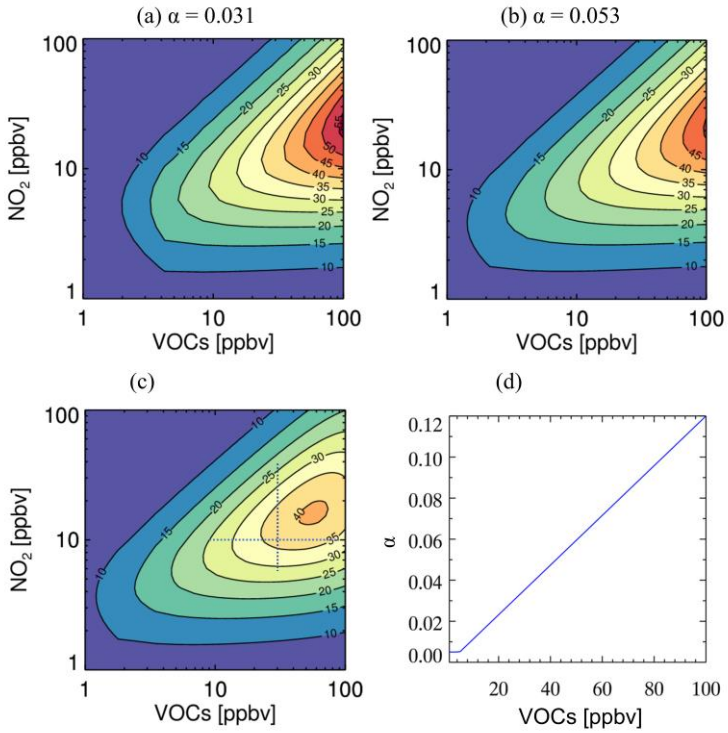

Figure 8. Ozone production ($P(O_3)$, ppb h-1) derived from a simplified analytic model is plotted as a function of NO_x and VOCs under three different organic nitrate scenarios with branching ratios of (a) 0.031 for the Xinjin campaign, (b) 0.053 for the Shanghai campaign, and (c)VOC-dependent branching ratios for Shanghai campaign, where the branching ratio decreases linearly from 12 to 0.5% with VOCs from 100 to 5 ppbv as shown in (d).

ferences

Arey, J., Aschmann, S. M., Kwok, E. S. C., and Atkinson, R.: Alkyl nitrate, hydroxyalkyl nitrate, and hydroxycarbonyl formation from the NOx-air photooxidations of C-5-C-8 n-alkanes, J. Phys. Chem. A, 105, 1020-1027, 10.1021/jp003292z, 2001.

Butkovskaya, N., Kukui, A., and Le Bras, G.: Pressure and Temperature Dependence of Methyl Nitrate Formation in the CH3O2+NO Reaction, J. Phys. Chem. A, 116, 5972-5980, 2012.

Cassanelli, P., Fox, D. J., and Cox, R. A.: Temperature dependence of pentyl nitrate formation from the reaction of pentyl peroxy radicals with NO, Phys. Chem. Chem. Phys., 9, 4332-4337, 10.1039/b700285h, 2007.

Farmer, D. K., Perring, A. E., Wooldridge, P. J., Blake, D. R., Baker, A., Meinardi, S., Huey, L. G., Tanner, D., Vargas, O., and Cohen, R. C.: Impact of organic nitrates on urban ozone production, Atmos. Chem. Phys., 11, 4085-4094, 10.5194/acp-11-4085-2011, 2011.

Liu, Y., Shen, H., Mu, J., Li, H., Chen, T., Yang, J., Jiang, Y., Zhu, Y., Meng, H., Dong, C., Wang, W., and Xue, L.: Formation of peroxyacetyl nitrate (PAN) and its impact on ozone production in the coastal atmosphere of Qingdao, North China, Sci. Total Environ., 778, 10.1016/j.scitotenv.2021.146265, 2021.

Perring, A. E., Bertram, T. H., Wooldridge, P. J., Fried, A., Heikes, B. G., Dibb, J., Crounse, J. D., Wennberg, P. O., Blake, N. J., Blake, D. R., Brune, W. H., Singh, H. B., and Cohen, R. C.: Airborne observations of total RONO2: new constraints on the yield and lifetime of isoprene nitrates, Atmos. Chem. Phys., 9, 1451-1463, 10.5194/acp-9-1451-2009, 2009.

Perring, A. E., Bertram, T. H., Farmer, D. K., Wooldridge, P. J., Dibb, J., Blake, N. J., Blake, D. R., Singh, H. B., Fuelberg, H., Diskin, G., Sachse, G., and Cohen, R. C.: The production and persistence of Sigma RONO2 in the Mexico City plume, Atmos. Chem. Phys., 10, 7215-7229, 2010.

Perring, A. E., Pusede, S. E., and Cohen, R. C.: An Observational Perspective on the Atmospheric Impacts of Alkyl and Multifunctional Nitrates on Ozone and Secondary Organic Aerosol, Chemical Reviews, 113, 5848-5870, 10.1021/cr300520x, 2013.

Reisen, F., Aschmann, S. M., Atkinson, R., and Arey, J.: 1,4-hydroxycarbonyl products of the OH radical initiated reactions of C-5-C-8 n-alkanes in the presence of N0, Environ. Sci. Technol., 39, 4447-4453, 10.1021/es0483589, 2005.

Rosen, R. S., Wood, E. C., Wooldridge, P. J., Thornton, J. A., Day, D. A., Kuster, W., Williams, E. J., Jobson, B. T., and Cohen, R. C.: Observations of total alkyl nitrates during Texas Air Quality Study 2000: Implications for O-3 and alkyl nitrate photochemistry, J. Geophys. Res.-Atmos., 109, 10.1029/2003jd004227, 2004.

Russell, M., and Allen, D. T.: Predicting secondary organic aerosol formation rates in southeast Texas, J. Geophys. Res.-Atmos., 110, 10.1029/2004jd004722, 2005.

Wennberg, P. O., Bates, K. H., Crounse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng, A. P., Zhang, X., and Seinfeld, J. H.: Gas-Phase Reactions of Isoprene and Its Major Oxidation Products, Chemical Reviews, 118, 3337-3390, 10.1021/acs.chemrev.7b00439, 2018.

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, Environ. Pollut., 252, 1910-1919, 10.1016/j.envpol.2019.06.004, 2019.