Response to Editors and Reviewers

We appreciate the reviewers for their careful reading and constructive comments on our manuscript. As detailed below, the reviewer's comments are shown in black, our response to the comments is in blue. New or modified text is in red.

All the line numbers refer to Manuscript ID: acp-2023-622.

Referee 2

The chemistry of NO3 with VOC affects the budget of nocturnal SOA, and regulates regional photo chemistry indirectly. This study presents a detailed analysis about the nitrate radical reactivity towards VOC based on the one-year VOC measurement in a typical urban site. The level, compositions and seasonal variation of NO3 reactivity are well characterized. The results showed isoprene and styrene dominated NO3 reactivity on average, and proposed a month-resolved parameterization scheme to predict NO3 reactivity by using one or several VOCs species data. They tried to rebuilt the dataset of NO3 reactivity by using the scheme and collecting the historical VOC measurement data, and showed an overall decrease trend in recent years. Although this result may be highly uncertain, it provided a new and interesting perspective of the nighttime chemistry in a long-term period. This topic certainly within the scope of ACP and the manuscript is overall well-written. I would like to recommend it be accepted after the authors address the following comments listed below:

Thanks for the review's overall positive comments.

Major comments:

1. In section 3.2, the authors constructed a parameterization to estimate NO3-VOCs reactivity using one or several VOCs concentration based on one-year data in 2019. For robustness, it is better to evaluate this parameterization on datasets of other years, since you have collected the historical data of VOC concentrations in Beijing for several years before 2019.

   We highly acknowledge this suggestion. We used the collected historical data of VOC concentrations in Beijing for several years before 2019 and selected isoprene, styrene and other indicators to estimate the corresponding NO_3 reactivity towards VOC by parameterization method 1. Error analysis was conducted and it was found that the parameterization method 1 estimated the reactivity with relatively small error, indicating that our parameterization schemes based on the indicators concentrations in Beijing is reasonable.

   In brief, we have added histograms to demonstrate the effectiveness of parameterization method 1 as follows.

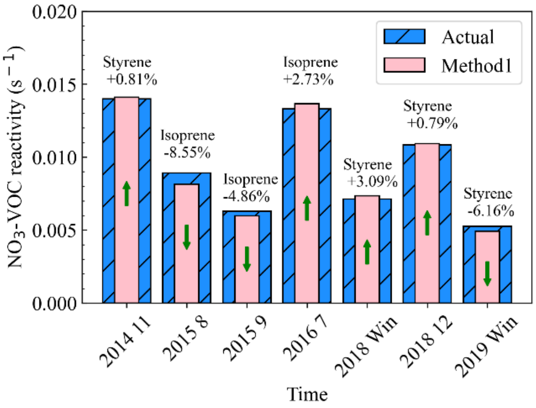

Figure S12. Histograms of actual NO_3 reactivity towards VOC and reactivity estimated through parameterization method 1 at different times in Beijing. The figure displays the indicators introduced in parameterization method 1 and the relative errors of estimation at different times. The (up/down) arrows represent the estimated effect (overestimation/underestimation) of the parameterized method 1.

Line 354. We evaluated this parameterization on datasets of other years (shown in Fig S12) and showed a robustness performance.

2. 5: The title 'Regulation of nighttime VOC oxidation' is somewhat vague for readers to follow. Maybe it is better to use 'The relationship between NO/Ox and nighttime VOC oxidation by NO3 radical'. I also found that the dependence of RNO3 on NOx has shown similar messages with the dependence on NO, which could be confusing in this figure as it is not related to the regions defined. Since the RNO3 has a relatively good exponential correlation with NO, I am wondering if Fig 6 can first focus on NO dependence and divide it into three regions, which might be regarded as NO-limited, transition and NO-saturated. In NO-saturated region, RNO3 is closed to zero and shows no dependence on both NO2 and O3. In the other two regions, RNO3 can reach up to 80%, and then it could be of interest to look into how the attribution of Ox influence the RNO3 variation.

Thanks. We have adjusted the previous title of Section 3.5 (Section 3.4 now) to "Relationship between NOx/O_3 and nocturnal VOC oxidation by NO_3 radical ".

We divided the nonlinear region of NO into two regions: NO-limited and NO-saturated region (NO-transited region was merged into the NO-limited region). Within the NO-limited region (NO concentration < 7 ppbv), we fitted the oxidation ratio with O_3 and NOx concentrations. It was found that within the NO-limited region, the oxidation ratio was sensitive to O_3 at 0-25 ppbv and NOx at 25-50 ppbv. Finally, we displayed three regions: O_3- limited region within NO-limited region, NO_X-limited region within NO-limited region and NO-saturated region. There is no significant difference between the modified fitting results and the previous one, indicating good consistency in this result. In brief, we have revised Figure 6 as follows to better demonstrate the synergistic control relationship and process of different species on the oxidation ratios.

