

Dear editor,

Thank you for handling our submission and we really appreciate your comments to improve the paper!

We also thank the reviewer #3 for the fruitful comments and suggestions. In this version, we have revised the manuscript accordingly and addressed all the reviewers' comments point-by-point for consideration as below. The remarks from the reviewers are shown in black, and our responses are shown in blue color. All the page and line numbers mentioned following are refer to the revised manuscript without change tracked.

Yours sincerely,

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### Reviewer # 3

The authors revised the manuscript with improvements, but massive problems, mainly language issue, still exist and need to be revised before publication.

Response: We have revised the manuscript accordingly and addressed the comments and suggestions raised by the reviewer point-by-point. We also corrected some mistakes and contradictions in the context. The Sect. 2.6, Sect. 3.3 and Sect. 3.4.3 have been deleted in the revised version. Besides, the paper has been subjected to editions for language by a native English speaker.

1. As the author replaced the OH and NO<sub>3</sub> radical concentrations by model calculation rather than parameterization, the title of the manuscript may not appropriate.

Response: We have followed the comments and the title of the manuscript has been corrected to ‘Atmospheric reactivity and oxidation capacity during summer at a suburban site between Beijing and Tianjin’.

2. The reviewer is still missing an argument why all OH, NO<sub>3</sub> and O<sub>3</sub> reactivity are calculated and compared if OH reactivity dominated 98.2% of the AOC. In the Line 141-144, the authors say previous study has analyzed OH reactivity but not NO<sub>3</sub> or O<sub>3</sub>. Isn't it one of the reasons that AOC is dominated by OH oxidation? In the abstract and conclusion, the authors claimed that the present study provide useful suggestions for VOC pollution control in North China Plain. Maybe the combined integration of OH, NO<sub>3</sub> and O<sub>3</sub> reactivity analysis could shed light on this topic but it's hidden in the current manuscript.

Response: Hydroxyl (OH), nitrate radicals (NO<sub>3</sub>) and O<sub>3</sub> play a centrally important role in cleansing the atmosphere of trace gas emissions resulting from both anthropogenic and biogenic activity (Atkinson and Arey, 2003; Heard and Pilling, 2003; Lu et al., 2018). OH can react both by addition and H abstraction to organic and inorganic trace gases and may be considered to be more reactive and much less selective than the NO<sub>3</sub> radical. The distinct reaction modes lead to significant differences in the lifetimes of both radicals, which for OH are typically less than 1 s and for NO<sub>3</sub> can exceed 1 h (Liebmann et al., 2018). The large NO<sub>3</sub> mixing ratios at night-time and the large rate constants for the reaction of NO<sub>3</sub> with several unsaturated biogenic VOCs result in NO<sub>3</sub> being the dominant sink of many BVOCs (Liebmann et al., 2018b; Liebmann et al., 2018a). Although for most NMVOCs, their reaction rate with O<sub>3</sub> is much lower than that with either OH or NO<sub>3</sub>, O<sub>3</sub> is very important because it is present at elevated mixing ratios in clean or contaminated atmospheres (Wang et al., 2013). The rate constants of the reactions for some alkenes with O<sub>3</sub> are even comparable to those with NO<sub>3</sub> (Atkinson and Arey, 2003). As mentioned above OH radicals, NO<sub>3</sub> radicals and O<sub>3</sub> react with atmospheric trace gases via different mechanisms, resulting in profoundly different rate coefficients and thus reactivities. Therefore, comprehensive evaluations of OH, NO<sub>3</sub> and O<sub>3</sub> reactivities is a key to understanding atmospheric oxidation capacity and identifying the controlling active species of secondary pollution in the atmosphere. The combined integration of OH, NO<sub>3</sub> and O<sub>3</sub> reactivities analysis could provide useful suggestions for VOC pollution control in North China Plain. The related statements have been added to the revised context. Please refer to Line 49-51 and 129-133 in the revised version.

