Response to Referee # *2*

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 #2:

This study conducted field measurements of gaseous organic nitrates at an urban site and assessed their effects on local O3 production using a box model incorporating an updated mechanism. Organic nitrates formation and its contribution to SOA and effect on O3 are of great concern to the researchers.

Major comments:

My main question about this work is the performance of the model simulations. The author used three mechanisms to simulate ONs, but as can be seen in Figure 4, the model simulated the concentration levels of ANs but poorly simulated the trend of ANs. It appears that the trend of simulated and observed ANs are opposite. The effectiveness of the model simulation affects the later analysis of ANs and the authors need to give an explanation. What about the R2 of the model simulation? Why does Zare's model that considers the ON formation initiated by OH and NO3 not work well compared to other models? Some specific comments are also provided below.

Thanks for the valuable comments. The simulated and measured levels of ANs are comparable, but there are some differences in the diurnal profiles, which may be caused by the following reasons. Firstly, the box model majorly simulates local chemistry budgets of ANs. As mentioned in 3.1 section, the transport might contribute to extra ANs from upwind areas. For example, on May 28th, there were high concentrations of both PNs and ANs in the morning accompanied by a change in wind direction and an increase in wind speed. In addition, the underestimation of PAN through box models has been reported in previous studies (Zeng et al., 2019;Sun et al., 2020;Xu et al., 2024). Secondly, the extremely high NO_x in the morning and evening rush hours will introduce larger errors to the ANs measurement during these periods. In addition, the error ratios (MSE) between measured and simulated ANs concentration based on Zare and Berkeley mechanism are 0.049 and 0.031 respectively, which are capable of reproducing the ANs chemistry. The impact of ANs on O_3 production are mainly qualified during the daytime period with high O_3 production, when ANs are better modeled.

The poor performance of the Zare mechanism on ON formation simulation can be

attributed to its modification of BVOCs oxidation by OH or NO_3 to produce ANs based on the Berkeley mechanism. The Zare mechanism refined the subsequent reactions of RO_2 generated by oxidation of BVOCs and would lead to a decrease in the ANs production from BVOCs. For example, after NO_3+ISO produce nitrooxy peroxy radical (INO_2), the Zare mechanism sets the C5 carbonyl nitrate (ICN) yield at 54% and 72% for INO_2+NO_3 and INO_2+INO_2, respectively. These modifications might introduce extra uncertainty since the yield of these newly added species could change in different conditions (e.g. high NO_x and anthropogenic VOCs). To clarify this point, the following explanation is added in 3.2 section "It should be noted that the Berkeley mechanism failed to fully reproduce the diurnal pattern of observed ANs. This is mainly due to the atmospheric transport that contributes to the ANs as mentioned in section 3.1. In addition, the drastic changes in NO_x during rush hours will introduce errors to the ANs measurements. In addition, the Zare mechanism refined the oxidation of BVOCs by OH or NO_3 by introducing extra species with uncertain yields, which might bring biases to the simulations under high NO_x and anthropogenic VOCs. In general, the Berkeley mechanism performs better on simulation of ANs than Zare mechanism.".

Minor comments:

1. *section 3.1, The authors divided the entire campaign into ozone pollution days, clean days, and background days. What are the specific criteria for dividing the clean and background days? How do precursors and environmental factors affect ANs and PNs on different days? The authors are also suggested to compare the effects of ANs and PNs on O3 on different days in the later analysis.*

Thanks for pointing the issue. To better clarify this point, we revised the description of classification in mentioned in 3.1 section as "The days without ozone pollution are categorized as clean or background days. For clean days, parameters, including K_{OH}, SO_2, and CO, show significant diurnal variations (Fig S1), and no rain occurs. The days that are neither ozone pollution days nor clean days are then classified as background days."