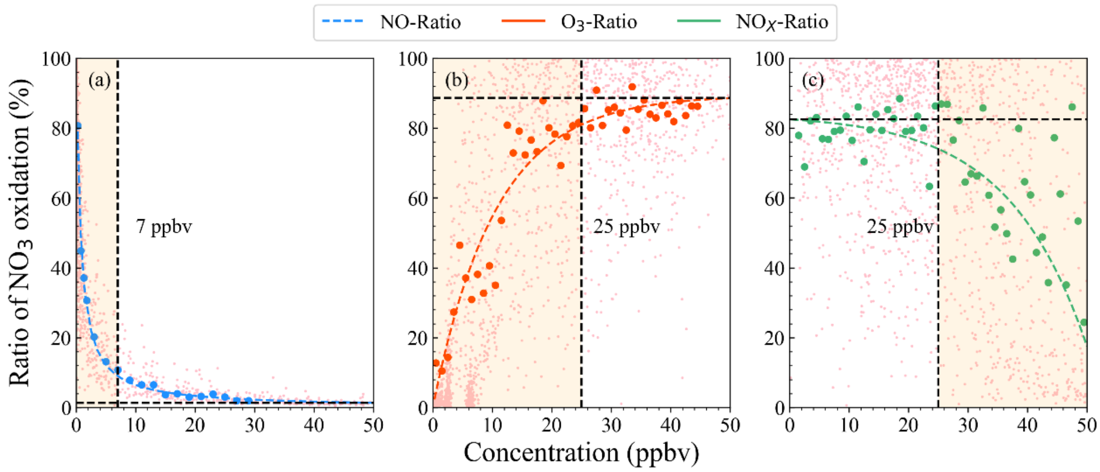

Figure 6. Fitting diagrams between the ratios of nighttime VOC oxidized by NO_3 and the concentrations of NO (a), O_3 (b) and NO_X (c). The light pink scattered dots represent the oxidation ratios at different concentrations and the solid dots represent the median value of each bin of oxidation ratios corresponding to each concentration range. Colored dot lines represent fitting results of the solid median dots. And the black dot line in each panel shows a threshold to divide the curve into two regimes. In (a), the regime divided into NO-limited (<7 ppbv) and NO-saturated (>7 ppbv), in (b) and (c), a threshold of 25 ppbv divide the curves into NO_X (O_3) limited and saturated regimes. The results showed in (b) and (c) are representative of low NO condition (< 7 ppbv).

Technical corrections:

1. Line 25: Please change 'the' to 'that'
2. Corrected accordingly.
3. Line 49: This equilibrium reaction can also take place during the day.

   We revised the wording throughout the manuscript accordingly.
4. Line 62: Please delete 'type'

   Deleted accordingly.
5. Line 86: Please change ';' to '.'.

   Corrected accordingly.
6. Line 102: Please change 'varies' a verb to an adjective.

   Corrected accordingly.
7. Line 117: Suggest adding 'newly' before 'proposed'.

   We added 'newly' accordingly.
8. Line 118: The word 'regulation' is a bit of vague here.

   We rewrote it as follows

   Line 115. At last, the nocturnal VOC oxidation by NO_3 during different seasons was further evaluated.

9. Line 138~139: Does this factor vary temporally? If so, please provide the specific values

Yes. We added a table to show the temporal variation of this factor as follows.

