Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-801-RC1, 2018

Atmospheric Chemistry and Physics Discussions

Open Access

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 #2

Received and published: 9 October 2018

This manuscript presents an extensive dataset of radical measurements in the Pearl River Delta region (China). The authors use these data to examine the budget of OH, HO2 and total RO2. There are not many co-located measurements of OH, HO2 and RO2, so this dataset and its analysis provide a rather unique and interesting look into the chemistry of the polluted atmosphere. The presentation of the data is well laid out and the discussion is clear. I have a few questions and comments for the authors, but, other than that, I recommend publication in ACP.

page 4, lines 19-20. "The interference is most effective when the amount of added NO is sufficiently high to convert most of the atmospheric HO2 to OH in the LIF cell" This

Printer-friendly version

Discussion paper

sentence is followed by the statement that the concentration of NO was reduced by a factor of 10. Does this mean that the conversion of HO2 to OH in the HO2 cell is not complete? Could this lead to underestimation of HO2?

page 5, lines 32-34. "The main reactants are NO and the peroxy radicals themselves, all of which were measured allowing the total loss rates from the individual reactions to be calculated." I am not sure this statement is correct. The ROxLIF technique certainly provides new information, but it still measures the sum of peroxy radicals, so I don't think the authors can claim that all of the peroxy radicals were measured.

The assumption that all RO2 have similar rate coefficients (with HO2, other RO2 and/or NO) is a very common one, but it is still a rather big assumption. The MCM itself uses two different generic rate coefficients for RO2+RO2, RO2+NO and RO2+HO2 reactions, depending on the type of peroxy radical. This issue is also mentioned on pages 6 and 7, and may be relevant for the discussion of the RO2 budget in Section 3.7. Moreover, if part of the argument is that the RO2 budget is closed within the instrumental uncertainty, but still slightly negative (page 12) than this could be a factor to consider. The authors correctly discuss on page 13 how the assumptions on the nitrate yields, which are a similar issue, affect the conclusions of the paper. But I don't see a similar discussion for the rate coefficients.

page 7. The two methods to calculate RO2 production from OH+VOC reactions take into consideration the possibile effect of unmeasured VOC, which is correct. However, a similar approach was not taken with regard to unmeasured alkene that react with ozone. Such missing VOC may be an issue for the calculation of OH sources in E4 and the discussion of the HO2 budget in Section 3.6. The potential problem is acknowledged on page 6, but there is no discussion of how it may affect the conclusions of the paper.

page 12, lines 1-2. It is not clear if the authors are discarding the hypothesis of Yang et al (2017) that the missing reactivity is at least partly due to OVOC and, if so, why.

Figure 3, panels f and g. In one panel the difference between destruction and production is compared to that derived from VOC(1) and in the other is compared to that derived from VOC(2). I see what the authors are trying to do, but it is a bit misleading. Maybe both differences could be shown by adding a third panel for both RO2 and RO2# or maybe different colors could be used.

page 11, line 25. Typo: "by developed".

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-801, 2018.