We thank the referees for their comments (shown in black below). Our responses are shown in red and the revisions to the manuscript are shown in green:

This paper presents measurements of OH, HO2 and RO2 radicals in London during the ClearfLo campaign in 2012. The authors compare the measured radical concentrations to both a simple steady-state model as well as a model based on the Master Chemical Mechanism. The authors find that the simple steady-state model can reproduce the observed OH concentrations reasonably well. However, model calculations using MCM v. 3.2 resulted in variable agreement with the measurements. The model tended to overpredict the measured OH, HO2, and RO2 concentrations, especially under low NO conditions typically observed during the afternoon. The discrepancy with the measured HO2 was especially high during easterly flows that passed over central London that brought high concentrations of VOCs and in particular higher concentrations of biogenic and diesel related VOCs. These results suggest that the model is either overestimating the sources of peroxy radicals or is underestimating peroxy radical sinks. Because the measured total OH reactivity is in reasonable agreement with the modeled total OH reactivity, the authors suggest that the modeled peroxy radical source from reaction of VOCs with OH is well characterized, and that the model is likely missing a significant peroxy radical sink under these conditions. The authors suggest that auto-oxidation of biogenic and large VOCs during the easterly flows may account for some of the discrepancies, as these mechanisms can reduce the rate of RO2 conversion to HO2 and lead to loss of these low volatility species to SOA formation, thus acting as a radical sink. Including a surrogate auto-oxidation mechanism into their model improves the agreement with measurements of HO2 and RO2 during the afternoon. The modeled overprediction of HO2 and RO2 during the low NO periods suggests that the model is overpredicting the instantaneous rate of ozone production during these periods. In contrast to the discrepancies observed under low NO conditions, the model significantly underpredicted the observed concentrations of RO2 radicals under high NO conditions, suggesting that the model is significantly underestimating the instantaneous net rate of ozone production, similar to that observed in other urban areas. The authors suggest that interferences associated with the measurement of total RO2 radicals from decomposition of CH3O2NO2 in their reactor may account for the discrepancy. The measurements appear to be of high quality and the paper is well written and suitable for publication in ACP after the authors have addressed the following comments.

1) In the introduction (page 3), the summary of the results of Griffith et al. (2016) during CalNex is misstated. Similar to the results reported here, Griffith et al. found that the model underestimated the measured HO2* by a factor of 3 during the week when NO mixing ratios were greater than 4 ppb. On the weekends, the modeled HO2* concentrations were in good agreement with the measured concentrations when NO mixing ratios were less than 4 ppb.

We apologise for this misrepresentation and will modify the text as follows:

Griffith et al. (2016) found that the level of agreement between modelled and measured HO_2 was dependent on whether it was a weekday or weekend; the model under-predicted HO_2^* by a factor of 3.4 during the week when NO mixing ratio were greater than 4 ppbv but agreed well on weekends (observed to modelled $HO_2^* = 1.3$) when NO concentrations were below 4 ppbv.

2) The large overestimation of the modeled RO2 concentrations in the evening during the easterly flows is disconcerting. Even though the majority of these episodes occurred at night and may not impact the conclusions of the paper regarding daytime ozone production (page 13) it appears that similar events occurred in the morning on August 5th and 15th. In contrast to the nighttime events, these events appear to have resulted in increases in the modeled HO2. The authors should also comment on these morning model episodes and potential reasons for the discrepancy with the measurements. Although there are only a handful of these modeled events, are the authors certain that these are isolated model events and not an indication of a more general problem with the model? Since these events appeared to correlate with high NO and VOC episodes (page 13), where fast radical propagation could lead to rapid changes in constrained species, could this indicate a problem with the 15-min re-initiation of the model constraints (page 10)? Are the authors sure that the concentration of constrained species is not changing during the 15-minute integration period during these episodes or at any other time? Related to the above, the authors speculate that these episodes may indicate "a problem in the representation of the oxidation chemistry of the complex VOCs which were present at these times." Can the authors provide more information on the composition of the peroxy radicals during these episodes and provide insight into the VOC oxidation chemistry in the model that is responsible for the large RO2 overestimations? What does a radical budget analysis indicate about the sources and sinks of radicals during these episodes? The paper would benefit from an expanded discussion of these model episodes to give the reader more confidence in their model results.

We thank the reviewer for spotting these daytime spike in the modelled radical concentrations and we have investigated the cause of these. We have found that we do not have NO concentrations for these times and the model was initialised with NO = 1×10^5 molecule cm^{-3} at these times so these model data could subsequently be filtered out – something we omitted to do. (See revised figure 2 below).

However, missing NO data is not the cause of the high nighttime modelled RO_2. These high modelled values relate to active nitrate radical chemistry (on page 13 we should have written '..evenings when NO_2 and VOC concentrations were elevated' rather than '..evenings when NO and VOC concentrations were elevated', NO concentrations were actually very low at these times). Although most of the VOC species seem to be elevated during these events, the model is particularly sensitive to the high levels on monoterpenes that were observed – this is illustrated in figure 9 in the model run constrained to standard VOCs only where the modelled nighttime RO_2 spike is reduced substantially.

We will modify the text as follows:

These high nighttime [RO_2] were not observed, to the magnitude predicted by the model, and other radical types (OH and HO_2) were not observed nor predicted to increase at the same time. These high modelled RO_2 excursions correspond to evenings when VOC concentrations were elevated and NO concentrations low and reflect periods of active nitrate chemistry in the model (see brown area, fig. 6). The RO_xLIF technique is likely insensitive to some NO_3-adduct alkene peroxy radicals. Only around 20% of the short-chain alkene derived NO_3-adduct peroxy radicals (e.g. those deriving from ethene and propene) are expected to convert to HO_2 in the reactor with the dominant reaction pathway (around 80%) instead leading to the formation of two aldehydes and NO_2 (according to the MCM). For the NO_3-adduct peroxy radical deriving from isoprene, however, the MCM assumes 100% yield of HO_2. The insensitivity of RO_xLIF to certain NO_3-adduct alkene peroxy radicals may explain the RO_2 model measurement discrepancy in the nighttime.

