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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric OH reactivity in central London: observations, model predictions and estimates of in situ ozone production" *by* L. K. Whalley et al.

Anonymous Referee #1

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This papers reports on measurements of the total OH reactivity (kOH) in the megacity London. Measurements of kOH are sparse. Therefore, the presentation of these measurements are important. Measurements of kOH are completed in this campaign by the detection of a large set of different VOCs. The authors nicely show, to which extend contributions of all measured OH reactants can explain measured OH reactivity. If also contributions of unmeasured oxygenated VOCs that are calculated by models are taken into account, the authors can show that kOH is explained. As the authors emphasize, missing reactivity that is discussed in literature always needs to be seen in the context of the completeness of measurement of OH reactants. These messages are clearly presented in the manuscript. However, the focus of the paper on

these points could be improved specifically in the second part of the manuscript. The authors should consider the following points:

(1) I assume that the measurement site was close to sources of VOCs. This may have consequences for the applicability of a box model, which assumes that oxygenated VOCs can accumulate. If the transport time between the source and the site is short, concentrations of products could be over-estimated.

(2) In my opinion, the presentation of instruments that are used for the analysis is not well-balanced. The major progress of this work is that a large set of VOC measurements was detected. However, the authors present their FAGE system in much greater detail than their GC systems. The authors may want to move Fig. 4 in the context of a more detailed description of these instruments. It is not clear to me, if all details of the FAGE system that are currently given are required.

(3) The authors discuss results of model calculations for HCHO, OH, HO2, and RO2. This discussion seems partly misplaced in this paper, especially because the authors announce to publish details of the comparison of modelled and measured radical concentrations in a separate paper. The context of the discussion is not always clear here and the information that is given to understand the results is not sufficient. I understand that the authors want to emphasize the importance of the increased number of VOC species that could be detected in this campaign. In this context, the discussion of HCHO might be justified. However, I do not see that the discussion of OH and RO2 makes much sense here. Only sparse information is given concerning important other species like for example ozone, HONO, details of NOx, HO2, CO that are needed to understand the production and destruction of radicals. Specifically, the model run of OH which is constrained to measured HO2 requires at least to show the diurnal profile of measured HO2 and NO. I understand that this will be the topic of separate paper, but then I would suggest to remove the discussion here and to focus the paper on kOH.

(4) The authors use measured OH to calculate steady state RO2, that is then used

to calculate ozone production rate. It seems a bit arbitrary to use measured OH, but not to use measured RO2 instead of calculated RO2. If the calculated RO2 concentration is used, the reader needs more quantitative information, if simplifications in this calculation are justified.

(5) Concerning the simplification of the calculation of the ozone production rate, it is not clear, why the authors do not include ozone production from HO2. In my opinion, the discussion of the ozone production rate does not fit the topic of the paper well, because the only conclusion is that radical concentrations needs to be correct in the model. If RO2 is measured like in this campaign, however, there is no need to use kOH at all.

(6) Fig. 8 is mostly showing results that are already included in other figures. I would suggest to reduce this figure to the new aspects (physical loss, HO2 constrained model). Why do the authors use the model run, in which HO2 is constrained? If I understand the point correctly, the purpose is to get the modelled OH correct. In this case, however, the use of measured OH as constraint would make much more sense.

(7) Technical remark regarding figures: The font size and thickness of lines may be not adequate in the final publication for one-column figures.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 31247, 2015.