



EGUsphere, referee comment RC1
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Comment on egusphere-2022-820

Anonymous Referee #1

Referee comment on "Experimental chemical budgets of OH, HO₂, and RO₂ radicals in rural air in western Germany during the JULIAC campaign 2019" by Changmin Cho et al., EGU sphere, <https://doi.org/10.5194/egusphere-2022-820-RC1>, 2022

This manuscript reports an interesting investigation of radical budgets (OH, HO₂, RO₂ and RO_x) in ambient air flushed through the SAPHIR chamber. This chamber is well equipped to measure each radical - or group of radicals - together with ancillary data that is necessary to compute the radicals' production and destruction rates.

The authors report on measurements covering each season of 2019 and focus on the spring and summer seasons when radical concentrations were significantly larger than instruments' detection limits. Great care was taken to rule out potential instrumental issues on the measured radical concentrations. Contrasting production and destruction rates for the above-mentioned radicals, the authors highlighted significant gaps in our understanding of radicals' sources and sinks in air masses characteristic of the Julich atmosphere (urban area impacted by biogenic emissions). It is shown that at low and moderate levels of NO_x, an additional source of RO_x is needed to close the RO_x production-destruction balance. At low NO (< 1ppb), it is shown that additional processes leading to the production of OH and the destruction of HO₂ are needed to close the budget of these radicals. At higher NO (1-3 ppb), no imbalance is observed for OH and HO₂ but an unknown source of RO₂ is needed to balance their production and destruction rates. The authors did a great job assessing how uncertain chemical processes could contribute to the observed imbalances.

This reviewer thanks the authors for the effort put in providing an easy-to-read manuscript - very well structured, clear and concise information - which is not an easy task when dealing with such complex dataset of measurements. This work will be of great interest for the atmospheric community and this reviewer recommends publication after the authors address the following comments:

Main comments:

P8 L204-207: It is stated that the ROx-LIF system is calibrated for CH₃O₂. Since the sensitivity of this instrument is species dependent, this will lead to a measurement bias for RO₂. By how much could the measured RO₂ deviate from the true value? Is this bias factored in the measurement uncertainty? If not, how could it affect the calculations of P_{OH, isop}, (Eq. 4), P_{HO₂} (Eq. 6), D_{HO₂} (Eq. 7), D_{RO₂} (Eq. 11) and D_{ROx} (Eq. 13)?

P10 L306: "First, the contributions from CO, NO, NO₂, HCHO and O₃ is removed from the measured OH reactivity as these species do not form RO₂ radicals in the reaction with OH. It is then assumed that the remaining fraction can be attributed to organic compounds (VOC reactivity (kVOC)) including measured and unmeasured VOCs, which produce RO₂ radicals in their reaction with OH" – For some VOCs the reaction with OH can lead to the prompt formation of HO₂ together with RO₂. For instance, toluene+OH will form 28% HO₂ and 72% RO₂. Assuming only the formation of RO₂ could lead to an underestimation of P_{HO₂} and an overestimation of P_{RO₂}. Could the authors comment on this aspect? Can the prompt formation of HO₂, which occurs with a few VOCs, be neglected when the total pool of VOCs is considered?

Table 2: This table indicates that NO₂ was measured using a chemiluminescence instrument. Was this instrument equipped with a photolytic NO₂ converter or a molybdenum converter? This should be clearly stated. Instruments equipped with a molybdenum converter are known to be prone to interferences when measuring NO₂. If a molybdenum converter was used, the authors should discuss how interferences on NO₂ measurements could impact the calculations of ROx destruction rates (Eq. 13) and Ox production rates (Eq. 14).

Minor comments:

P8 L226-228: "Photolysis frequencies inside the chamber were derived from the solar actinic flux densities measured by a spectroradiometer mounted on the roof of the nearby institute building (Bohn et al., 2005; Bohn and Zilken, 2005)." – How is the Teflon sheet transmission determined when the cleanliness changes from day-to-day?

P11 L338-339: Was the humidity dependence of k₁₇ accounted for in the calculation of D_{ROx}? It seems so from Table 1 where k₁₇ is reported for 1% water but it should be clearly stated in the text.

P12 L370-371: Please include O₃+alkenes in the list of minor Ox destruction pathways

Figures 3, 4, S3, S4: Please indicate in the caption what the error bars represent for OH. Also please add error bars for the other measurements.

Figures 8-12 & S6-S7: Please clarify in the caption whether uncertainties are displayed as 1-sigma? 2 sigma? Other?

Edits:

P2 L55: "the lower are summarized in" should read "the lower atmosphere are summarized in"

Table 1: The authors may want to add the reaction of OH+O₃ in the radical interconversion section

P32 L819: "the formation of OH from their reaction with NO could only explain up to" should read "the formation of OH from their reaction with HO₂ could only explain up to"