Referee 1

This paper presents the measurements of OH, HO2, and RO2 radicals and OH reactivity in central Beijing in the summer of 2017 as part of the APHH campaign. It reportes the highest ever observed OH concentration of 2.8×107 cm-3 in urban area, even slightly higher than that reported in PRD in China by Lu et al. (2012).

Experimental budget analysis of OH, HO2, RO2, and ROx was performed in the similar way as Tan et al. (2019) did in PRD in 2014. Consistent with other studies in China, the authors found a missing OH source under low NO (<0.5 ppbv) and high VOC condition. Besides, the authors found the opposite trends in HO2 budget and RO2 budget. The HO2 production rate exceeded the destruction rate by the similar rate as the RO2 destruction rate exceed production rate. The authors explained the opposite difference as the substantially slower than assumed net propagation rate of RO2 to HO2. If only 10% of the RO2 radicals propagate to HO2 upon reaction with NO, the HO2 and RO2 budget would be closed. The authors also performed a model simulation based on MCM 3.3.1, and found consistent results with the experimental budget analysis, except for the OH radical. The model simulated OH concentration very well due to a cancellation of missing OH source and sinks terms in its budget. The model underpredicted the kOH consistently across all NOx levels. To understand the model biases, the authors performed several sensitivity tests. The inclusion of heterogeneous loss of HO2 to aerosol surfaces and ClNO2 chemistry could not entirely explained the HO2 overestimation and RO2 underestimation, respectively. Several sensitivity tests were done to see the impact of missing OH reactivity on the modelled radical concentrations by assuming reactants convert OH to CH3O2, OHCH2CHO2O2, CH3(O)O2, and C96O2. The authors proposed that missing OH reactivity converted OH to a larger RO2 that undergo several reaction with NO, before eventually generating HO2, could improve the agreement between observation and simulation, and they used an α-pinene-derived RO2 species (C96O2) as an example. The results are of interest to the atmospheric chemistry community, enriching the ROx measurement in megacity, and the paper is worthy of publication. However, there are some critical issues and mistakes have to be addressed and corrected in advance before publication. Also, the paper could be shortened quite a bit and the writing could be more concisely and logically.

We thank referee 1 for their useful comments and have responded to each specific comment in bold below. The changes to the manuscript that we will make are in red.

1. Line 337, Alkyl nitrates are not formed from aldehydes + NO3.

This was a typo and should have been:

Alkyl nitrates, formed from isoprene + NO3 were also enhanced at these times at this site (Reeves et al., 2019).

This will be corrected in the revised manuscript

2. According to the Fig.4, the RO2 neutral reaction rate (RO2+NO->RO2) has no dependence towards NO concentration since the P:D(HO2) showed no tendency towards lower NO. However, as the NO decreased, the competitive reaction of RO2 with HO2 or RO2 isomerization would become more and more important, and was even comparable to the rate between RO2 and NO. Thus, the multiple conversion of one RO2 to another should be reduced towards low NO.

In response to a comment from the second reviewer, we have added model scenario 'Missing k(OH) (OH to C96O2)' to part of the radical measurement time-series, alongside the base model scenario to highlight that additional VOC reactivity which produces RO_2 radicals that isomerise after reaction

with NO is able to increase the modelled total RO_2 concentration both under the lower NO conditions experienced between the 16th – 22nd June as well as on the higher NO days 9th – 12th June indicating that NO is still at sufficient concentrations to dominate the fate of RO_2 between the 16th – 22nd June, despite NO concentrations being lower.

However, as the referee states, in the afternoon low-NO chemistry (e.g. RO_2+HO_2 reactions) does play a greater role (30%), see Newland et al., (2020). Under these conditions, the reaction of RO_2 with NO and, therefore, the subsequent RO isomerisation, becomes less efficient and this trend is demonstrated when we overlay the RO_2 median measured to modelled (Missing k(OH) (OH to C96O2)) ratio vs NO on figure S3. We hypothesise that the production rate of HO_2 exceeds the destruction rate of HO_2 by a similar amount across the whole NO range encountered because we are neglecting both RO_2+NO reactions that lead to an RO radical that is able to undergo isomerisation reactions which would serve to reduce alpha most strongly under high NO conditions, whilst under low NO conditions we are neglecting RO_2 unimolecular reactions which may form OH directly rather than HO_2.

