Referee 2

This paper presents measurements of OH, HO2, and RO2 radical concentrations in addition to measurements of total OH reactivity in Beijing during the AIRPRO campaign in summer 2017. A radical budget analysis using the measured sources and sinks of these radicals revealed a potential missing source of OH during most of the campaign, although rates of OH production and destruction were in better balance under the higher NOx periods. The measured rates of HO2 production were found to be significantly greater than the rates of destruction, while the measured rates of destruction of RO2 radicals was found to be greater than the rates of production, especially under the higher NOx periods. These results suggest that the rate of conversion of RO2 to HO2 may be significantly slower than currently assumed. The authors also present the results of several 0-D box models using the MCM 3.3.1 chemical mechanism. The model was able to reproduce the measured OH concentrations, but underestimated the measured total OH reactivity, suggesting that the agreement may be fortuitous. The model also overestimated the measured HO2 concentrations and underestimated the measured RO2 concentrations, consistent with the experimental radical budget suggesting that the model may be overestimating the rate of conversion of RO2 to HO2 under high NO conditions. The model was found to be in better agreement with the measurements if the missing reactivity was assumed to be composed of VOCs that produced a-pinene derived RO2 radicals that upon reaction with NO results in isomerization reactions that reform other RO2 species before eventually producing HO2 effectively reducing the rate of conversion of RO2 radicals to HO2. While this model scenario improved the model agreement with the measurements of HO2 and RO2, it significantly underestimates the measured OH concentrations, consistent with a missing OH source. However, the proposed RO2 isomerization reactions may lead to the production of OH radicals and contribute to the missing OH source. The significant underestimation of the observed RO2 concentrations implies that the model is significantly underestimating the observed rate of ozone production under high NOx conditions. The measurements appear to be of high quality and include measurements of unknown interferences, which except for a few instances were found to be negligible. The measured radical concentrations are consistent with previous ROx measurements in several urban areas and is of interest to the atmospheric chemistry community. I recommend publication after the authors have addressed the following comments.

We thank referee 2 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) The analysis generally focuses on the campaign average and the measurements under higher NOx conditions, but there is little discussion regarding the measurements under lower NO conditions, and in particular the extended period at the end of the campaign where the measured RO2 concentrations were the highest. The scale used in Figure 2 makes it difficult to see, but the discrepancy between the measurements and the model appears to be as significant as the discrepancies at higher NOx for this period. Unfortunately, this is not apparent from the information provided in Figure 6. It is not clear whether the additional VOC reactivity producing RO2 radicals that isomerize after reaction with NO to form additional RO2 would improve the model agreement for this period, as it is not clear whether reaction with NO still dominates the fate of peroxy radicals during this portion of the campaign. While the manuscript is already long, it would still benefit from a discussion of this aspect of their measurements.

We will extend the discussion on the model measurement comparison under the low NOx periods by including the following discussion:

Pg 14, line 440 onwards: The model under-estimates total RO$_2$ throughout the measurement period, although the level of disagreement (in terms of 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 (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
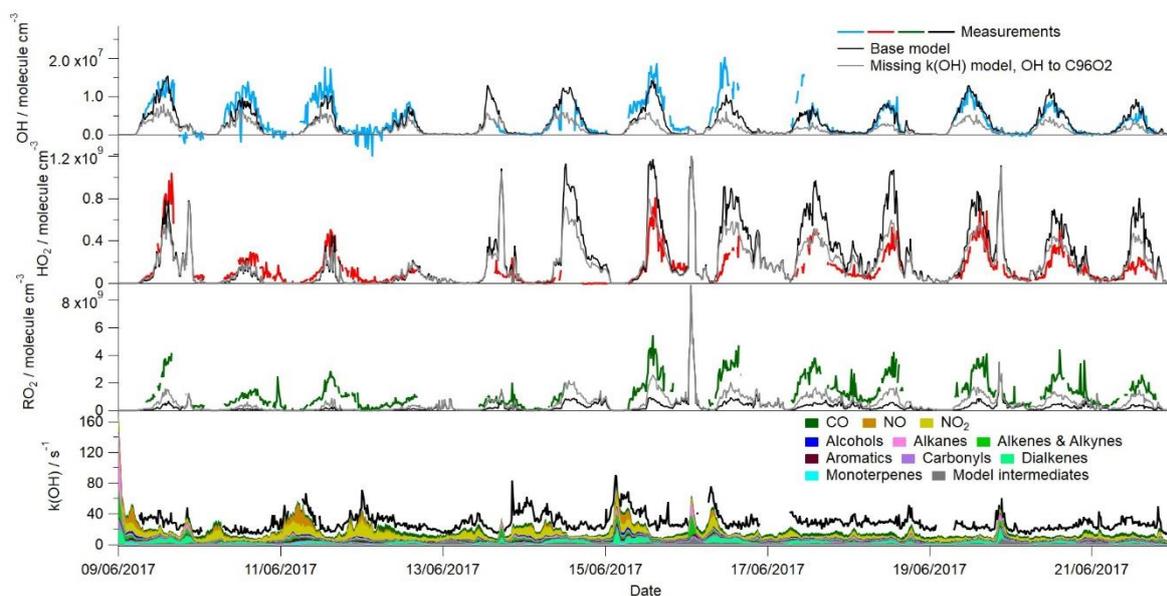
Figure S2: Time-series of the measured and modelled OH, HO$_2$, total RO$_2$ and OH reactivity from the 9th – 22nd June which encompasses high NO days (9th – 12th June) and low NO days (16th – 22nd June).
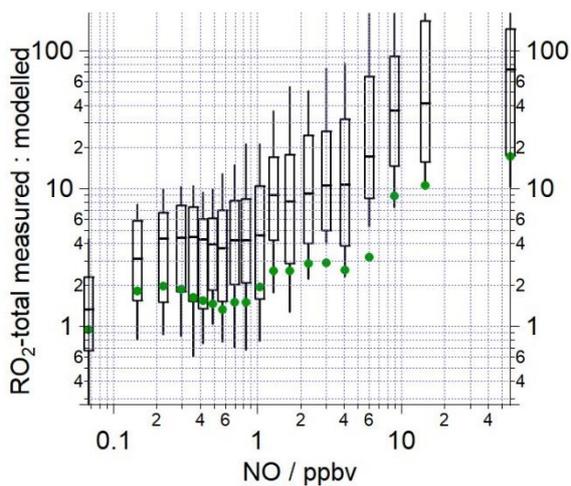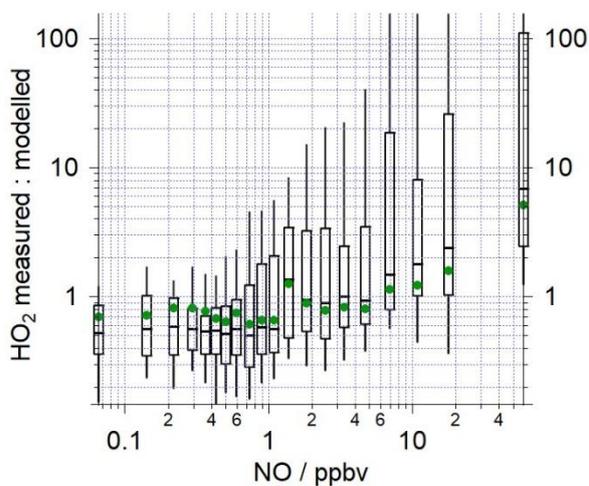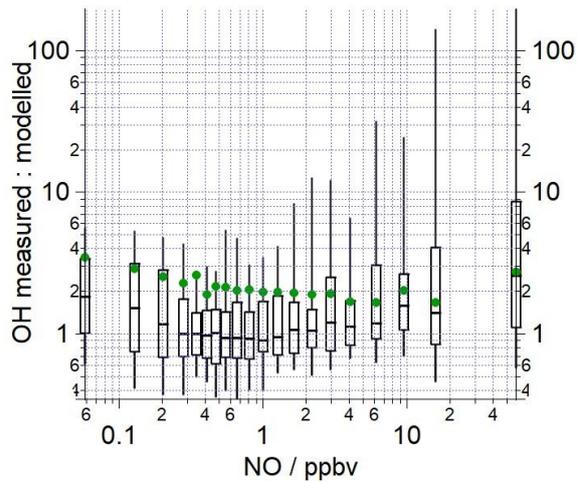
Figure S3: The median ratio (-) of the measured to modelled (base) OH, HO₂ and total RO₂ binned over the NO mixing ratio range encountered during the campaign on a logarithmic scale. The box and whiskers represent the 25th/75th and 5th/95th confidence intervals. The green circles display the measured to modelled OH, HO₂ and total RO₂ 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.

