Response to Editor:

Comments:

1. In your reply to reviewer #1 regarding the RO_2 interference yields applied, you state 'The RO_2 interference yields which have been used for correction were the reported data in Lu et al. (2012).' It is not clear from your response nor from the changes made in the manuscript whether this correction considers possible differences in the RO_2 interference yields owing to differences in the amount of NO added to the detection cell in the two studies? I suggest that the concentration of NO added in both studies is stated in this manuscript and, if they are different, an explanation of how the RO_2 interference yield was scaled for the 2018 campaign should be provided.

Reply

Thanks for your helpful suggestions. In the PRIDE-PRD2006 campaign, Lu et al. (2012) injected pure NO into the HO_2 detection cell, and the high NO concentration is sufficient to achieve the complete HO_2-to-OH conversion. Fuchs et al. (2011) reported that the relative RO_2 detection sensitivities are approximately constant when the NO concentration is so high that HO_2 conversion in the detection is nearly complete. Thus, the relative RO_2 detection sensitivities reported by Lu et al. (2012) can be used for the correction of HO_2 concentrations as long as the HO_2-to-OH conversion efficiencies reach 100%. In this study, in the high NO mode (the NO concentration was 50 ppm, and the HO_2-to-OH conversion efficiencies reached 100%) in this study, we used the relative RO_2 detection sensitivities reported by Lu et al. (2012). We revised the description in Section 2.2 in the revised version.

Revision

Section 2.2

(1) Fuchs et al. (2011) reported that the relative RO_2 detection sensitivities are approximately constant when the NO concentration is so high that HO_2 conversion in the detection is nearly complete. Thus, when the HO_2-to-OH conversion efficiencies reach 100%, the relative RO_2 detection sensitivities reported by Fuchs et al. (2011) and Lu et al. (2012) can be used for the correction of HO_2 concentrations.

(2) Herein, we simulated the HO_2 and HO_2^* concentrations by the model, and the RO_2 interference yields which were used for correction were the modeled values reported by Lu et al. (2012) in the PRIDE-PRD2006 campaign in which the HO_2-to-OH conversion efficiencies also reached 100% due to the injection of pure NO in the HO_2 detection cell.

2. In your response to reviewers #2 and #3 regarding the possible impact of heterogeneous losses of HO_2 in the study, you have provided a discussion on how heterogeneous losses can impact the agreement between the modelled and measured HO_2* and put this into the context of previous ambient measurements of γ. Further to this, however, I think the manuscript would benefit from a discussion on how inclusion of HO_2 uptake in the model impacts the modelled OH concentrations also - as figure 6 highlights that the modelled OH

concentration decreases as the HO_2 uptake coefficient is increased (leading to an increase in the modelled to measured OH discrepancy); this should be acknowledged and a discussion provided on how the impact of including heterogeneous HO_2 loss impacts on the required concentration of species X needed to close the OH budget (and how this then compares to the concentration of species X in earlier studies).

Reply

Thanks for your suggestions and we revised Section 4.3 and the Supplementary Information.

Revision

Section 4.3:

It should be noted that the HO_2 heterogeneous uptake (γ = 0.3) reduced the modeled OH concentrations by around 20% compared to the OH simulations in the base model during the daytime (08:00-18:00). Sensitivity tests illustrated that good agreements of OH observations-simulations and HO_2^* observations-simulations were both achieved when the amount of X changed from 0.1 ppb to 0.25 ppb and the HO_2 effective uptake coefficient was 0.3, as shown in Fig. S6 in the Supplementary Information. Compared to the Backgarden and Heshan sites, the amount of X in Shenzhen was lower despite a significant HO_2 heterogeneous uptake, which might be closely related to the environmental conditions as discussed in Sect. 4.2.