Table S2. The averaged diurnal variations of Factor ($=\frac{MNT_{sim}}{ISO_{sim}}$) during different months.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0:00	1.66	1.66	1.56	1.26	1.56	1.34	1.34	1.49	1.20	1.68	1.66	1.84
1:00	2.05	1.96	2.01	1.69	2.20	1.71	1.69	2.00	1.46	2.05	1.93	2.16
2:00	2.21	2.11	2.22	1.94	2.59	1.95	1.99	2.51	1.75	2.24	2.08	2.28
3:00	2.26	2.15	2.30	2.04	2.72	2.06	2.26	2.91	1.96	2.34	2.18	2.31
4:00	2.66	2.52	2.86	2.48	3.19	2.06	2.68	3.45	2.37	2.85	2.63	2.69
5:00	3.72	3.57	4.45	3.54	1.24	0.68	1.00	2.07	3.28	4.38	3.71	3.79
6:00	3.69	3.67	4.46	3.56	0.81	0.49	0.71	1.39	3.34	4.53	3.76	3.92
7:00	2.61	2.66	2.69	2.04	0.45	0.31	0.32	0.43	0.73	2.16	2.60	2.81
8:00	1.73	1.76	1.39	0.94	0.18	0.13	0.14	0.16	0.24	0.98	1.64	1.85
9:00	1.36	1.35	0.95	0.62	0.13	0.09	0.10	0.10	0.14	0.63	1.26	1.42
10:00	1.20	1.18	0.80	0.49	0.11	0.08	0.08	0.09	0.11	0.49	1.07	1.24
11:00	1.24	1.23	0.84	0.50	0.11	0.08	0.07	0.08	0.10	0.46	1.05	1.29
12:00	1.17	1.18	0.79	0.46	0.11	0.07	0.06	0.08	0.09	0.42	0.97	1.22
13:00	1.01	1.04	0.68	0.39	0.10	0.07	0.06	0.07	0.09	0.36	0.86	1.08
14:00	0.90	0.93	0.60	0.35	0.09	0.06	0.06	0.07	0.08	0.32	0.78	0.98
15:00	0.93	0.94	0.62	0.37	0.10	0.07	0.07	0.07	0.09	0.34	0.82	1.03
16:00	1.32	1.26	0.86	0.52	0.13	0.08	0.08	0.08	0.11	0.54	1.20	1.46
17:00	1.86	1.80	1.20	0.74	0.17	0.09	0.09	0.11	0.17	0.97	1.83	2.04
18:00	2.10	2.19	1.47	0.87	0.21	0.11	0.11	0.14	0.29	1.41	2.14	2.28
19:00	2.37	2.43	1.97	1.17	0.34	0.14	0.14	0.23	0.58	1.91	2.42	2.58
20:00	2.45	2.46	2.16	1.49	0.74	0.44	0.34	0.50	0.87	2.20	2.48	2.69
21:00	2.13	2.16	1.82	1.33	0.94	0.84	0.77	0.77	0.94	2.03	2.16	2.38
22:00	1.59	1.70	1.32	0.95	0.88	0.88	0.95	0.91	0.85	1.59	1.70	1.85
23:00	1.47	1.57	1.32	1.01	1.13	1.08	1.15	1.16	0.98	1.49	1.59	1.72

10. Line 140: Please delete the first ‘is’.

Corrected accordingly.

11. Line 190: Please add the ‘reason that’ before ‘the calculated’.

Revised accordingly.

12. Line 205: Please change ‘of’ to ‘among’.

We polished the language throughout the manuscript accordingly.

13. Line 207: What is the ‘another individual VOC’? I guess it means other?

Yes. We revised it to ‘other VOC’.

14. Line 213~214: I think the conclusion sentence here is not so necessary here. Or the authors could just put it at the beginning of this paragraph.

Thanks, we deleted it accordingly.

~~Overall, the k_{NO3_mea} displayed a characteristic of high in summer and autumn and low in winter and spring~~

15. Fig 1: In my opinion, the information in this figure is a little bit overlapped by presenting NO3-VOC reactivity levels in both months and seasons of a year. I think the months of year style is enough to demonstrate the temporal variations of reactivity. And the seasonal variations can be just provided in the text. In addition, it is not easy to identify daytime and nighttime reactivity with thin frames in black and blue. Shadow padding could be better.

    We appreciate for the reviewer's suggestion to revise Figure S1 in order to clearly display the daily and diurnal average levels of NO_3 reactivity towards VOC in different seasons. The revised figure is as follows.

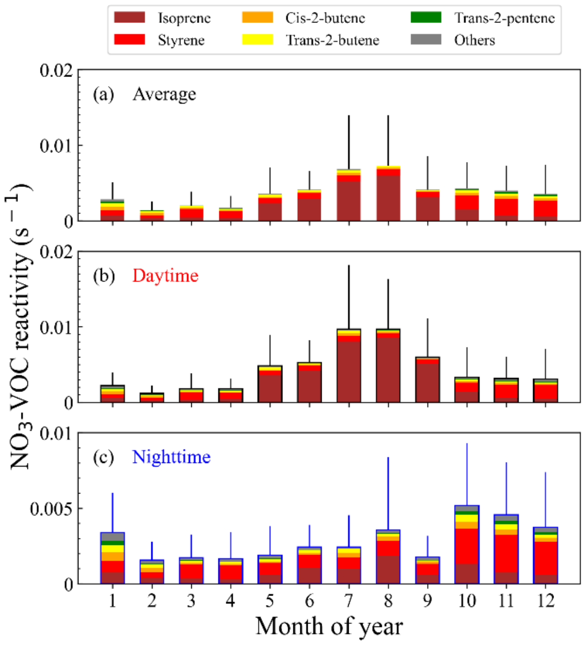

Figure 1. Histograms of monthly-averaged k_{NO3_mea} and the compositions during all the day (a), daytime (b) and nighttime (c). The color denotes the contributions of different VOC species. The lines represent the error bars of the reactivity (± standard deviations).

