

Interactive comment on “Experimental budgets of OH, HO₂ and RO₂ radicals and implications for ozone formation in the Pearl River Delta in China 2014” by Zhaofeng Tan et al.

Anonymous Referee #3

Received and published: 17 October 2018

The article "Experimental budgets of OH, HO₂ and RO₂ radicals and implications for ozone formation in the Pearl River Delta in China" by Tan et al. analyses the radical budgets for a polluted region utilising comprehensive observations of radical species, total OH reactivity and radical precursors. The total budgets of RO_x and OH, HO₂, RO₂ are compared pointing to a conversion between RO_x to HO₂ and OH by an unknown component X as formerly hypothesised by Hofzumahaus et al. 2009, in the Pearl River Delta and unmeasured VOC species. The implications for the O₃ production potential are discussed to be less effective as assumed by total OH reactivity measurements. The article is well written with an unique dataset, calculating the budgets with a measurement approach only. I recommend publication after following remarks have

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been addressed:

page1, line 17: Typo: "radical interconversion" instead of "radical interconveresio"

page 1, line 19: "In case of RO₂, the budget can only be closed when the missing OH reactivity is attributed to unmeasured VOCs. Thus, the existence of unmeasured VOCs is directly confirmed by RO₂ measurements." This is a likely but not exclusive explanation. I recommend to rephrase the sentences: "In case of RO₂, the budget could be closed by attributing the missing OH reactivity to unmeasured VOCs. Thus, unmeasured VOCs are directly linked to the RO₂ measurements."

page 1, line 25: "These observations suggest the existence of a chemical mechanism that converts RO₂ to OH without the involvement of NO. Please quantify the average contribution of this channel to the total turnover rate.

page 2, line 17: Please explain the abbreviation of "PRIDE-PRD" already here.

page 2, line 36: "... tendency to underpredict OH under low-NO_x conditions" . Please define the term "low-NO_x conditions".

Page 4, line 4: Please explain in the supplement table caption the term "RO₂#".

Page 4, line 12: Please quantify how much OH is internally removed.

Page 4, line 13: How did you account for possible impurities in N₂?

Page 4, line 21: Please quantify the upper limit of the HO₂ interference .

Page 4, line 33: How did you quantify the HO₂ background signal?

Page 5, line 8: It is unclear which instruments have been used for CO and CO₂ in this study.

Page 6, line 36: Please quantify the impact of the assumption that the nitrate yield is 5%. Please add a reference for the nitrate yield.

Page 7, line 17: Despite the fast NO₃ photolysis Liebmann et al. , 2018, found during

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daytime a fractional loss of NO₃ of 25% by reaction with BVOC. What is the daytime NO₃ production rate in this study and what would be an upper limit for its contribution ?

Page 9, line 38, What is the upper limit of RO_x production by NO₃ during night time, i.e. what is the NO₃ production rate ?

Page 10, line 24 Is it the only exclusive explanation or a possible explanation that fits the result ?

Page 11, line 6: "The completeness of the radical measurements allows a budget analysis for all radicals (OH, HO₂, RO₂) based on experimental data only, ...". Please add: "under the assumption that for the production and loss rates all relevant species were measured."

Page 11, line 9: How do you define daytime?

Page 11, line 25: typo : "... comparative method developed by ..."

Page 11, line 30: It is not obvious that under NO_x regimes, controlling radical propagation and termination schemes, the resulting intermediates or even the emitted VOC found in Yang et al are comparable with the ones in this study.

Page 12, line 4: Please specify uncertainties.

Page 13, line 35 Please quantify "negligible" including upper limit for dry deposition

Page 13, line 36&37; Page 14 line 7 : Specify uncertainties

Page 14, line 4: Please include the statement that the loss term HO₂*NO generating NO₂ can be replaced by the production term of HO₂ under the assumption that other HO₂ losses, like HO₂+RO₂, HO₂+HO₂ are negligible.

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