Newland, M. J., Bryant, D. J., Dunmore, R., Bannan, T., Acton, W. J., Langford, B., Hopkins, J., Squires, F. A., Dixon, W. J., Drysdale, W. S., Ivatt, P. D., Evans, M. J., Edwards, P., Whalley, L. K., Heard, D. E., Slater, E. J., Woodward-Massey, R., Ye, C., Mehra, A., Worrall, S. D., Bacak, A., Coe, H., Percival, C., Hewitt, C. N., Lee, J. D., Cui, T. Q., Surratt, J. D., Wang, X., Lewis, A. C., Rickard, A. R., and Hamilton, J.: Rainforest-like atmospheric chemistry in a polluted megacity, Atmospheric Chemistry and Physics Discussions, 35, 2020.

Pg 14, line 440 onwards: The model under-estimates total RO_2 throughout the measurement period, although the level of disagreement (in absolute concentration) is most severe from the 16th – 22nd June when NO concentrations were at their lowest. During this period, the average NO mixing ratio was ~0.4 ppbv during the afternoon hours, whilst the average NO mixing ratio for the entirety of the campaign was ~0.75 ppbv during the afternoons (Fig S1 in SI). The average peak NO mixing ratio observed in the morning between 16th – 22nd June was just over 6 ppbv, whilst the average peak NO mixing ratio for the entirety of the campaign was close to 16 ppbv.

Pg 18, line 566 onwards: The modelled radical concentrations predicted from the 'Missing k(OH) (OH to C96O2)' scenario are overlaid with the radical observations and modelled radicals from the base model scenario in Fig S2, SI. The additional VOC reactivity which produces RO_2 radicals that isomerise after reaction with NO is able to increase the modelled total RO_2 concentration both under the lower NO conditions experienced between the 16th – 22nd June as well as on the higher NO days 9th – 12th June indicating that NO is still at sufficient concentrations to dominate the fate of RO_2 between the 16th – 22nd June, despite NO concentrations being lower. The median measured to modelled (Missing k(OH) (OH to C96O2)) ratio vs NO (Fig S3, SI) highlights that the inclusion of alkoxy isomerisation following RO_2 + NO reaction increases the modelled RO_2 across the entire NO range but, considering the log scale, has the biggest impact on the ratio (from the measured to modelled (base) ratio) at the highest NO concentration. Both the simple- and complex-RO_2 species are enhanced, as the first 3 generations of RO_2 species formed would be detected during the RO_x-mode in the RO_x-LIF instrument and, hence, contribute to RO_2-simple.