3) The authors highlight the model underestimation of RO2 radicals under high NO conditions, and suggest that decomposition of CH3O2NO2 in their reactor may result in an overestimation of the measured RO2 concentration (pages 15-16). Since they do not know the contribution of this interference, they choose not to correct for it. If this interference is small, can the authors speculate what may be missing from the model to explain the underestimation of the measured RO2 concentrations under high NO conditions?

The photolysis of ClNO2 to Cl atoms may provide an additional source of RO2 radicals early in the morning as reported by Riedel et al. (2014) We have explored this for our London observations as ClNO2 was measured during the project (Bannan et al., 2015)and we find that although Cl atom chemistry increases the modelled RO2 concentrations in the morning when NOx levels are high, the predicted increase is only 20% and so cannot reconcile the model under-prediction in RO2. If the rate or branching ratio of RO2+NO to alkyl nitrate are over-estimated in the model, or the rate of PAN decomposition is faster than assumed in the model, this could help to bring the model into better agreement. Similar to our speculation that it is uncertainties in the degradation of biogenic and large VOCs that are leading to model biases under low NOx conditions, it may be uncertainties in the rate and branching ratio of alkyl nitrates formed from the larger VOCs that are leading to model bias under high NOx conditions also.

The photolysis of $ClNO_2$ to Cl atoms may provide an additional source of RO_2 radicals early in the morning as reported by Riedel et al. (2014). $ClNO_2$ was measured during the ClearfLo project (Bannan et al., 2015) and, although Cl atom chemistry can increase the modelled RO_2 concentrations in the morning when NO_x levels are high, the predicted increase is modest, ~ 20%, and so cannot fully reconcile the model under-prediction in RO_2. For the more complex VOCs present (e.g. biogenics and the long-chain alkanes) the rate of RO_2 propagation vs RO_2 termination may be faster than assumed in the model which would help to bring the model into better agreement with the observations.

 Minor points: Pages 8 and 12: The authors corrected the OH measurements for an expected laser generated interference based on laboratory calibrations. What was the magnitude of the OH laser-generated interference relative to the ambient measurements?

The median correction made is 20% of the ambient OH that was measured

Page 9-10: The authors should comment on why they chose to use MCM v3.2 rather than the updated v3.3.1, and whether the updated biogenic chemical mechanisms for isoprene and monoterpenes would impact their results.

As we used MCMv3.2 to model OH reactivity from the campaign (Whalley et al., 2016) and compare to these results in the manuscript we really needed to use the same model version for consistency. We are now working with the latest version of the MCMv3.3.1 and using this model mechanism to compare to some recent radical observations that we made in Beijing in China in 2016/2017. Under low NOx conditions, our preliminary model measurement comparisons from Beijing are consistent with findings reported in this manuscript from London – i.e. the model over-estimates HO2. From these findings we do not expect the latest version of the MCM which includes updates to the biogenic degradation mechanisms to change the findings we report here.

Page 11: Similar to that done in Whalley et al. (2016), the authors should consider highlighting the easterly flow periods in Figures 1 and 2 for clarity.

