Dear Editor and Referee,

Thanks for your suggestions which significantly help us to improve the manuscript. Hereby, we submit our responses and the manuscript has been revised accordingly. If there are any further questions or comments, please let us know.

Best regards

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Reviewer #1 (Minor Comments)

1. ***I just suggest changing 'NO gas was mixed with 2% in N2' to 'NO gas (2% in N2)'***

Reply:

Thanks for your suggestion. We modified the description in Line 187-188.

Revision:

Line 187-188: For HO_2 measurement, the NO gas (2% in N_2) was utilized to achieve HO_2-to-OH conversion.

2. ***Change 'laser beam was amplified to a diameter of 8 mm' to 'laser beam had a diameter of 8 mm'***

Reply:

Thanks for your suggestion. We modified the description in Line 158-160.

Revision:

Line 158-160: The radical detection module utilized a single pass laser configuration, and the laser beam had a diameter of 8 mm.

3. ***For the following question: '27. Fig. 10, line 532 - 539: Some further details on how the model was run when it was used to predict ozone are needed. What model constraints were changed to variables other than ozone (presumably NO2 was also changed to a variable)? ' If NO2 remained as a model constraint, this doesn't test the models ability to predict ozone as it is formed from the photolysis of NO2 (which was left constrained), so it isn't clear why the model predicted ozone changes when HONO is left unconstrained? Could additional model runs be performed where O3 and NO2 are unconstrained (constrained and unconstrained to HONO) as I think this would be a better test of the impact of HONO on O3?***

Reply:

Thanks for your suggestion. In the ozone-prediction mode, we use the 0-D chemical box model incorporating a condensed mechanism, the regional atmospheric chemistry mechanism version 2-Leuven isoprene mechanism (RACM2-LIM1). The utilization of a box model significantly reduces the computational power and simplifies the transport processes to derive the chemical response efficiently. In the box model mechanism, no emission rates were input into the traditional box model, so the concentrations of NO, NO_2, and VOCs need to be constrained to measurements in order to explore the ozone-related chemical processes.

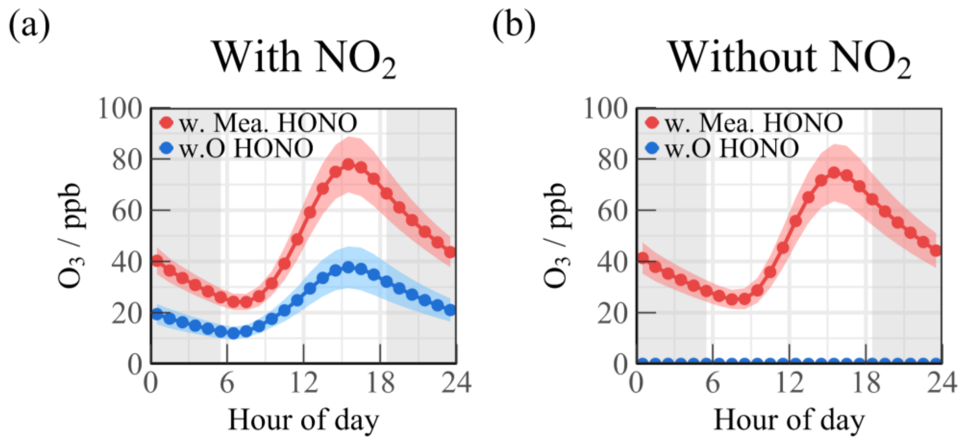

Fig. The O_3 concentration output by the ozone-prediction mode in different scenarios (Scenario 1: with input of NO_2, Scenario 2: without input of NO_2). The HONO concentration was constrained by measurement (w. Mea. HONO, red line) and unconstrained (w. O. HONO, blue line), respectively.

We attempted to follow the suggestions of the reviewers and did not constrain the concentrations of ozone and NO_2. The simulated results of ozone in this scenario are shown in the Figure above. The predicted daytime distribution of ozone concentration is basically the same in Scenario 1 (Fig.(a), with NO_2 constrained, adopted in this paper) and Scenario 2 (Fig.(b), without NO_2 constrained, recommended by the reviewer). However, due to the lack of sources in Scenario2, the box model cannot predict ozone concentrations normally without HONO input, and the obtained ozone concentration is approximately 0 (Fig.(b), blue line). The effect of HONO on ozone generation cannot be investigated under the condition that no NO_2 is input. Comparatively, removing the constraints on ozone and NO while keeping NO_2 as a constraint is a commonly used method in the box model for ozone prediction (Tan et al., 2018a). We added the description in the manuscript.