Supplementary Information

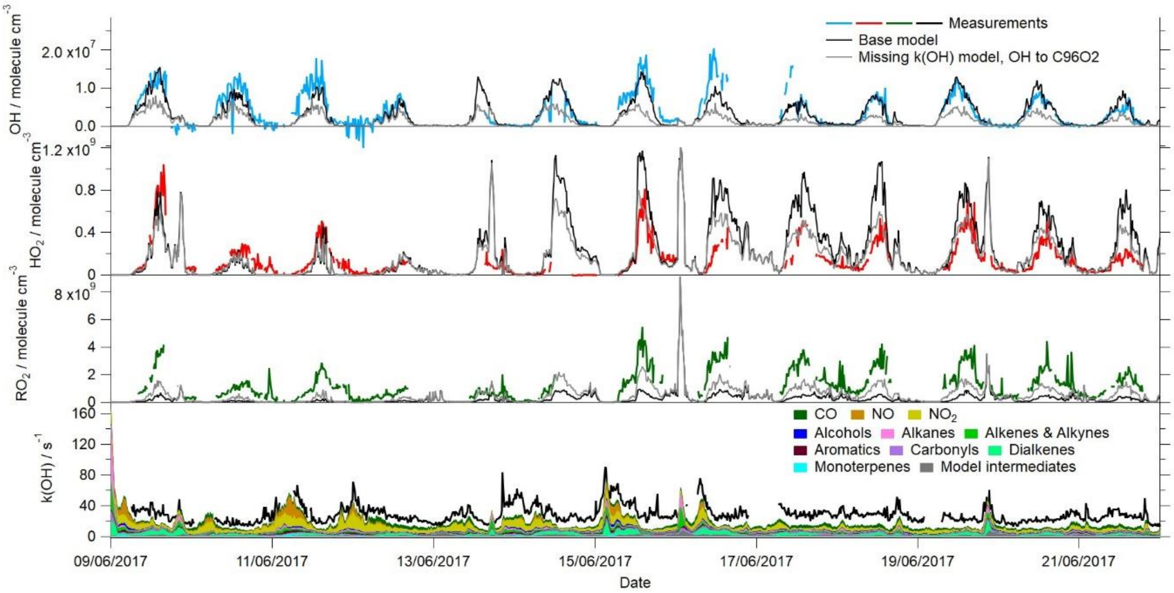
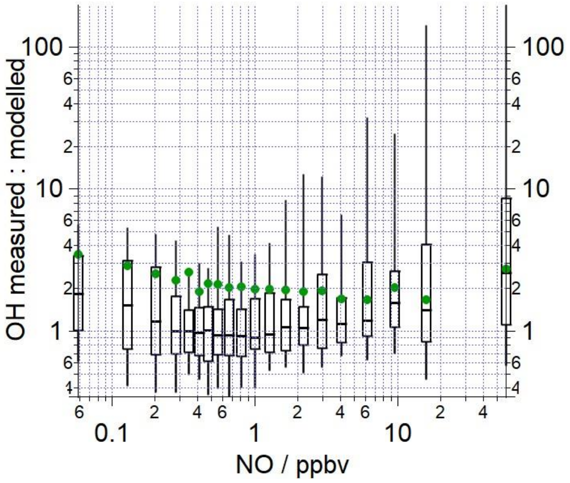
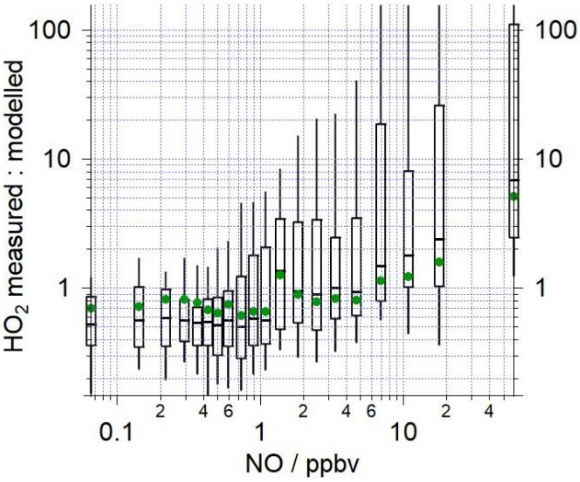


Figure S2: Time-series of the measured and modelled OH, HO_2, total RO_2 and OH reactivity from the 9th – 22nd June which encompasses high NO days (9th – 12th June) and low NO days (16th – 22nd June).





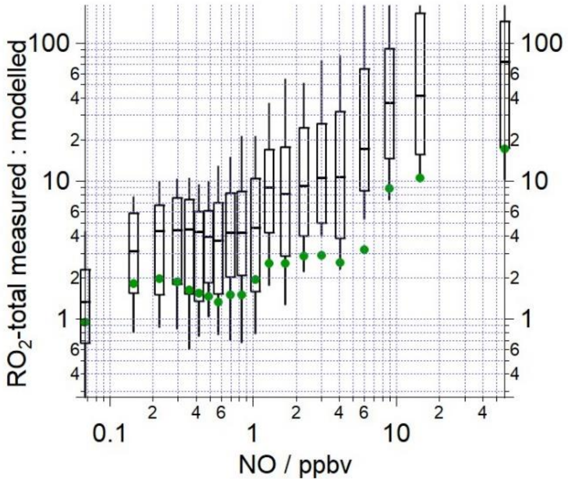


Figure S3: The median ratio (-) of the measured to modelled (base) OH, HO_2 and total RO_2 binned over the NO mixing ratio range encountered during the campaign on a logarithmic scale. The box and whiskers represent the 25th/75th and 5th/95th confidence intervals. The green circles display the measured to modelled OH, HO_2 and total RO_2 ratio when the model includes missing OH reactivity in the form of a single reaction which converts OH to C96O2. The number of data points in each of the NO bins is ~80

The median measured to modelled (Missing k(OH) (OH to C96O2)) ratio vs NO (green circles) is displayed in figure S3 alongside median measured to modelled (base) ratio. The inclusion of alkoxy isomerisation following RO_2 + NO reaction increases the modelled RO_2 concentration across the entire NO range but, considering the log scale, has the biggest impact on the ratio (from the measured to modelled (base) ratio) at the highest NO concentration. The HO_2 median measured to modelled (Missing k(OH) (OH to C96O2)) ratio vs NO in the middle panel increases from the measured to modelled (base) ratio at NO mixing ratios <1 ppbv, indicating improved agreement. At higher NO mixing ratios, where the base model begins to underpredict HO_2, due to the large under-prediction in RO_2, this under-prediction is reduced in the missing k(OH) (OH to C96O2) scenario owing to the increase in modelled RO_2.