2) Related to this, Berndt et al. (2018) report that RO2 + RO2 accretion reactions for a-pinene may be significant under low NOx conditions, and this type of accretion reaction may also be important for the peroxy radicals of other large VOCs. It's not clear whether these reactions could impact the modeled RO2 concentrations overall, but could be important during the low NOx period at the end of the campaign when the RO2 concentrations are high. Given that the authors are hypothesizing that isomerization of peroxy radicals of large VOCs produce additional peroxy radicals, the authors should comment on the potential impact of these reactions on the model results.

We have taken the rate of accretion from Berndt et al and the observed RO_2 and NO concentrations to assess if accretion reactions may be competitive under low NO conditions experienced. If we assume that all RO_2 species measured undergo accretion reactions with a rate coefficient of 9.7×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, and compare this to the production rate of RO radicals from the reaction of RO_2 with NO we find that under the low NO_x period, the production rate of accretion products is comparable to the production rate of alkoxy radicals. If we use the faster rate coefficient of accretion of 79×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, the production rate of accretion products is ~8.5 times faster than the RO production rate during the low NO_x period, although this should be viewed as an upper limit as the total RO_2 concentration measured will contain a contribution from small RO_2 radicals, such as CH_3O_2, for which the rate of accretion is negligible. Nevertheless, we expect the inclusion of accretion reactions in the MCM would serve to reduce the modelled RO_2 concentration under low NO_x conditions as the reaction represents a RO_x sink. This suggests that the missing RO_2 source may be even larger than reported here. Accretion reactions effectively remove RO_2 radicals without conversion of NO to NO_2 and so have implications for modelling in situ O_3 production, if models rely only on the rate of VOC oxidation when investigating O_3 production.

We will add the following discussion to the manuscript:

Pg 19, line 602 onwards: In addition to missing unimolecular RO₂ reactions, the model may be missing other RO₂ reaction pathways, for example, RO₂ accretion reactions, as identified by Berndt et al (2018). Although it is difficult to fully assess how competitive these RO₂+RO₂ reactions may be compared to RO₂+NO reactions from the total RO₂ observations made (the concentration of each individual RO₂ would be needed), the inclusion of accretion reactions in the MCM would serve to reduce the modelled RO₂ concentration under low NOₓ conditions as the reaction represents an overall ROₓ sink. This suggests that the missing RO₂ source identified may be even larger under the lower NO conditions.

Pg 20, line 609 onwards: Under low NO conditions there is emerging evidence that unimolecular isomerisation reactions occur for a range of RO₂ radicals (Jokinen et al., 2014; Ehn et al., 2014; Berndt et al., 2016; Wang et al., 2017b) as well as RO₂ accretion reactions (Berndt et al., 2018). These reactions will effectively remove RO₂ radicals without conversion of NO to NO₂ and so also have implications for modelling in situ O₃ production, if models rely only on the rate of VOC oxidation when investigating O₃ production.

3) The authors should provide plots of some of the diurnal averaged constraints for their model (NO, NO2, O3, CO, isoprene, etc.) to allow comparisons with other urban measurements and to put the results shown in Figure 5 into context. Adding the diurnal average of the low NOx period at the end of the campaign would also assist in interpreting the radical measurements during this period. This information could go into a supplement.