We will highlight the periods of Easterly flow in Figures 1 and 2 in the revised manuscript:
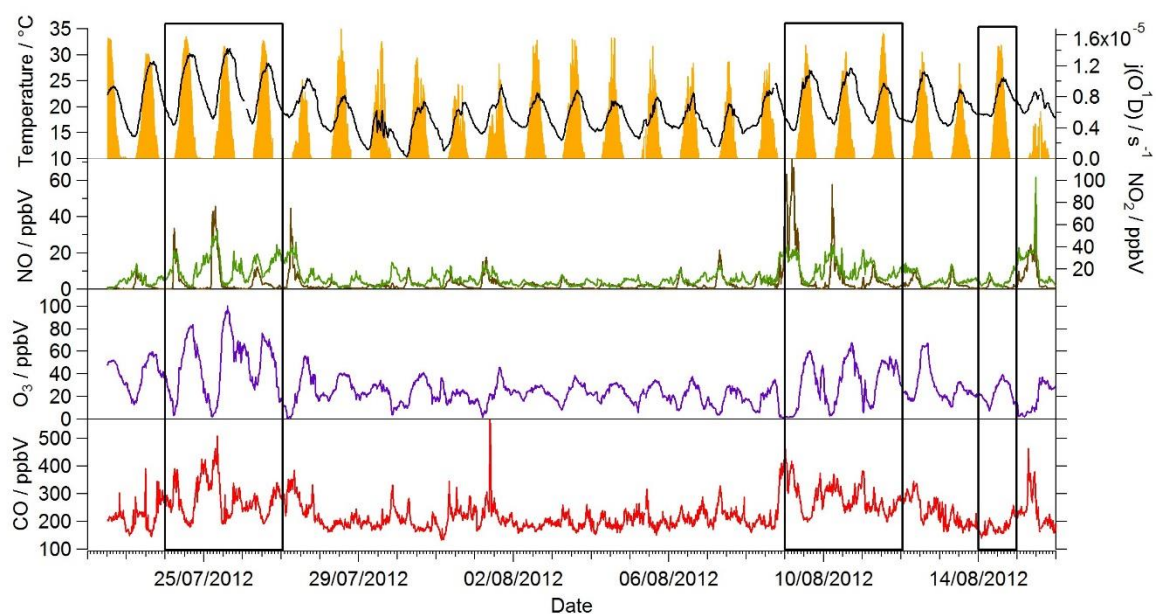
Figure 1: Observed temperature (black line), j(O^{1}D) (yellow area), NO (brown line), NO$_2$ (green line), O$_3$ (purple line) and CO (red line) mixing ratios during the summer ClearfLo IOP. Data time resolution is 15 minutes. Periods of Easterly flow are highlighted inside the black boxes.
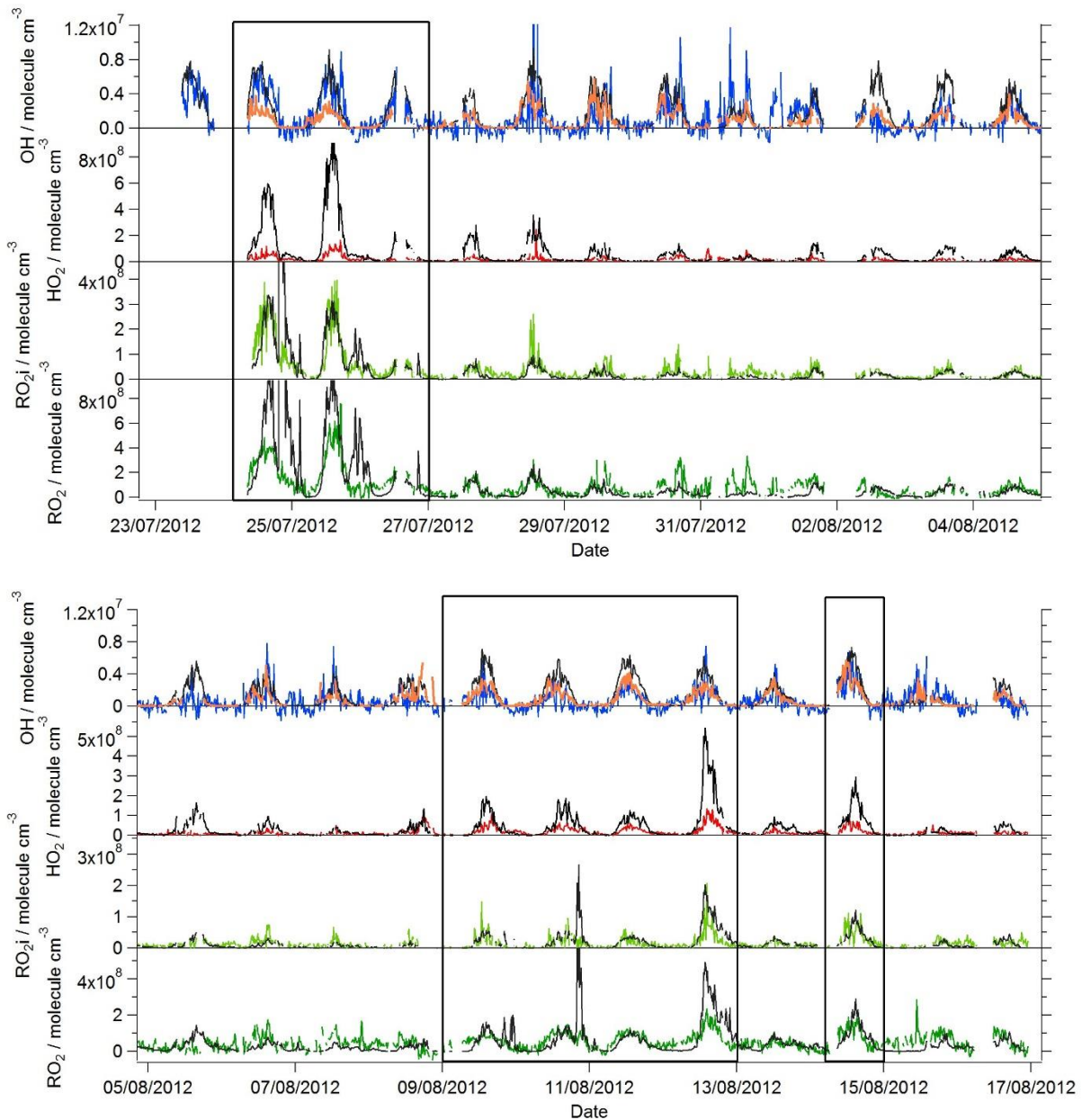
Figure 2: Observed (coloured lines) and MCM-BASE modelled (black lines) OH, HO₂, RO₂*i* and RO₂ during the summer ClearfLo IOP; steady state [OH] ([OH]_PSS) is displayed by the orange line. Periods of Easterly flow are highlighted inside the black boxes.

Page 11: What were some of the VOC concentrations? Isoprene and other biogenics? Although this information is given in Whalley et al. (2016), providing some additional information on the VOC concentrations would be useful.

We will add and additional table including average concentrations for the model species:

Table 3: Model constraints and their average and maximum noontime concentrations during South westerly and Easterly flows

