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Atmospheric Chemistry and Physics Discussions

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 #1

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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.

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.

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?

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?

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.

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? 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.

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?

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.

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.

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

Technical comments:

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

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

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.

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.

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.

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.

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

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.

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