The HO_2 median measured to modelled (Missing k(OH) (OH to C96O2)) ratio vs NO in the middle panel increases from the measured to modelled (base) ratio at NO mixing ratios <1 ppbv, indicating improved agreement. At higher NO mixing ratios, where the base model begins to underpredict HO2, due to the large under-prediction in RO_2, this under-prediction is reduced in the missing k(OH) (OH to C96O2) scenario owing to the increase in modelled RO_2.

The OH median measured to modelled (Missing k(OH) (OH to C96O2)) ratio vs NO (top panel) highlights a missing OH source, the magnitude of which deceases as NO concentrations increase.

3. The experimental configuration of RO2 convertor is missing.

We have provided an experimental description of the RO_xLIF instrument on pg 6 and provide references to previous papers (Whalley et al., 2018 and Slater et al., 2020) where further details can be found. We will add details on the physical dimensions of the RO_2 convertor to the revised manuscript.

Pg6, line 176: In the RO_xLIF reactor, which is an 83 cm long, 6.4 cm internal diameter flow-tube, in HO_x-mode, a flow of CO (10% in N_2) was added just beneath the sampling inlet and this rapidly converted any ambient OH sampled to HO_2. Within the RO_xLIF FAGE cell, a continuous flow of NO (99.95%) titrated ambient HO_2, the converted OH and also a large % of RO_2-complex radicals (see below) to OH for detection. In RO_x-mode, a total-RO_2 + HO_2 + OH measurement was made by addition of a dilute flow of NO (500 ppmv in N_2) alongside the CO which promoted the conversion of all HO_2 and RO_2 radicals to OH; the OH formed was rapidly re-converted to HO2 by reaction with CO. Within the RO_xLIF FAGE cell, the HO_2 was titrated back to OH, by reaction with NO, for detection.

4. In Line 573, the estimated NO concentration is the reactor is 4e13 cm-3. The reaction time scale of RO2+NO reaction is 0.003s. If such large flow was used in the reactor, the conversion to OH could be finished and the OH could further react with NO to form HONO. How do the author account for such conversion?

Excess CO (CO:NO = 50) was added continuously to the ROxLIF reactor, so the dominant reaction of OH, once formed, was with CO to reform HO_2 rather than reaction with NO.

5. The RO2 and ROx budget is missing the part of Cl oxidation.

Nitryl chloride measurements were only made for part of the campaign period, so it is not possible to add the production of RO_2 radicals from Cl atoms to the campaign averages. We will add the following sentence to the revised manuscript to help the reader gauge the impact Cl oxidation rates can have on RO_2 production:

Pg16, line 488: The production rate of RO_2 from Cl-initiated VOC oxidation on these mornings would serve to enhance P(RO_x) by up to 2.1 ppbv hr^{-1}.

6. How sensitive of the experimental budget of HO2 and ROx radical towards the organic nitrate yield in the reaction of RO2 and NO? The organic nitrate yield varies from 0.01 to 0.5 among different RO2 species and it might have notable influence on the ROx and HO2 budget. Tan et al. (2019) not only set the yield to 0.05 but also performed the sensitivity tests by varying the yield from 5% to 20%, and notable influence was observed for their study although the bias was still within the experimental errors. Considering the large measured RO2 concentration, the yields might play significant role on this budget analysis in this study.

Increasing the alkyl nitrate yield will decrease the production rate of HO_2, and would lead to an improved agreement with the HO_2 destruction rate. However, an increased alkyl nitrate yield would serve to increase both the RO_2 and the total RO_x destruction rates, enhancing the discrepancy between the known RO_2 and RO_x production rates further. The MCM, which takes into account the different types of RO_2 present from the VOCs observed, predicts a mean alkyl nitrate yield of 6%, so we feel that our choice of a 5% yield in the budget analysis is appropriate.