Species	Mean / ppbV South Westerly flow	Mean / ppbV Easterly flow	Max noontime / ppbV South Westerly flow	Max noontime / ppbV Easterly flow
Ozone	24.2	37.4	34.4	87.8
Nitric oxide	2.5	5.5	33.4	11.9
Nitrogen dioxide	10.6	18.8	101.6	39.3
Carbon monoxide	213.8	272.7	298.4	311.0
Nitrous acid	0.32	0.56	0.89	0.89
Nitric acid	0.67	1.54	1.59	3.89
Peroxyacetyl nitrate	0.07	0.23	0.09	2.63
Methanol	2.4	5.2	5.5	8.9
Ethanol	2.4	5.7	5.2	6.8
Propanol	0.3	0.64	0.83	1.5
Butanol	0.6	0.84	1.42	2.1
Methane	1853.0	1903.2	1939.0	1971.5
Ethane	3.1	6.8	4.6	6.0
Propane	1.2	2.7	3.1	3.6
i-Butane	0.5	1.1	1.5	1.8
n-Butane	1.0	2.2	2.9	4.3
i-Pentane	0.5	1.2	1.5	2.4
n-Pentane	0.2	0.6	0.6	1.0
Hexane	0.3	0.7	1.7	1.4
Heptane	0.2	0.4	0.5	0.5
Octane	0.1	0.3	0.5	0.4
2-Methyl pentane	0.2	0.3	0.5	0.8
Nonane	0.2	0.4	0.8	0.5
Decane	0.2	0.4	0.6	0.4
Undecane	0.3	0.7	1.0	0.6
Dodecane	0.6	1.3	2.4	1.3
Dichloromethane	0.03	0.06	0.08	0.09
Acetylene	0.3	0.5	0.9	0.8
Ethene	0.5	0.9	1.7	1.7
Propene	0.2	0.3	0.5	0.3
Trans-2-butene	0.02	0.03	0.04	0.05
But-1-ene	0.05	0.08	0.1	0.12
Metyl propene	0.04	0.07	0.1	0.1
Cis-2-butene	0.01	0.02	0.03	0.03
Pent-2-ene	0.02	0.04	0.06	0.06

	Mean / ppbV South Westerly flow	Mean / ppbV Easterly flow	Max noontime / ppbV South Westerly flow	Max noontime / ppbV Easterly flow

Pent-1-ene	0.02	0.04	0.04	0.05
Trichloroethene	0.01	0.02	0.03	0.03
Benzene	0.12	0.2	0.3	0.3
Toluene	0.36	0.7	1.0	1.0
Ethylbenzene	0.06	0.1	0.2	0.2
1,3-Dimethylbenzene	0.04	0.08	0.1	0.1
1,4-Dimethylbenzene	0.04	0.08	0.1	0.1
1,2-Dimethylbenzene	0.05	0.11	0.1	0.2
1,2,3-Trimethylbenzene	0.01	0.01	0.04	0.02
1,3,5 -Trimethylbenzene	0.01	0.01	0.13	0.03
1,2,4-Trimethylbenzene	0.02	0.03	0.25	0.11
Phenylethene	0.02	0.05	0.06	0.07
1-Methylethylbenzene	0.002	0.003	0.01	0.01
Propylbenzene	0.03	0.09	0.17	0.24
3-Ethyltoluene	0.01	0.02	0.14	0.08
4-Ethyltoluene	0.01	0.02	0.07	0.05
2-Ethyltoluene	0.01	0.01	0.11	0.03
Benzaldehyde	0.01	0.01	0.03	0.06
α-Pinene	0.12	0.2	0.31	0.46
Limonene	0.04	0.07	0.12	0.23
Formalydehyde	6.7	13.8	10.1	29.9
Acetaldehyde	3.3	6.6	7.6	9.2
Acetone	2	3.4	3.7	5.3
Methacrolein	0.02	0.03	0.06	0.12
Methylvinylketone	0.02	0.04	0.07	0.13
2-Methylpropanol	0.04	0.06	0.1	0.2
Acetic Acid	0.04	0.06	0.1	0.2
Butan-2-one	0.05	0.08	0.14	0.25
n-Butanal	0.01	0.02	0.03	0.06
2-Penanone	0.02	0.04	0.07	0.13
n-Pentanal	0.02	0.03	0.06	0.1
4-Methyl-2-pentanone	0.04	0.07	0.12	0.23
Hexan-2-one	0.03	0.05	0.09	0.15
Cyclohexanone	0.01	0.02	0.04	0.08
1,3-Butadiene	0.01	0.02	0.05	0.02
Isoprene	0.1	0.2	0.3	0.48

Page 11: Including campaign averaged NO / NO2 in Figure 3 would help to highlight the model/measurement discrepancies under the difference NO regimes.

Good idea. We will modify figure 3 as suggested:
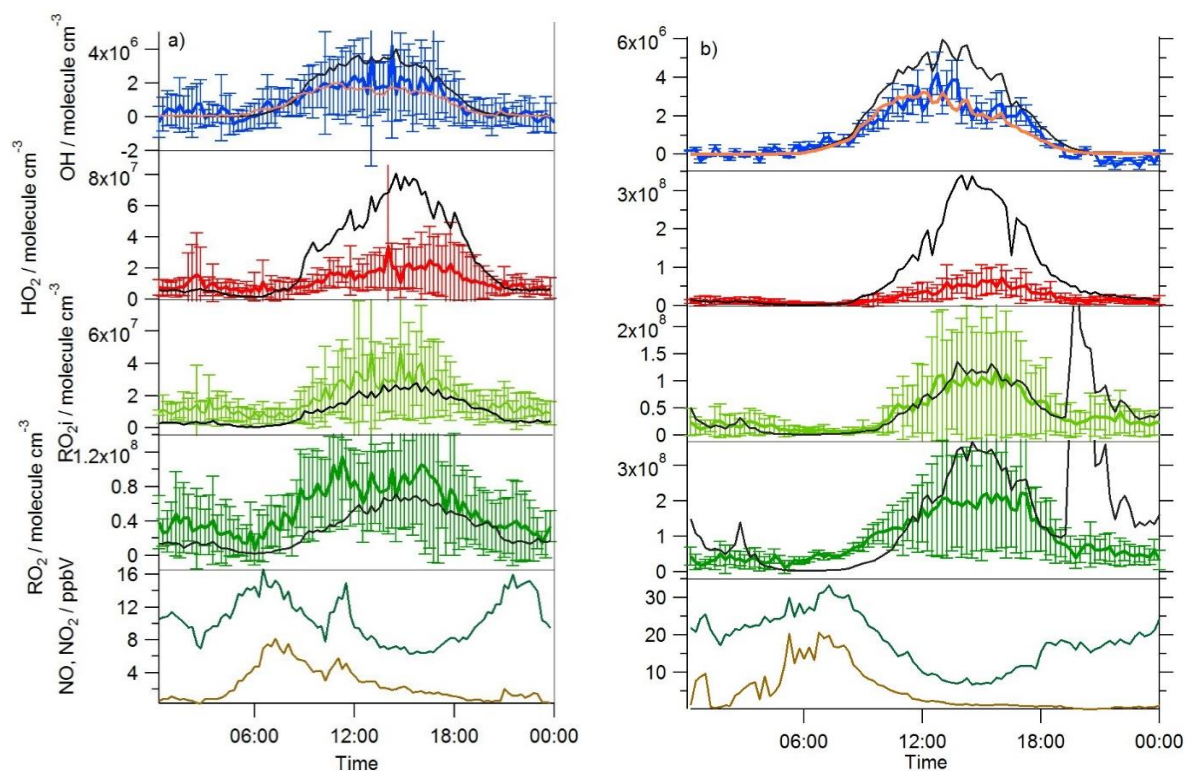
Figure 3: Average diel observed (coloured lines with error bars) and MCM-BASE (black line) OH, HO₂, RO₂i and RO₂ profiles during a) south-westerly and b) easterly flows; [OH]ₚₛₛ is displayed by the orange line. The error bars represent the 1σ variability in the observations. The average diel observed NO (brown line) and NO₂ (green line) are displayed in the bottom panels.

