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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Experimental budgets of OH, HO_2 and RO_2 radicals and implications for ozone formation in the Pearl River Delta in China 2014" *by* Zhaofeng Tan et al.

Anonymous Referee #1

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This paper presents an analysis of OH, HO2, and RO2 radical budgets based on direct measurements of these radicals as well as measurements of their sources and sinks during the PRIDE-PRD2014 (Program of Regional Integrated Experiments of Air Quality over the Pearl River Delta) in 2014. Because this study involved direct measurements of the concentration of each radical family, the authors are able to provide an analysis of the radical budgets based on measured concentrations in contrast to previous studies that used the results of chemical models to estimate concentrations of unmeasured radical concentrations. The results illustrate that while the radical budgets for HO2 and total ROx are balanced to within the uncertainty of the measurements, the budget for RO2 radicals can only be balanced if the observed missing OH reactivity

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is due to reaction of unmeasured VOCs leading to the production of RO2 radicals. In addition, the analysis suggests a missing RO2 sink and a missing OH source in the afternoon which cancel each other in the total ROx budget. The budgets could be closed by including an additional chemical mechanism that converts RO2 radicals to OH that does not involve reaction with NO. While an interference with their measurements of OH could explain these discrepancies, the authors provide some evidence that their measurements were free of unknown interferences. However, they acknowledge that additional measurements with more continuous testing for interferences are needed to confirm these results. The authors use the measurements to calculate integrated net rates of ozone production, and find that a missing RO2 sink would reduce ozone production by approximately 30% compared to that expected from the VOC oxidation rate.

The paper is well written and provides a new perspective on our understanding of radical chemistry. It is suitable for publication in ACP after the authors have addressed the following minor comments.

1) The authors provide evidence that the missing OH reactivity is due to missing VOCs that react to produce RO2 radicals. While this provides strong evidence that the missing OH reactivity is not due to radical termination reactions, it is not clear from the discussion on pages 11 and 12 that this rules out that the missing reactivity is due to unmeasured OVOCs as discussed by Yang et al. (2017). This should be clarified.

2) One of the main conclusions of the paper is that the budget analysis suggests a missing RO2 radical sink and an OH radical source in the afternoon. While the authors suggest that RO2 isomerization reactions from isoprene and methacrolein may not be important given the low concentrations of isoprene measured, there may be other autoxidation processes that could be important in the afternoon when NO concentrations are low (see Praske et al., PNAS, 115, 64-69, 2018). This should be discussed in more detail.

3) The authors provide some evidence that their OH measurements are free from interferences through some chemical modulation tests. While the majority of these measurements appear to be below the detection limit for the instrument, it is not clear from Table 3 whether the data presented represent an average of multiple tests during the time period indicated, or a single modulation experiment. It would useful clarify the number and duration of the modulation experiments, perhaps by showing some of the raw data from the experiments in the supplement.

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