We will include the following figure in the SI to assist in the interpretation of the radical observations and for comparison with other urban measurements.
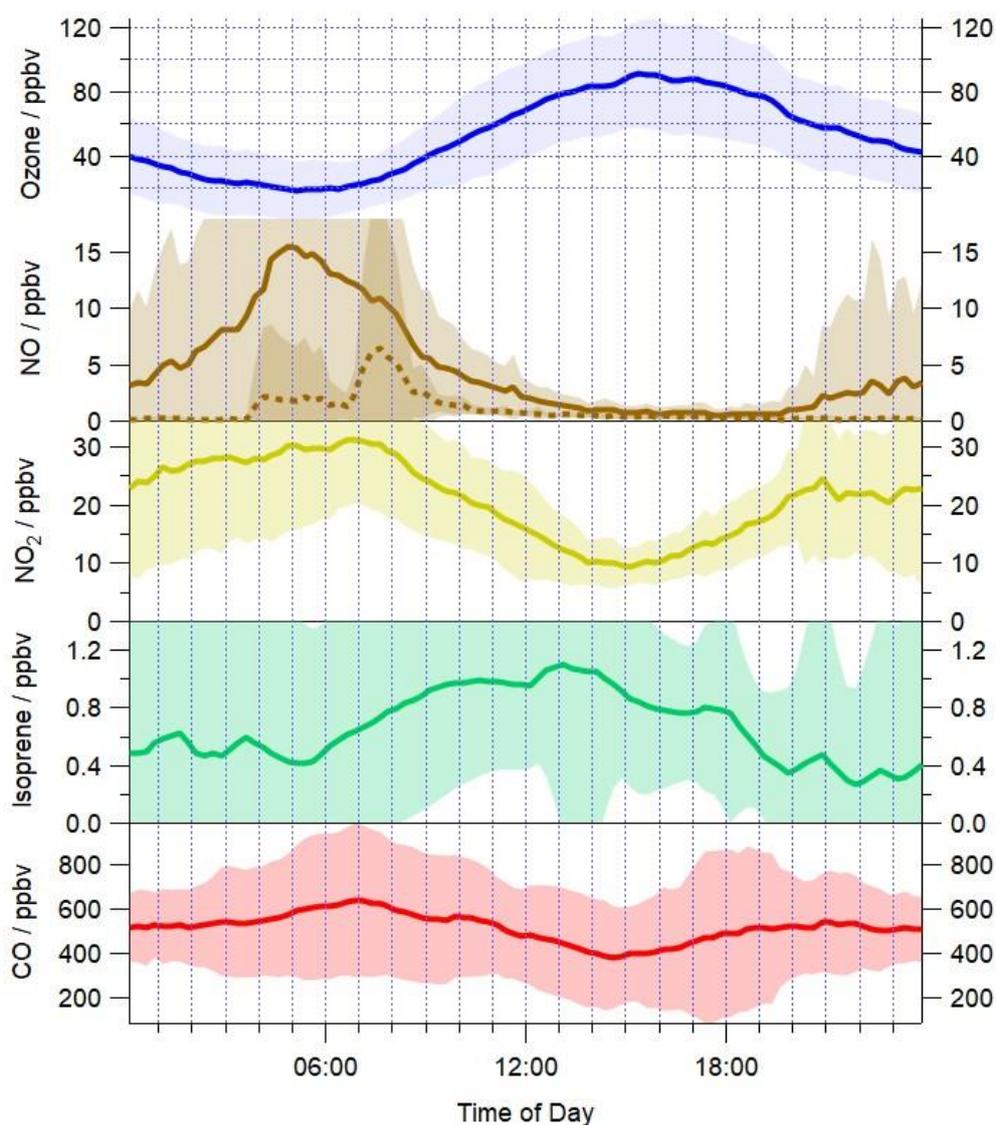
Figure S1: Average profiles for the observed O₃, NO, NO₂, isoprene, and CO at 15 minute intervals over 24 hours. The solid lines represent the campaign average whilst the dashed line is the average NO profile between 16th – 22nd June.

4) The definition of alpha on page 17 line 513 appears to be an error as it is not consistent with the value and the definition described on page 8 line 246. This should be clarified.

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.

This will be changed in the revised manuscript.