Referee 2

This paper presented the measurements of OH, HO2 and specious RO2 concentrations in London in 2012 summer. The OH experimental budget was closed. However, a box model based on MCM v3.2 overestimated HO2 concentrations by up to a factor of ten. The authors believed that the discrepancy was caused by the uncertainties in the degradation mechanism of biogenic and diesel related VOCs in low NOx. On the other hand, the model started to underestimate measured RO2 concentrations. Finally, the influence on ozone production prediction caused by such measurement and model discrepancy was discussed. The full set of free radical measurement is sparse in the literatures. With this comprehensive data set, the radical budget was nicely diagnosed, which provide deep insights into the radical chemistry of the current urban atmosphere. This manuscript is well written and structured. I suggest publication after the authors addressed the comments below.

Specific comments:

1. The name of alkene and aromatic related RO2 needs to be standardized in the community. The authors used RO2i in this paper while some people used RO2#. Due to the essence of the detection mechanism, would it be possible to use R(OH)O2 for this kind of peroxy radicals? This is a comment for the consideration of the authors.

Although we think this is a good suggestion, we have used RO_2i to represent RO_2 species that convert to OH within a FAGE cell in the presence of NO both in the current manuscript and in our previous paper (Whalley et al., 2013) and, as the referee points out, others have adopted different nomenclature. We would prefer to use RO_2i here rather than introduce a third term into the literature so we are, at least, consistent with our earlier paper.

2. In the part of experimental, it would be nice if a small subsection shortly before the model description with a brief description (e.g. measurement techniques, uncertainties, LOD, et al.) of the relevant parameters (e.g. total OH reactivity, NO, NO2, O3, CO and VOCs). Even some redundancy compared to Whalley et al. 2016 is helpful for the readers to better understand the results.

We do include these details in Table 2 but plan to include an additional table in the revised manuscript to include typical concentrations for the species that are used to constrain the model. (See Table 3 above).

3. The RO2 correction due to PAN decomposition is relative large. Fuchs et al. (2008) and Tan et al. (2017) found the PANs interference in atmospheric relevant conditions is negligible. Could the authors comment on the possible difference between two instruments?

The correction we make is for the decomposition of CH3O2NO2 in the flow tube. The correction is larger in this work both because of the experimental conditions we experienced (temperatures were generally below 298K and NO2 concentrations were frequently greater

than 10 ppb) and slight differences in the equilibrium rate constant we use ($K_{eq} = 3.6 \times 10^{-12}$ cm^3 at 298 K, taken from the MCM vs $K_{eq} = 2.7 \times 10^{-12}$ cm^3 at 298 K,(Fuchs et al., 2008)). The equilibrium rate coefficient displays a strong negative temperature dependence, increasing by over an order of magnitude if we calculate it using the highest (304K, $K_{eq} = 1.65 \times 10^{-12}$ cm^3) vs lowest temperatures (283.55K, $K_{eq} = 2.26 \times 10^{-11}$ cm^3) experienced during the campaign. As the coolest temperatures were experienced in the morning, the correction is most significant in the morning (and during the cooler south westerlies). Furthermore, Fuchs et al.(2008) calculate the % interference at 10 ppb NO_2. We frequently observed NO_2 concentrations greater than 10 ppb, with NO_2 peaking at 50 ppb during the morning rush-hour so the correction becomes more significant in this work due to these factors.

4. The authors choose MCMv3.2 for their base case but not the latest version MCMv3.3.1. The later discussion talked about the possible influence of VOCs autooxidation pathways of which to my knowledge is included and improved in MCMv3.3.1. Could the authors comment on this choice?

As we used MCMv3.2 to model OH reactivity from the campaign (Whalley et al., 2016) and compare to these results in the current manuscript we really needed to use the same model version for consistency. We are now working with the latest version of the MCMv3.3.1 and using this model mechanism to compare to some recent radical observations that we made in Beijing in China in 2016/2017. Under low NOx conditions, our preliminary model measurement comparisons from Beijing are consistent with findings reported in this manuscript from London – i.e. the model over-estimates HO_2. From these findings we do not expect the latest version of the MCM which includes updates to the biogenic degradation mechanisms to change the findings we report here.

5. The mean diurnal profiles are averaged for different air sector. But the budget analysis in figure 4 only show the average for the whole campaign. The authors should make it consistent. Especially the OH budget is different between different flow regimes. Also the same applied to the figure 5 and figure 6.