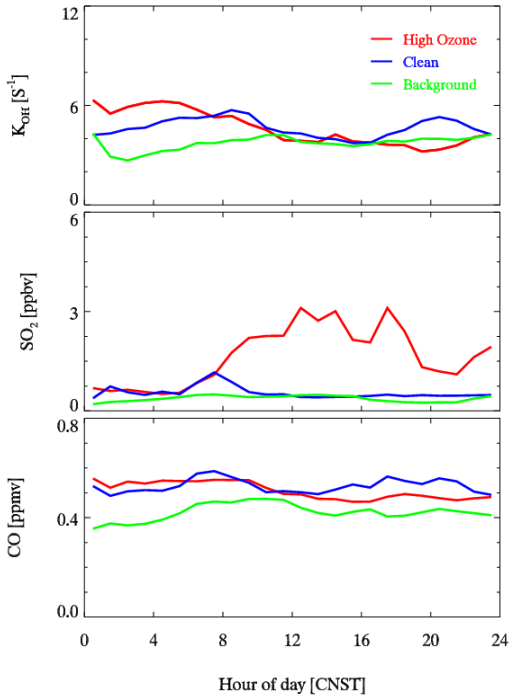

Figure S1. Mean diurnal profiles of VOC reactivity (K_{OH}), SO_2 and CO during different observation periods.

The factors affecting ANs and PNs are indeed an important topic, however, it is beyond scope of this study. We prefer to address this in our next study, where we will comprehensively analyze the budgets of ANs and PNs from a collections of several historical campaign case by case.

As suggested by reviewer, we further compare the effects of PNs and ANs on O_3 during different days. The results of comparison for PNs are added in section 3.3 and Fig. S3 as "The impacts of PNs photochemistry on O_3 vary across different days. As shown in Fig. S4, the integrated $P(O_3)$ change reaches 6.9 ppbv due to PNs photochemistry during ozone pollution period. For the background and clean periods, the changes are close to each other with a value of 3.8 and 4.2 ppbv, respectively. Therefore, the PNs photochemistry contributes to more $P(O_3)$ inhibition during the ozone pollution period, which should be considered in ozone pollution prevention.".

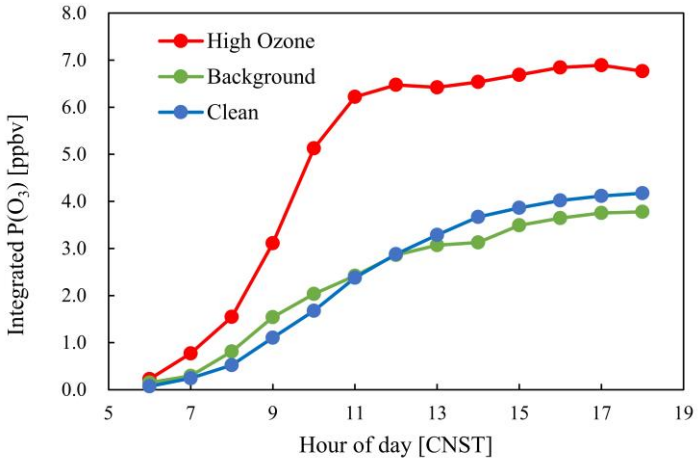

Figure S4. The integrated $P(O_3)$ changes constrained by PNs photochemistry during different observation periods.

For ANs, the effects are simulated via simplified box model, due to the wide variety of ANs and the related complex mechanism. During the different days, the branching ratio of ANs are 0.055, 0.054 and 0.052, respectively. Therefore, the ANs chemistry are similar across different days. The effects of ANs formation on O_3 production during different days are added in section 3.4 as below.

"To further investigate the effect of ANs formation on O_3 production during different days, sensitivity tests on VOCs reactivity and α are conducted based on typical conditions during different periods. The α values are derived as 0.055, 0.054 and 0.052, for the high ozone, clean and background periods, respectively. As shown in Fig. S4, the $P(O_3)$ exhibits a similar trend with the increase of NO_x across different periods. The $P(O_3)$ peak during the background period (30.3 ppbv/h) is slightly lower than that during both the high ozone days and the clean days (32.5 and 32.4 ppbv/h). Therefore, the ANs chemistry has similar effects on O_3 production within different periods during the Shanghai campaign."