Supplementary Information:

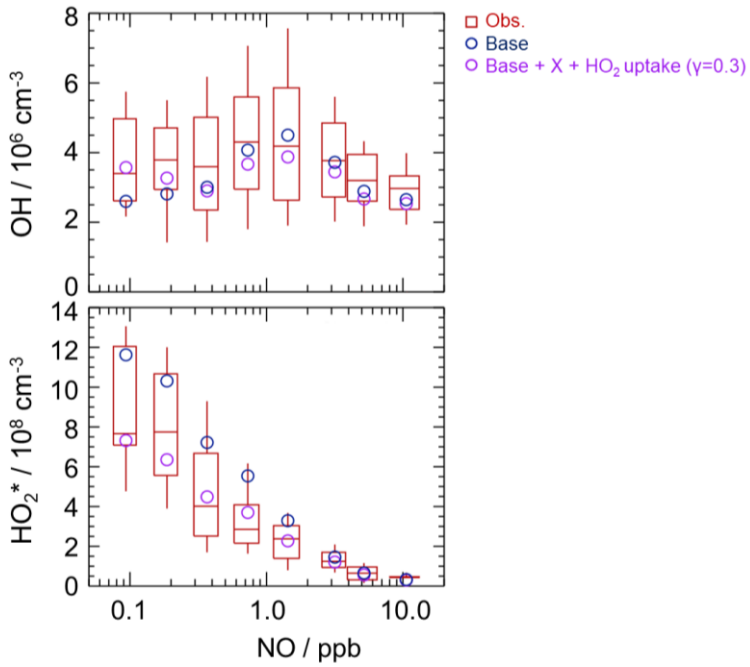

Figure S6: NO dependence on OH and HO_2^* radicals. The red box-whisker plots give the 10%, 25%, median, 75%, and 90% of the HOx observations. The blue circles show the median values of the HOx simulations by the base model, and the purple circles show the HOx simulations by the model with X mechanism (X = 0.25 ppb NO) and HO_2 heterogeneous uptake (γ = 0.3). Only daytime values and NO concentration above the detection limit of the instrument were chosen.

3. With regards to ROOOH species acting as potential OH interferences within the FAGE detection cell, I believe the manuscript (and readers) would benefit from some further details at the beginning of this section on how OH may be formed from the decomposition of ROOOH species within FAGE detection cells. In the Fittschen et al. 2019 paper, they suggest heterogeneous decomposition of ROOOH on the walls of the FAGE cell or the entrance nozzle could yield OH.

Reply

Thanks for your suggestions, and we added the description of how OH may be formed from the ROOOH decomposition in the revised manuscript.

Revision

Section 2.2

Fittschen et al. (2019) reported that the OH interference signals might come from the ROOOH heterogeneous decomposition on the walls of the FAGE cell or the entrance nozzle, but they also noted that the ROOOH interference is highly dependent on the design and measurement conditions of different FAGE instruments.

4. In response to reviewer #3 regarding gross vs net ozone production rates I suggest changing '…while it was much higher than the O_3 production rate in Beijing in winter despite being the gross production rate (Tan et al., 2018).' to '…while the net ozone production rate in Shenzhen was much higher than the gross O_3 production rate in Beijing in winter (Tan et al., 2018).'

Reply

We have revised the expression in the revised version.

Revision

The modeled $P(O_3)_{net}$ in this study was comparable to the net O_3 production rate in Wangdu in summer (Tan et al., 2017), while the net ozone production rate in Shenzhen was much higher than the gross O_3 production rate in Beijing in winter (Tan et al., 2018)

References

Tan, Z., Fuchs, H., Lu, K., Hofzumahaus, A., Bohn, B., Broch, S., Dong, H., Gomm, S., Haeseler, R., He, L., Holland, F., Li, X., Liu, Y., Lu, S., Rohrer, F., Shao, M., Wang, B., Wang, M., Wu, Y., Zeng, L., Zhang, Y., Wahner, A., and Zhang, Y.: Radical chemistry at a rural site (Wangdu) in the North China Plain: observation and model calculations of OH, HO2 and RO2 radicals, Atmospheric Chemistry and Physics, 17, 663-690, 10.5194/acp-17-663-2017, 2017.

Tan, Z., Rohrer, F., Lu, K., Ma, X., Bohn, B., Broch, S., Dong, H., Fuchs, H., Gkatzelis, G. I., Hofzumahaus, A., Holland, F., Li, X., Liu, Y., Liu, Y., Novelli, A., Shao, M., Wang, H., Wu, Y., Zeng, L., Hu, M., Kiendler-Scharr, A., Wahner, A., and Zhang, Y.: Wintertime photochemistry in Beijing: observations of ROx radical concentrations in the North China Plain during the BEST-ONE campaign, Atmospheric Chemistry and Physics, 18, 12391-12411, 10.5194/acp-18-12391-2018, 2018.