The radical budget does not really differ in terms of the importance of particular reactions, rather the flux is just over twice as fast for many reactions under the easterly flows (See Fig. 7 below). An exception to this are the low NO_x RO_2 termination pathways: HO_2+RO_2 reactions are ~ six times faster and RO_2+RO_2 reactions are ~ eight times faster under easterly flows. These pathways are minor compared to the RO_2+NO_x pathways, however, and owing to this, we feel that the manuscript would not benefit from splitting figure 4 and figure 6. We will include Figure 7 in the revised manuscript to highlight the magnitude of the radical flux under South westerly and Easterly conditions respectively.
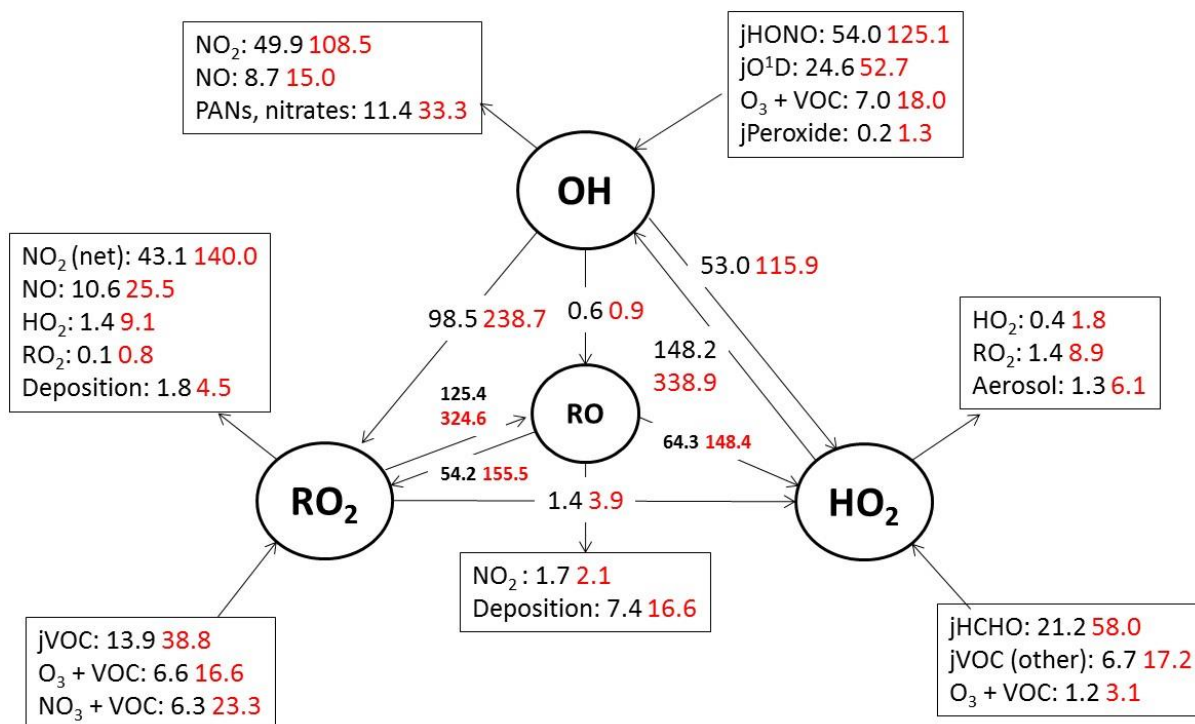
Fig. 7: Mean daytime (6am – 9pm) rates of reaction for formation, propagation and termination of radicals in units of 10^5 molecule cm^{-3} s^{-1} for south westerly (black) and easterly (red) air masses.

The relative importance of the individual formation, propagation and termination reactions under south westerly and easterly flows remains similar. However, as highlighted by Fig. 7, the rate of many of the reactions are at least twice as fast under the easterly flows with HO_2+RO_2 and RO_2+RO_2 reactions approximately 6 and 8 times faster respectively and NO_3+VOC reactions close to 4 times faster.

6. The comparison between measured and modelled RO2 radicals is presented in the paper. However, the modelled RO2 species should be explained in more detail. To our knowledge, not all the RO2 species can be detected by the chemical conversion because no HO2 is generated (e.g. some of the NO3-adduct alkenes peroxy radicals according to RACM2). Could it be one of the cause of the RO2 excursions in the model calculations?

The modelled RO2 radicals is simply the sum of all individual RO2 species that the model predicts from the VOCs it is constrained to. We have not attempted to subtract the contribution of modelled RO2 species that ROxLIF has low sensitivity towards.

The MCM assumes that a small fraction of NO3-adduct alkenes peroxy radicals (deriving from simple alkenes such as ethene and propene) do decompose to HO2 (~20%), but the dominant channel does not yield HO_2 radicals. As the modelled total RO2 presented does include 100% contribution from these NO3-adduct alkenes peroxy radicals this may indeed be one explanation for the high modelled RO2 concentration at night that is not observed in the observations.

Similarly, the low sensitivity of ROxLIF to certain RO2 species could also explain some of the model over-predictions during the daytime (e.g. on the 24th, 25th July and 12th August). If we compare the observed total RO2 radicals to model predicted RO2i (which are able to convert

to HO2 on the FAGE cell time-scale and so will be converted efficiently in the ROxLIF reactor also) the model RO2i is slightly lower than observed RO2 on these days, suggesting that we have low sensitivity for other RO2 species that either convert to HO2 on a longer time-scale or that do not convert to HO2 at all. We will explain what exactly the modelled total RO2 species represents in the revised manuscript:

… The model over-estimates the total RO_2 concentration observed by close to a factor of two during the easterly flows but predicts RO_2i well in this airmass. It should be noted that the model RO_2 is simply the sum of all individual RO_2 species that the model predicts from the VOCs it is constrained to and no attempt is made to subtract the contribution of RO_2 species that RO_xLIF may have a low sensitivity to. This model-measurement RO_2 discrepancy could, therefore, indicate the presence of RO_2 species which do not readily convert to HO_2 in the RO_xLIF reactor in these easterly flows. Alternatively the modelled RO_2 over-estimate…

As described in the section 2.6, the model was constrained to the measured PANs, which may potentially introduce large flux between acetyl peroxy radicals and PANs as shown in Figure 5. Can the authors comment on the treatment of PANs in the model and its consequence.