Revision:

Line 606-608&Supplement S1: Comparatively, removing the constraints on ozone and

NO while keeping NO_2 as a constraint is a commonly used method in the box model for ozone prediction (Tan et al., 2018a).

Reviewer #2 (Minor Comments)

1. ***L44-46 : "Without the HONO constraint, simulated O3 decreased from ~75 ppb to a global background (~35 ppb), and daytime HONO concentrations were reduced to a low level (~70 ppt)." – Was HONO the only species that was unconstrained here? Or was O3 also unconstrained together with HONO? It is hard to believe that O3 decreased from 75 to 35 ppb, especially when the authors indicate on L41-42 that the ozone production rate increases by 33-39% when HONO is constrained.***

Reply:

Thanks for your suggestion. The ozone production rate increases by 33-39% when HONO is constrained. In the ozone prediction scenario, the constraints on observed ozone and NO concentrations were removed, upon the basis the effect of constrained/unconstrained HONO were investigated. We acknowledge the reviewer's opinion that the drop in ozone concentration from ~75 ppb to 35 ppb is somewhat strange, and suspect that there may be other factors related to nitrogen chemistry at play, making the change in ozone concentration without HONO input more complex. Therefore, and we emphasize that this is a result of sensitivity testing for ozone prediction. We conducted an additional test to investigate the changes in ozone concentration prediction and added a new Fig. S8 in the supplement. The HONO concentration was constrained by measurement (w. Mea. HONO, red line in Fig. S8), unconstrained (w. O. HONO, blue line in Fig. S8) and calculation (w. Cal. HONO, green line in Fig. S8). The calculated HONO concentration was limited to 2% of NO_2 concentration. This simple calculation method for HONO concentration has been validated in multiple field observations (Tan et al., 2019; Elshorbany et al., 2012). Compared to the condition without HONO input, the addition of calculated HONO concentration slightly improved the O_3 simulation effect, but the peak value remained at around 40 ppb. Therefore, the contribution of HONO to ozone concentration prediction has some rationality. We added the description in the manuscript.

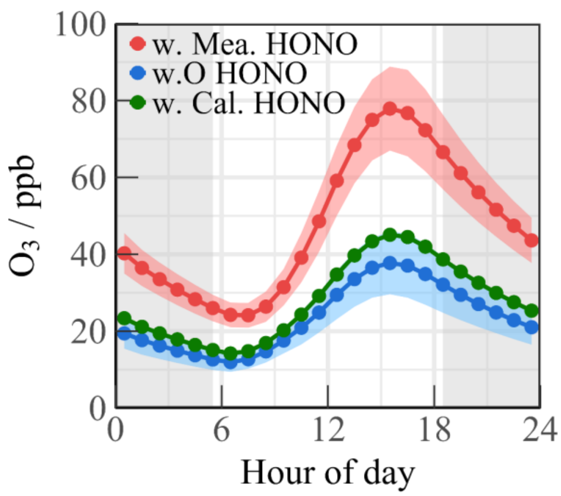

Fig. S8. The O_3 concentrations simulated by the ozone-prediction mode. The HONO concentration was constrained by measurement (w. Mea. HONO, red line), unconstrained (w. O. HONO, blue line) and calculation (w. Cal. HONO, green line). The calculated HONO concentration was limited to 2% of NO_2 concentration.

Revision:

Line 608-611: Considering the complexity of HONO chemistry, this is more emphasized as a sensitivity test for ozone prediction, and its validity has been examined through simulated comparisons under different HONO concentrations (Fig. S8).

Line 44-46: In the ozone-prediction test, simulated O_3 decreased from ~75 ppb to a global background (~35 ppb) without the HONO constraint.

2. ***L215-216: Is the measurement accuracy given as 1σ? Please indicate it in the text.***

Reply:

Thanks for your suggestion. We modified the description in Line 216-217.

Revision:

Line 216-217: At a typical laser power of 15 mW, the measurement accuracy for OH and HO_2 measurement was 13% and 17% (1σ), respectively.

3. ***L527-528: "which also affects the quantum yield of NO2" – The reviewer does not understand what is meant here. Do the authors mean that it affects the amount of NO2 that is produced? Please clarify.***

Reply:

Thanks for your suggestion. Regarding the modification on Eq.8, it was suggested by Reviewer 2 (Question 18) during the discussion process. Considering the reaction between RO_2 and NO, the formation of organic nitrates affects affects the amount of NO_2 that is produced. Therefore, we added α_i represents the organic nitrate yield in Eq.8 to determine the effective generation of NO_2 (Tan et al., 2018b). We modified the misleading description in Line 528-529.