### References:

- Atkinson, R., and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds., *Chemical Reviews*, 103, 4605-4638, doi:10.102/cr0206420, 2003.
- Heard, D. E., and Pilling, M. J.: Measurement of OH and HO<sub>2</sub> in the troposphere, *Chemical Reviews*, 103, 5163-5198, doi:10.1021/cr020522s, 2003.
- Liebmann, J., Karu, E., Sobanski, N., Schuladen, J., Ehn, M., Schallhart, S., Quéléver, L., Hellen, H., Hakola, H., Hoffmann, T., Williams, J., Fischer, H., Lelieveld, J., and Crowley, J. N.: Direct measurement of NO<sub>3</sub> radical reactivity in a boreal forest, *Atmos Chem Phys*, 18, 3799-3815, doi:10.5194/acp-18-3799-2018, 2018a.

Liebmann, J. M., Muller, J. B. A., Kubistin, D., Claude, A., Holla, R., Plass-Dülmer, C., Lelieveld, J., and Crowley, J. N.: Direct measurements of NO<sub>3</sub> reactivity in and above the boundary layer of a mountaintop site: identification of reactive trace gases and comparison with OH reactivity, *Atmos Chem Phys*, 18, 12045-12059, doi:10.5194/acp-18-12045-2018, 2018b.

Lu, K., Guo, S., Tan, Z., Wang, H., Shang, D., Liu, Y., Li, X., Wu, Z., Hu, M., and Zhang, Y.: Exploring the Atmospheric Free Radical chemistry in China: The Self-Cleansing Capacity and the Formation of Secondary air Pollution, *National Science Review*, doi:10.1093/nsr/nwy073, 2018.

Wang, Y., Hu, B., Tang, G., Ji, D., Zhang, H., Bai, J., Wang, X., and Wang, Y.: Characteristics of ozone and its precursors in Northern China: A comparative study of three sites, *Atmos Res*, 132-133, 450-459, doi:10.1016/j.atmosres.2013.04.005, 2013.

3. The manuscript needs proofreading, especially for Introduction section. It is difficult to follow the writing, and there are some obvious mistakes and contradictions in the context. For instance, in line 343-345, why it is 'as expected'? and it said 'with the accumulation of NMVOCs' in the first part of the sentence, but followed by 'the concentration of NMVOCs gradually decreases' in the second part. This sentence is confusing. In line 407, it said 'the majority of OH reactivity towards total NMVOCs values were below 2 s<sup>-1</sup>', but it was not the case for OH reactivity towards total NMVOCs. The expressions and collocations of some sentences need to be considered again. For instance, in line 610-612, '....., which even dominated the photochemical loss of NO<sub>3</sub>'. It is confusing of the 'dominated'.

Response: We have proofread the introduction section and corrected some confusing sentences in the context. We have modified into 'The trend of NMVOCs was inversely related to that of O<sub>3</sub>. When the NMVOCs concentrations in the atmosphere accumulates to a certain level, as photochemical reactions progress, the O<sub>3</sub> concentration gradually increases, and the NMVOCs concentrations gradually decreases (Kansal, 2009; Song et al., 2018)'. Please refer to Line 244-247 in the revised version. We are really sorry for the mistakes in line 407. We have modified into 'The majority of OH reactivity towards total NMVOCs values were below 13 s<sup>-1</sup> (Figure S4a-d)'. Please refer to Line 310-311 in the revised version. In line 610-612, we have modified into 'The diurnal variation of in the hourly median NO<sub>3</sub> concentration showed two peaks which were consistent with the high chemical production from NO<sub>2</sub> + O<sub>3</sub> (Figure S9d)'. Please refer to Line 507-508 in the revised version.

#### References:

Kansal, A.: Sources and reactivity of NMHCs and VOCs in the atmosphere: a review, *J Hazard Mater*, 166, 17-26, doi:10.1016/j.jhazmat.2008.11.048, 2009.