We only constrain the model to CH3CO(O)2NO2; other higher molecular weight PAN species are left unconstrained. We have, however, run the model unconstrained to CH3CO(O)2NO2 to see how well the model was able to capture the observed concentration of this species and to gauge the level of deposition (physical loss from the box) we should include for other unconstrained model-generated PAN species. There was no discernible difference in model-predicted RO2 species in the runs with PAN constrained and unconstrained so we don't think the treatment of PAN is the cause of the model under-estimation. We do speculate (see the response to reviewer 1 above) that the under-prediction of RO2 species under high NOx conditions is likely caused by problems with the Termination:Propagation ratio for RO2 in the model vs reality and uncertainites in the net formation of PAN species (particularly more complex PAN species) as well as uncertainties in alkyl nitrate formation rates and branching ratios could contribute to this.

7. The α derived from the HO2 experimental budget analysis is very useful parameter to show the discrepancy in the current chemical mechanisms. As the observed-to-modelled HO2 ratio shows large dependence on ambient NO concentrations, could it be possible that α also depends on NO concentrations?

We find that good agreement between HO2 observed and HO2 calculated can be achieved if α equal to 0.15 is assumed. Although we should note (and will do in the revised manuscript) that assuming α = 0.15 does lead to the model under-predicting HO2 for the higher NOx conditions experienced in the early morning, and so this does indicate that α is dependent on NO concentrations but likely also on the VOC speciation too.

Using the observed RO_2 and OH concentrations in equations E8 – E11 above to calculate [HO_2], generally good agreement between HO_2 observed and HO_2 calculated can be achieved if α equal to 0.15 is assumed as shown in Figure 11. Using an α = 0.15, leads to a model under-prediction of HO2 for the higher NO_x conditions experienced

in the early morning, however. This may indicate that α is dependent on NO concentrations and likely the VOC speciation too.

8. With respect to the diagnosis of the OH budget shown in Figure 4, the OH production rate by HONO photolysis is almost comparable to that of HO2 + NO. In this case, the chain length of the HOx reaction system is close to 1 which potentially imply the dominance of the low NOx air masses. The authors shall then have some discussion of the quality of the NO and HONO measurement results.

This is certainly the case after the morning rush hour period and we will highlight the lower NOx regimes in figure 3 by including the NOx diurnal profiles alongside the radical profiles for the two air-masses. We will direct the readers to the discussion on the quality of HONO measurements in Lee et al., (2016) as well as the NOx instrumental paper (Lee et al., 2009) that is referenced in Table 2.

The campaign median ratio of the rate of OH production to the turnover rate of OH (D_{OH}), equal to the product of the total OH reactivity and the observed [OH] concentration, is close to 1 throughout the day (Fig. 4) highlighting consistency between the OH, HO_2 and OH reactivity observations as well as the ancillary, co-located HONO (Lee et al., 2016) and NO observations (Lee et al., 2009). From late morning and throughout the afternoon, when NO concentrations dropped, the production rate of OH from HONO photolysis becomes competitive with the rate of production of OH from the secondary reaction of HO_2 with NO.

9. Line 13-14, Page 14: The comparison between OH measurement and model calculation below 1 ppbv of NO only refers to one statistical box in Figure 7, which could be expanded to more bins in low NO regime to determine the trend, so that more information could be drawn from the NO dependence. Or the authors think all the NO lower than 1 ppb is not well determined.