16. Line 251: Fitting equations are not displayed in Fig 2.

    Thanks for your comments. Figure 2 is to demonstrate the correlation between VOC concentrations and NO3 reactivity towards VOC, and the fitting equations are shown in Table S3 in detail. It's organized to select indicators through heat map firstly and estimate through the fitting equations in parametrization scheme. The relevant description has been provided in the text as follows.

    Line 289. Fig. 3 shows the correlation coefficients and the fitting equations between VOC concentrations and k_{NO3} in each month (detailed in Table S3). According to the correlation coefficients, we can select the strongest indicator corresponding to the certain month as the variable of the parameterization method.

17. Eq 10: If the author chose only one species, which has the strongest correlation coefficient with total NO3 reactivity, to develop parameterization, then what does the subscript i mean? Is it month? Please specify it because it could be a little bit misleading after comparing to Eq 11.

    Yes, the subscript i means the months. Specifically, [VOCi] is the concentration of VOC selected as an indicator for each month, and a_i, b_i are the corresponding fitting slope and intercept. To avoid misleading, we removed the subscript i from Eq. 10 and only used a single indicator concentration for characterization. In brief, we have revised Eq. 10 as follows.

    Line 297.

$$NO_3\, reactivity_{sim1} = a \times [VOC] + b \qquad \text{Eq. 10}$$

    where, a, b and [VOC] respectively represent the slope, the intercept and the VOC species concentrations (ppbv) used for parameterization in each month.

18. Fig 2: It is called heat map not thermodynamic diagram. And the description in the figure legend is not so clear.

    Thanks for the correction and we revised it accordingly. We added explanation of the heat map to describe clearly in the figure legend as follows.

    Line 305.

    Figure 3. The heat map of the correlation between VOC concentrations and k_{NO3_mea}. Colored blocks indicate different correlations, by which the best indicator can be selected for parameterization method of each month. The darker the color of the blocks, the better the correlation between the corresponding VOC concentration and k_{NO3_mea}, and the better the indicator tend to be.

19. Line 308: Please also mention the method used here to account for MNT reactivity which has been described in methodology section.

    Thanks for your comments. We added a mention to account for MNT reactivity described the methodology section as follows.

    Line 257. The NO_3 reactivity towards MNTs (named as k_{NO3_MNTs}) was estimated by the method mentioned in section 2.2. After taking MNTs into account, the total k_{NO3} (named as k_{NO3_total}) was greatly enlarged, with campaign-averaged value of 0.0061 ± 0.0088 s^{-1}, resulting in our results comparable with previous research results. The NO3 reactivity towards MNTs was higher in autumn and winter and lower in spring and summer (Fig. S7).

20. Line 317: Is this sentence trying to say ‘to compare the monoterpene and the total’? It could be confusing here because it is followed by the fraction of MNT-NO3 reactivity.

    Yes. To avoid confusing, we polished the language as follows.

    Line 267. To evaluate the contribution of monoterpenes to the total k_{NO3}, we calculated the fraction (FMNTs) by Eq. 12.

21. Line 352: Please change ‘highlight’ to ‘highlighting’.

    Corrected accordingly.

22. Line 356~371: Suggest moving Fig S11 to the main text. I think the seasonal variation of VOC reactivity attribution is more suitable to be presented here.

    Thanks, we moved it in the main text accordingly.

23. Line 374: Please specify the RNO3 and add the statement ‘see method 2.3 for its calculation’ here. Furthermore, it is not clear how the authors derive the Fig 6. It means the values of each bins?

    We appreciate for the reviewer’s suggestion to add the statement as follows

    Line391. To understand the importance of nighttime VOC oxidized by NO_3, we defined the fraction of VOC oxidation rate by NO_3 to the total oxidation rate as nocturnal VOC oxidation ratio of NO_3 (R_{NO3}, see method 2.3 for its calculation) and explored the relationship between the ratio and the nighttime concentrations of NO, O_3 and NO_X.

    We added an explanation in the caption of Fig 6 as follows.

Figure 6. Fitting diagrams between the ratios of nighttime VOC oxidized by NO_3 and the concentrations of NO (a), O_3 (b) and NO_X (c). The light pink scattered dots represent the oxidation ratios at different concentrations and the solid dots represent the median value of each bin of oxidation ratios corresponding to each concentration range. Colored dot lines represent fitting results of the solid median dots. And the black dot line in each panel shows a threshold to divide the curve into two regimes. In (a), the regime divided into NO-limited (<7 ppbv) and NO-saturated (>7 ppbv), in (b) and (c), a threshold of 25 ppbv divide the curves into NO_X (O_3) limited and saturated regimes. The results showed in (b) and (c) are representative of low NO condition (< 7 ppbv).