

Responses to Editor's Comments

We are grateful to your thoughtful comments on the early version of the manuscript and the suggestions you made to improve the manuscript. We have revised the manuscript accordingly by making full use of these comments and suggestions. Below is our point-to-point responses to your comments, which are marked in blue color, while those modified in the revised manuscript and the revised Supplement are highlighted in red color.

Editor comments

1. L. 58: It is not clear why you cite Buxton et al., 1997 here. This is a kinetic study and does not report on any products.

Response: Thanks for your kind suggestion. We have deleted this reference.

2. l. 93 – 95: I do not understand this new sentence. Either it seems that a word is (or several ones are) missing or the grammar is not correct. Please either clarify it or remove it.

Response: Thanks for your kind suggestion. We have removed it.

3. l. 168: Remove 'greatly'.

Response: Done.

4. l. 192 – 196: What is the point you are trying to make here?

This sentence is way too convoluted and long. What is a direct result from your study? What is relevant to the discussion of your results? What is a logical continuation of the preceding sentence (Firstly, ..., Secondly...).

The meaning of the preceding sentence is clear: Low NO₂ leads to low NO which, in turn, weakens the titration effect of O₃.

In my opinion, you could end the next sentence after ‘NO₃⁻’: “Secondly, the reduction of NO₂ during the LCD could reduce the concentration of NO₃⁻”.

The remainder of the sentence is unclear. Does it refer to your observations? Is all this information relevant for your discussion? – If you want to keep it, split this long sentence into at least three so it is clear how it relates to the discussion of your data.

Response: The remainder of the sentence did not refer to our observations and our discussions, thus we have deleted them. Additionally, we have rephrased these discussions as follows:

Wang et al. (2021) demonstrated that O₃ in Chinese megacities during the LCD is primarily produced from the NO_x-saturated regime. The significant drop of NO₂ during the LCD led to the reduction of NO concentration (Xu et al., 2020), and further weakened the efficient titration effect of O₃ (Levy et al., 2014). Thus, the lower concentration of NO₂ during the LCD could increase O₃ concentration. O₃ exhibited a negative correlation with PM_{2.5} mass concentration ($R^2 = 0.57$) during the LCD, suggesting that the enhanced O₃ was also driven by lower PM_{2.5} concentration during the LCD, because PM_{2.5} could scavenge the precursors (HO₂· and NO_x radicals) of O₃ (Li et al., 2019) and alleviate the aerosol radiative effect on the photochemical formation of O₃ (Wu et al., 2020). Moreover, the more favorable atmospheric conditions such as the higher temperature and stronger solar radiation during the LCD were beneficial for the generation and accumulation of O₃ (Li et al., 2019).

Please see Lines 189-195, Pages 5-6 in the revised manuscript.

5. 1. 200: add ‘the concentration’: The concentration of OH radicals during the ...

Response: Done.

6. 1. 202: Add ‘concentrations of’: “... could lead to higher concentration of OH radicals...”.

Response: Done.

7. 1. 222: I assume that you mean ‘homologous’, not ‘homogenous’ here.

Response: Yes, we mean “homologous”. We have replaced “homogenous” with “homologous” in the revised manuscript. Please see Line 218, Page 6.

8. 1. 359: What do you mean by ‘equilibrium concentrations’ here? Why not simply ‘concentrations’? Or can you say for sure that the system was in equilibrium.

Response: We have deleted “equilibrium” in the revised manuscript.

9. 1. 383: I did not mean that you should include my example in the paper. I only wrote in my comments to give you one possible example to illustrate the difference between causation and correlation. There are likely many more possibilities why acidity and C₂ formation CORRELATE but are not CAUSED by each other.

As it is currently written it is not logical as two concepts (enhanced solubility vs acid catalysts) are mixed: You say that the acidity only affects the solubility of (M)Gly but then the reaction is acid-catalyzed. For simplicity, I suggest removing the following text:

Such negative correlations were possibly because more SO₂ could lead to more SO₄²⁻ and lower pH_{is}, which in turn enhanced the solubility of Gly and mGly and ultimately promoted C₂ formation. Therefore, an acid-catalyzed C₂ formation may occur in the aqueous phase under the present atmospheric conditions before the LCD.

Response: Thanks for your kind suggestion. We have rephrased this text as follows:

As shown in Fig. 4a, pH_{is} exhibited pronounced negative relationships with C₂ and its precursors such as Gly and mGly ($R^2 \geq 0.45$), which was also found in other field studies (Cheng et al., 2017; Meng et al., 2014; Wang et al., 2017; Yu et al., 2021), possibly suggesting an acid-catalyzed C₂ formation in the aqueous phase under the present atmospheric conditions before the LCD.

Please see Lines 379-380, Page 10 in the revised manuscript.

10. 1. 541 – 544: I do not understand the use of ‘offset’ in this sentence:

While previous studies focused on the importance of higher emission level and promoted secondary oxidation for producing more diacids and related compounds, this study strongly suggested that the

enhanced secondary formation of diacids and related species could offset the significant decline of organic precursors from anthropogenic pollutant emissions during the LCD.

Do you mean the following? (Please check the meaning – do not simply copy/paste this text!)

Previous studies focused on the correlation between higher emissions and enhanced production of diacids and related compounds. However, this study has shown that diacids are enhanced despite reduced emissions.

Response: Yes, we do. Thus we have rephrased this text as follows:

Previous studies focused on the relationships of higher diacids and related compounds with more source emissions or/and promoted secondary oxidation. However, this study strongly suggested that the secondary formation of diacids and related species were enhanced despite the significant decline of organic precursors from anthropogenic pollutant emissions during the LCD.