If we expand the number of bins in the low NOx regime we find that the MCM model and PSS under-estimate the observed OH at NO<0.5 ppb with the model-measured agreement improving at NO concentrations between 0.5 – 1 ppbv. We will include an illustration of this and discussion in the revised manuscript:
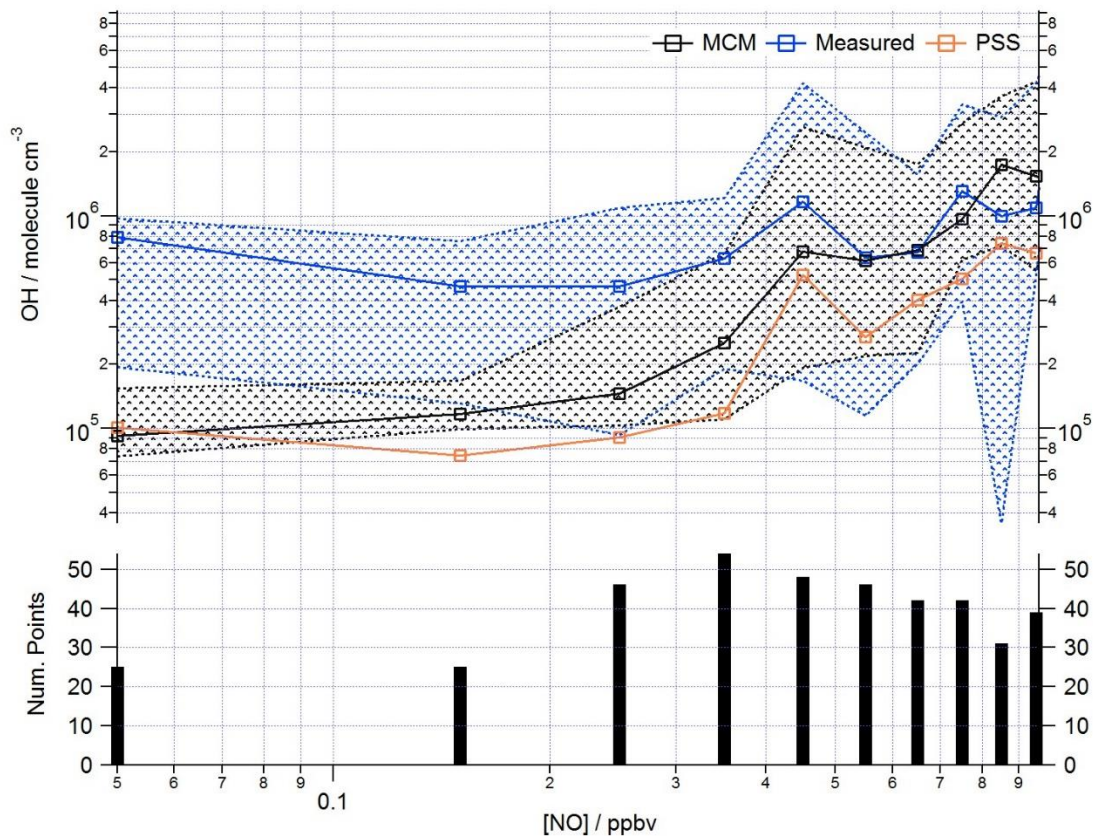
Fig 9: Observed and modelled OH behaviour as a function of NO (< 1 ppbv) for the whole campaign period. Median OH measured (blue squares), OH modelled (base MCM model = black squares, steady state calculation = orange squares). Patterned areas represents the 25/75th percentiles. Data are filtered for daytime hours between 6 am and 7 pm and binned by [NO] with a bin width = 0.1 ppbv. The number of points in each bin is displayed in the lower panel.

By expanding the number of bins representing the OH data at [NO] < 1 ppbv (Fig. 9) it is evident that both the MCM-BASE and PSS calculation under-estimate the observed OH at [NO]<0.5 ppbv, with the MCM-BASE agreeing with the observations between 0.5 − 1 ppbv [NO].

10. Equation 7 and Equation 11, the HO2 production from OH+HCHO reaction is missing.

This is an oversight in the text. We did include HO2 production from HCHO+OH reaction in the α determined and in the results presented in Fig. 10. We will correct the equations to reflect this:

$k_{CO+OH}[CO][OH] + k_{HCHO+OH}[HCHO][OH]+2\times j(HCHO_{radical\ channel)[}HCHO]+(\alpha\times k_{RO2+NO}[RO_2][NO])$
$= k_{HO2+HO2}[HO_2]^2+k_{HO2+NO}[NO][HO_2]+k_{HO2+RO2}[RO_2][HO_2]+k_{HO2+O3}[O_3][HO_2]+k_{Loss\ to\ Aerosols}[HO_2]$

$c=k_{CO+OH}[CO][OH]+ k_{HCHO+OH}[HCHO][OH]+2\times j(HCHO_{radical\ channel})[HCHO]+(\alpha\times k_{RO2+NO}[RO_2][NO])$

Technical comments:

1. Line 4, Page 3: Sub-urban should be suburban.

Corrected

2. Line 13, Page 5: The reference to Fuchs et al. 2017 is missed in the discussion of the Wangdu results.

We will add this reference in to the discussion of the Wangdu results:

In the recent study in the Wangdu region of China, POH was found to equal DOH within uncertainties throughout the day (Tan et al., 2017) demonstrating consistency between the observed radical concentrations and observed OH reactivity (Fuchs et al., 2017).

3. Line 23, Page 5: The definition of local ozone production usually only refers to chemical processes. Since the deposition is not discussed, the authors can delete the deposition term in the text and E1.

We will delete:

$P(O_3)=(k HO_2+NO[HO_2][NO]+k RO_2+NO[RO_2][NO])−(k OH+NO_2+M[OH][NO_2][M]+k RO_2+NO_2+M[RO_2][NO_2][M])$

4. Line 23-24, Page 7: The authors argued that the measured RO2 represented is the lower estimate in the context of the detection sensitivity of different RO2 species. Nevertheless, later on the authors also talked about RO2 measurement interference in Sect. 2.5.3. I think the general reader may feel confuse about this way of description. "the measured RO2 represented is the lower estimate" shall be rephrased.

We shall expand as follows:

..This assumption means that the concentration of RO_2 observed may be a lower estimate as certain RO_2 species will not convert as efficiently as methane-derived RO_2 radical. For example, the MCM predicts that only ~ 20% of NO_3-adduct RO_2 radicals which derive from the reaction of simple alkenes (e.g. ethene and propene) with NO_3 will convert to HO_2 in the presence of NO at the reduced pressures of the flow reactor and so we expect RO_xLIF to have low sensitivity to these RO_2 types.

5. Suggest to include the parts from NO3 oxidation during daytime in Figure 5, to keep consistent with Figure 6. The current budget is not fully balanced.

We have included NO3+VOC forming RO2 in Figure 5. Perhaps the referee over-looked this?

6. Line 1-4, Page 15: The authors claimed that HO2* follows more closely the decrease in modelled HO2 than measured HO2, which is not easily seen from the Figure 7b and may need more detail explanation.

We will add '..under low NO conditions' to clarify the conditions where this modelled HO2 and measured HO2* agreement is most apparent.

7. Line 12- 19, Page 15: The text is more suitable to move to Line 4 before 'It is possible. . .'

We will move this text as suggested

8. It's not clear why a subsection 4.1.1 is separated from section 4.1, since all the content is discussing the possible explanation for overestimation of HO2 in low NO.

We will remove subsection 4.1.1.

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