Song, M. D., Tan, Q. W., Feng, M., Qu, Y., Liu, X. G., An, J. L., and Zhang, Y. H.: Source Apportionment and Secondary Transformation of Atmospheric Nonmethane Hydrocarbons in Chengdu, Southwest China, *J Geophys Res-Atmos*, 123, 9741-9763, doi:10.1029/2018jd028479, 2018.

4. The manuscript still needs a significant reduction to be concise and informative before reconsidering. For instance, the manuscript introduced the O<sub>3</sub> formation regime analysis in Sect. 2.6 and Sect. 3.3, but it seems to be irrelevant to the subject and context of this article. The manuscript also analyzed the frequency distributions and cumulative frequency distributions of k<sub>OH</sub>, k<sub>O<sub>3</sub></sub> and k<sub>NO<sub>3</sub></sub>, but it not discussed in detail enough nor expressing a clear conclusion.

Response: This work was aiming to explore the OH, NO<sub>3</sub> and O<sub>3</sub> reactivities based on the measured VOCs and traditional trace gases concentrations. So, following the reviewer's suggestions, the Sect. 2.6 and Sect. 3.3 have been deleted in the revised version. As seen from the frequency distributions and cumulative frequency distributions of total OH, NO<sub>3</sub> and O<sub>3</sub> reactivities, the majority of total OH, NO<sub>3</sub> and O<sub>3</sub> reactivities values were dominated by the sum of low reactivity contributions and less by single compounds with high reactivity, highlighting the necessity of

considering a large number of species to obtain a complete picture of total OH, NO<sub>3</sub> and O<sub>3</sub> reactivities. Please refer to Line 301-304, 369-371 and 417-419 in the revised version.

5. Line 91-93: The OH reactivity is calculated by a global model in Ferracci et al. (2018) and by a box model based on Master Chemical Mechanism in Whalley et al. (2016)

Response: Following the reviewer's suggestions, the sentence of 'The total OH reactivity was also modeled using a zero-dimensional box model based on the Regional Atmospheric Chemical Mechanism to compare them with the measurements or calculations (Lou et al., 2010;Whalley et al., 2016;Ferracci et al., 2018;Yang et al., 2017).' has been modified into 'OH reactivity was also modeled by a global model by (Ferracci et al., 2018) and by a box model based on the Master Chemical Mechanism (MCM) (Whalley et al., 2016).'. Please refer to Line 88-90 in the revised version.

#### References:

Ferracci, V., Heimann, I., Abraham, N. L., Pyle, J. A., and Archibald, A. T.: Global modelling of the total OH reactivity: investigations on the "missing" OH sink and its atmospheric implications, *Atmos Chem Phys*, 18, 7109-7129, doi:10.5194/acp-18-7109-2018, 2018.

Whalley, L. K., Stone, D., Bandy, B., Dunmore, R., Hamilton, J. F., Hopkins, J., Lee, J. D., Lewis, A. C., and Heard, D. E.: Atmospheric OH reactivity in central London: observations, model predictions and estimates of in situ ozone production, *Atmos Chem Phys*, 16, 2109-2122, doi:10.5194/acp-16-2109-2016, 2016.

6. Line 325-327, it compared the temperature in this study to the four cities in Tan et al., 2019 without any introduction.

Response: The comparisons of temperature in this study and the four cities (Beijing, Shanghai, Chongqing and Guangzhou) in Tan et al., 2019 were untenable due to the differences of observation seasons. Besides, we have followed the suggestion that the manuscript needs a significant reduction to be concise. Therefore, we decided to delete the related description in the revised version.

7. Figure 10. The y-axis covers 10 orders of magnitude and its difficulty for me to read out the number. It's only mentioned once in the text and not really discussed.

Response: Thanks for the suggestion. First, the similarities and differences between section of overall characteristics of AOC and section of relative contributions of NMVOCs oxidation pathways were confusing because the concept of the oxidation rate is same as AOC. Second, the manuscript needs a significant reduction to be concise. Therefore, we decided to delete the section of relative contributions of NMVOCs oxidation pathways. So, we have moved the Figure 10 and Figures S12-S17 in the revised version.