Revision:

Line 528-529: α_i represents the organic nitrate yield, which affects the amount of NO_2 that is produced from the reaction between RO_2 and NO (Tan et al., 2018b).

4. ***Eqs. 4: How did the authors derived this equation? The general equation to calculate the HO2 uptake rate is k=γ*ASA*γ(HO2)/4.***

Reply:

Thanks for your suggestion. The HO_2 uptake rate in Eq.4 was incorrectly written in the previous manuscript. We have modified the Equation in Line 283.

Revision:

Line 283:

$$k_{HO_2+uptake} = \frac{\gamma \times ASA \times \nu_{HO_2}}{4} \quad (4)$$

Reviewer #2 (Edits)

1. ***L205: "Mercury lamp intensity is adjusted to establish." – Please clarify this sentence. It seems that something is missing.***

Reply:

Thanks for your suggestion. We have modified the sentence in Line 205-206.

Revision:

Line 205-206: Mercury lamp intensity is fine-tuned to establish a correlation between light intensity and ozone concentration.

2. ***L208: "In the YMK c ampaign , the humidity varied between 40 80%" should read "In the YMK campaign , the relative humidity varied between 40 80%"***

Reply:

Thanks for your suggestion. We have modified the sentence in Line 209.

Revision:

Line 209: In the YMK campaign, the relative humidity varied between 40 – 80% (Fig. S3).

3. ***L173-174: "Due to the synchronous reaction at 308nm , wavelength modulation is not applicable to ozone photolysis interference" should read "Since the ozone photolysis interference is due to the laser light itself, wavelength modulation does not allow removing it."***

Reply:

Thanks for your suggestion. We have modified the sentence in Line 173-174.

Revision:

Line 173-174: Since the ozone photolysis interference is due to the laser light itself, wavelength modulation does not allow removing it.

4. ***L272: "diagnose the impacts of the reactive bromine chemistry." Should read "diagnose the impacts of the reactive bromine and iodine chemistry."***

Reply:

Thanks for your suggestion. We have modified the sentence in Line 271-273.

Revision:

Line 271-273: Considering the environmental characteristics of the MBL, the gas-phase mechanisms for bromine (Br) and iodine (I) were introduced into the base model to diagnose the impacts of the reactive bromine and iodine chemistry

5. ***L527-528: "αi represents the side generation ratio of organic nitrate" – Should read "αi represents the organic nitrate yield".***

Reply:

Thanks for your suggestion. We have modified the sentence in Line 528-529.

Revision:

Line 528-529: α_i represents the organic nitrate yield, which affects the amount of NO_2 that is produced from the reaction between RO_2 and NO (Tan et al., 2018b).

References

Elshorbany, Y. F., Steil, B., Brühl, C., and Lelieveld, J.: Impact of HONO on global atmospheric chemistry calculated with an empirical parameterization in the EMAC model, Atmos. Chem. Phys., 12, 9977-10000, 10.5194/acp-12-9977-2012, 2012.

Tan, Z., Lu, K., Jiang, M., Su, R., Wang, H., Lou, S., Fu, Q., Zhai, C., Tan, Q., Yue, D., Chen, D., Wang, Z., Xie, S., Zeng, L., and Zhang, Y.: Daytime atmospheric oxidation capacity in four Chinese megacities during the photochemically polluted season: a case study based on box model simulation, Atmos Chem Phys, 19, 3493-3513, 10.5194/acp-19-3493-2019, 2019.

Tan, Z. F., Lu, K. D., Jiang, M. Q., Su, R., Dong, H. B., Zeng, L. M., Xie, S. D., Tan, Q. W., and Zhang, Y. H.: Exploring ozone pollution in Chengdu, southwestern China: A case study from radical chemistry to O3-VOC-NOx sensitivity, Sci Total Environ, 636, 775-786, 10.1016/j.scitotenv.2018.04.286, 2018a.

Tan, Z. F., Lu, K. D., Dong, H. B., Hu, M., Li, X., Liu, Y. H., Lu, S. H., Shao, M., Su, R., Wang, H. C., Wu, Y. S., Wahner, A., and Zhang, Y. H.: Explicit diagnosis of the local ozone production rate and the ozone-NOx-VOC sensitivities, Sci. Bull., 63, 1067-1076, 10.1016/j.scib.2018.07.001, 2018b.