



EGUsphere, referee comment RC2
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Comment on egusphere-2022-820

Anonymous Referee #2

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-RC2>, 2022

This paper presents measurements of OH, HO₂, and RO₂ radical concentrations and total OH reactivity in ambient air sampled from inside the SAPHIR chamber. OH radicals were measured by both an LIF-FAGE instrument and a DOAS instrument, while HO₂ and RO₂ radicals were measured using the ROx-LIF instrumental technique. The authors use the radical measurements together with measurements of ancillary measurements of photolysis rates, NO_x, and VOCs to calculate the radical production and destruction rates to determine whether they are balanced. The authors find that under lower NO conditions (less than 1ppb) the rate of OH radical destruction was consistently greater than OH production, while the rate of HO₂ radical production was greater than HO₂ radical destruction. At higher NO conditions, the OH and HO₂ radical budgets appeared to be in balance. In contrast, the total ROx radical budget was found to be generally balanced over the range of NO measured, with the destruction rate greater than the production rate at the highest and lowest mixing ratios of NO.

The authors demonstrate that instrumental errors associated with the radical measurements are minimal given that the LIF-FAGE measurements of OH (after accounting for interferences) were in good agreement with the DOAS measurements, and that the measurements of the rate of Ox production was consistent with the rate of the reaction of peroxy radicals with NO. As a result, the authors conclude that a missing OH radical source and a missing HO₂ loss process is needed to balance the radical budgets. At the highest NO concentrations, the authors suggest that an additional RO₂ production process is required to close the RO₂ radical budget.

The authors suggest several possible explanations for the missing sources and sink, including alkene ozonolysis, OVOC photolysis, and heterogeneous uptake of HO₂ radicals, although according to the conclusions the exact nature of the missing sources and sink could not be determined from the measurements.

The paper is well written and contains additional evidence that our understanding of radical chemistry under a range of NO concentrations is incomplete. The paper would be suitable for publication after the authors have addressed the following comments.

- In the abstract (lines 39-41), the authors state that the missing OH source “consists likely of a combination of a missing primary radical source ($0.5 \sim 1.4$ ppbv h^{-1}) and a missing inter-radical HO₂ to OH conversion reaction with a rate of up to 2.5 ppbv h^{-1} .” However, there appears to be little discussion of this potential OH source/HO₂ sink in the paper, except briefly on page 29 (lines 670-671) and page 43 (line 893) and it is not mentioned in the conclusions. If this is a major finding as suggested in the abstract, it should be emphasized more in the manuscript.
- The authors state that photolysis frequencies were “were derived from the solar actinic flux densities measured by a spectroradiometer mounted on the roof of the nearby institute building.” Given that an underestimation of radical production from photolysis could account for the missing OH radical source, the authors should clarify how potential differences in photolysis rates inside versus outside of the chamber were accounted for in their budget calculations.
- The authors measured total OH reactivity and use it to determine the total OH loss rate. However, as illustrated in Figure 5 there appears to be significant missing OH reactivity when compared to the calculated reactivity from measured OH sinks. Unfortunately, there is little discussion about the potential composition of the missing OH reactivity. The paper would benefit from a brief discussion of the missing OH reactivity and whether unmeasured OVOCs may be responsible. While the authors suggest that OVOCs such as acetaldehyde, methyl vinyl ketone, methacrolein, and methylglyoxal do not contribute significantly to radical production, have the authors considered other potential unmeasured OVOCs, perhaps through a model of the chemistry, that may be contributing to the missing reactivity as well as be a potential unmeasured radical source?

Minor comments:

Page 2, line 63: The Griffith et al. 2016 reference reports urban measurements. Did the authors mean to cite Griffith et al., Atmos. Chem. Phys., 13, 5403–5423, 2013, which reports measurements in a forest environment?

In Figure 12 I assume that the numbers at the top of the figure represent the number of points in each NO bin. This should be clarified in the caption. Also, the uncertainty should be clarified.