2. *Line 242-256, compare ANs and PNs in Shanghai and Xinjin. And Line 329-337, the reduced inhibition of PNs on ozone production in Shanghai compared to Xinjin was attributed to the lower PNs production rate. The authors did not do further modeling analysis here, but it is suggested that the authors provide a reasonable discussion.*

Thanks for your suggestion. Detailed discussion is added in section 3.3 as "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. *Line 378-411, The Fig. 10 was missing. Regarding the sensitivity of VOCs reactivity and α to the effect of ANs formation on O3 production, it is suggested that the authors make more comparisons of the results of the most recent studies or those from China. In addition, I would like to know if the authors have tested the sensitivity of VOCs reactivity and α for different days, i.e. ozone pollution, clean and background days and what are the differences in the results?*

Thank you for pointing out the mistake. The Fig. 10 should be Fig. 9. As the measurements of total ANs and PNs are pretty scarce in China, a comparison among different campaigns can be done in the future.

According to the suggestions by reviewer, we further test the sensitivity of O_3 production to VOCs reactivity and α for different periods. The results of sensitivity analysis are added as Fig. S4 and the detailed discussion are shown as below "To further investigate the effect of ANs formation on O_3 production during different days, sensitivity tests on VOCs reactivity and α are conducted based on typical conditions during different periods. The α values are derived as 0.055, 0.054 and 0.052, for the high ozone, clean and background periods, respectively. As shown in Fig. S5, the $P(O_3)$ exhibits a similar trend with the increase of NO_x across different periods. The $P(O_3)$ peak during the background period (30.3 ppbv/h) is slightly lower than that during both the high ozone days and the clean days (32.5 and 32.4 ppbv/h). Therefore, the ANs chemistry has similar effects on O_3 production within different periods during the Shanghai campaign."

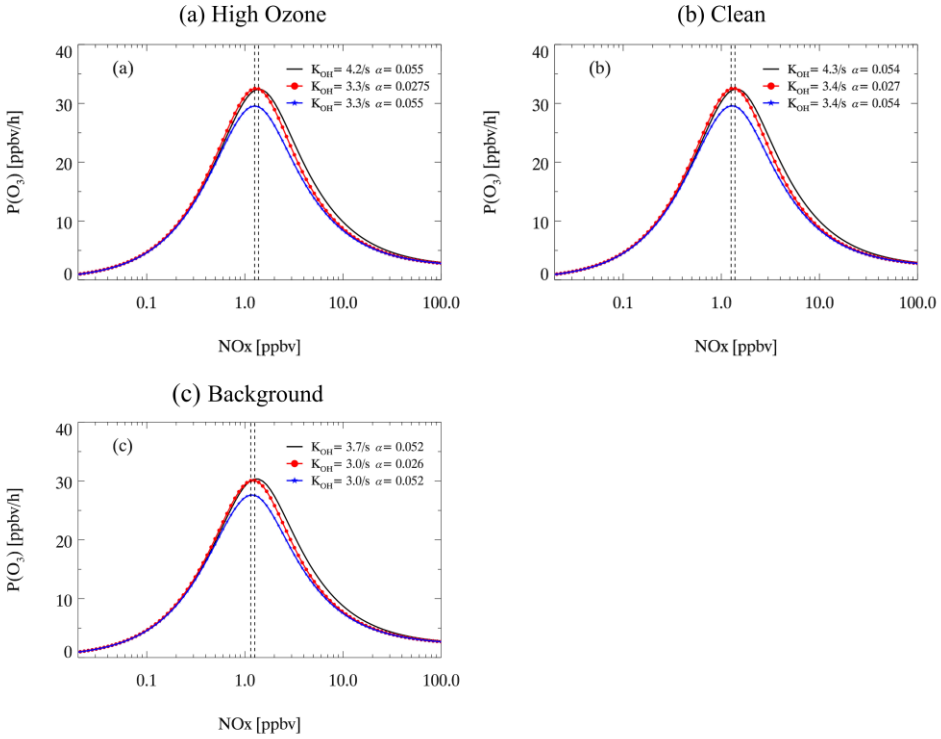

Figure S5. The ozone production rate ($P(O_3)$) varies as a function of NO_x under different VOC-NO_x regimes during Shanghai campaign: (a) under measured parameters during high ozone period; (b) during the clean period; (c) during the background period. The solid line shows the mean K_{OH} with effective α; the red dot line shows a 20% reduction in K_{OH} with a 50% reduction in α; the blue dot line shows a 20% reduction in K_{OH} with no change in α. Dash lines show the turning point in different cases.

References

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