

Interactive comment on “Understanding in situ ozone production in the summertime through radical observations and modelling studies during the Clean air for London project (ClearfLo)” by Lisa K. Whalley et al.

Anonymous Referee #2

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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 mea-

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sured 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

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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.

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.

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3) The authors highlight the model underestimation of RO_2 radicals under high NO conditions, and suggest that decomposition of $\text{CH}_3\text{O}_2\text{NO}_2$ in their reactor may result in an overestimation of the measured RO_2 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 RO_2 concentrations under high NO conditions?

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?

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.

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.

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.

Page 11: Including campaign averaged NO / NO_2 in Figure 3 would help to highlight the model/measurement discrepancies under the different NO regimes.

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