7. If it was the case as the author said, 90% of the measured RO2 would react with NO to produce another RO2, in which the majority of the RO2 was probably derived from long-chain alkanes,

monoterpenes, and other like-VOCs, this part of RO2 should be detected in the RO2-complex. According to Fig 5, the RO2-complex only made up less than 50% of the total RO2.

As we state on Pg 18, lines 566 – 569: both the simple- and complex-RO_2 species are enhanced (by including an alkoxy isomerisation mechanism in the model), as the first 3 generations of RO_2 species formed would be detected during the RO_x-mode in the RO_x-LIF instrument and, hence, contribute to RO_2-simple. The final RO_2 species formed, that does propagate to HO_2 via RO upon reaction with NO, would be detected during the HO_x-mode in the RO_xLIF instrument and, as such, contributes to the RO_2-complex fraction.

Besides, if the multiple bimolecular reaction of RO2 with NO made up such a proportion (90%), the ozone production would be inconceivably enhanced, but was not embodied in the observed O3 concentrations.

It is unwise to compare the ozone production rate to the observed ozone which will be impacted by physical processes such as advection, ventilation and deposition. The comparison of the model predicted glyoxal revealed that during the morning hours rapid ventilation effectively removed glyoxal from the model box. We can expect that ozone would be removed at the same rate and so the high rate of ozone production calculated from the observed peroxy radicals may not be reflected in the ozone concentration observed. We will comment on the losses of O_x in the revised manuscript. See response to Ezra Wood's comment.

Pg20, line 613 onwards: By approximating the rate of ozone production to the rate of NO_2 production from the reaction of NO with HO_2 and RO_2 radicals, urban radical measurements can be used to estimate chemical ozone formation (Kanaya et al., 2007; Ren et al., 2013; Brune et al., 2016; Tan et al., 2017; Whalley et al., 2018).

$$P(\mathrm{O_x}) = \left(k_{\mathrm{HO_2+NO}}[\mathrm{HO_2}][\mathrm{NO}] + k_{\mathrm{RO_2+NO}}[\mathrm{RO_2}][\mathrm{NO}]\right) \qquad (11)$$

Losses of O_x ($L(O_x)$) include chemical losses such as the reaction of NO_2 with OH, net PAN formation, the fraction of $O(^1D)$ (formed by the photolysis of O_3) that react with H_2O and the reaction of O_3 with OH and HO_2. Physical loss processes, such as O_3 deposition and ventilation out of the model box (see section 2.4) will also contribute to $L(O_x)$. Physical processes such as advection of O_3 into the model box would also need to be considered in the model to make a direct comparison to the observed O_3 concentrations.

Considering the chemical production of O_x (E.11), recent studies where OH, HO_2 and RO_2 observations (via RO_xLIF) were made, demonstrated that models may under-predict ozone production at high NO due to an underestimation of the RO_2 radical concentrations at high NO concentrations (Tan et al., 2017; Whalley et al., 2018).

8. Line 563, Line 574-575, and Table 3, the author attributed the missing OH reactivity to additional reaction converting OH to C96O2, which is an α-pinene derived RO2, but C96O2 is formed in the α-pinene reaction with O3 but NOT with OH. How do the authors justify this assumption? Some discussion to make such assumption is needed.

This is true, our motivation for choosing C96O2 was to investigate the impact of RO isomerisation forming RO2 in the model and so picked the C96O2 peroxy radical as this species undergoes several

isomerisation steps following RO_2+NO reaction and is already included in the MCM. We will add the following footnote to Table 3 in the revised manuscript to clarify this:

[1] Note, C96O2 is an α-pinene derived RO_2 that forms during the ozone-initiated oxidation of α-pinene. The additional production of C96O2 peroxy radicals in this model scenario was used to investigate the impact of an RO isomerisation mechanism on the modelled radical concentrations.

Technical comments:

1. Line 234, the last [RO2] should be out of the right bracket in Eq (6).

This will be corrected

2. Line 360, 'production and destruction'.

This will be corrected

3. There is no need for 2.4.1.

This will be removed and incorporated into section 2.4

4. Line 513, α = 0.87 seems to be wrong or the description of α was confusing.

The definition for alpha on page 17 line 513 should be α = 1 minus the rate at which RO forms RO2 or RC(O)O2 divided by the rate of RO conversion to HO2.

5. Conclusion should be section 4.

This will be corrected