Please see Lines 535-538, Page 14 in the revised manuscript.

11. 1. 549: This is overstating your findings and also the novelty of your study.

1) You did not measure OH in the aqueous phase. How can you state that you studied the effect of OH on C₂ formation?

2) It is by far not the first study that inferred OH-driven C₂ formation. There are many studies that – just like you – showed similar trends, e.g. (Crahan et al., 2004; Jiang et al., 2014; Mochizuki et al., 2017; Rinaldi et al., 2011; Sorooshian et al., 2006; Wonaschuetz et al., 2012; Zhu et al., 2020) This list is by far not complete or exhaustive. They also did not measure OH directly. Some of the studies used models with measured data as input and this way could indeed quantify the role of OH pathways, based on constrained OH concentration, exceeding your approach.

I am not saying that you should add any of this to the paper. Instead, I suggest removing ““for the first time successfully””.

Response: We agree with you. Thus we have deleted “for the first time successfully” and “To the best of our knowledge, this study was first conducted on the effect of OH · radicals on C₂ formation in the field campaign, though many studies have been performed in chamber experiments.”.

12. 1. 552: Do your data really support any conclusions on the reactivity of ^{13}C ? You saw a trend that C_2 was enriched in ^{13}C ...such a trend could be equally explained by slower loss processes of ^{13}C enriched oxalate. I suggest limiting your concluding section to facts that are supported by your results, e.g. “We found higher $\delta^{13}\text{C}$ values of C_2 during the LCD than before the LCD (Fig. 10).”

Response: We agree with you. Thus we rephrased this text as follows:

Moreover, the $\delta^{13}\text{C}$ values of C_2 during the LCD were higher than those before the LCD (Fig. 10), largely because the reactivity of ^{13}C was higher than that of ^{12}C in the gaseous photochemical oxidation. We also observed more enriched ^{13}C in C_2 during the aging processes of organic aerosols.

Please see Lines 545-547, Page 14 in the revised manuscript.

References

- Cheng, C., Li, M., Chan, C. K., Tong, H., Chen, C., Chen, D., Wu, D., Li, L., Wu, C., Cheng, P., Gao, W., Huang, Z., Li, X., Zhang, Z., Fu, Z., Bi, Y., and Zhou, Z.: Mixing state of oxalic acid containing particles in the rural area of Pearl River Delta, China: implications for the formation mechanism of oxalic acid, *Atmos. Chem. Phys.*, 17, 9519-9533, 10.5194/acp-17-9519-2017, 2017.
- Levy, M., Zhang, R., Zheng, J., Zhang, A. L., Xu, W., Gomez-Hernandez, M., Wang, Y., and Olaguer, E.: Measurements of nitrous acid (HONO) using ion drift-chemical ionization mass spectrometry during the 2009 SHARP field campaign, *Atmospheric Environment*, 94, 231-240, <https://doi.org/10.1016/j.atmosenv.2014.05.024>, 2014.
- Li, K., Jacob, D. J., Liao, H., Shen, L., Zhang, Q., and Bates, K. H.: Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China, *Proceedings of the National Academy of Sciences*, 116, 422, 10.1073/pnas.1812168116, 2019.
- Meng, J., Wang, G., Li, J., Cheng, C., Ren, Y., Huang, Y., Cheng, Y., Cao, J., and Zhang, T.: Seasonal characteristics of oxalic acid and related SOA in the free troposphere of Mt. Hua, central China: Implications for sources and formation mechanisms, *Science of The Total Environment*, 493, 1088-1097, <http://dx.doi.org/10.1016/j.scitotenv.2014.04.086>, 2014.
- Wang, J., Wang, G., Gao, J., Wang, H., Ren, Y., Li, J., Zhou, B., Wu, C., Zhang, L., Wang, S., and Chai, F.: Concentrations and stable carbon isotope compositions of oxalic acid and related SOA in Beijing before, during, and after the 2014 APEC, *Atmos. Chem. Phys.*, 17, 981-992, 10.5194/acp-17-981-2017, 2017.
- Wang, N., Xu, J., Pei, C., Tang, R., Zhou, D., Chen, Y., Li, M., Deng, X., Deng, T., Huang, X., and Ding, A.: Air Quality During COVID-19 Lockdown in the Yangtze River Delta and the Pearl River Delta: Two Different Responsive Mechanisms to Emission Reductions in China, *Environmental Science & Technology*, 55, 5721-5730,

10.1021/acs.est.0c08383, 2021.

Wu, J., Bei, N., Hu, B., Liu, S., Wang, Y., Shen, Z., Li, X., Liu, L., Wang, R., Liu, Z., Cao, J., Tie, X., Molina, L. T., and Li, G.: Aerosol–photolysis interaction reduces particulate matter during wintertime haze events, *P. Natl. Acad. Sci. USA*, 117, 9755-9761, 10.1073/pnas.1916775117, 2020.

Xu, K., Cui, K., Young, L.-H., Wang, Y.-F., Hsieh, Y.-K., Wan, S., and Zhang, J.: Air Quality Index, Indicatory Air Pollutants and Impact of COVID-19 Event on the Air Quality near Central China, *Aerosol and Air Quality Research*, 20, 1204-1221, 10.4209/aaqr.2020.04.0139, 2020.

Yu, Q., Chen, J., Cheng, S., Qin, W., Zhang, Y., Sun, Y., and Ahmad, M.: Seasonal variation of dicarboxylic acids in PM_{2.5} in Beijing: Implications for the formation and aging processes of secondary organic aerosols, *Sci. Total Environ.*, 763, 142964, <https://doi.org/10.1016/j.scitotenv.2020.142964>, 2021.