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# Comment on acp-2021-702

Anonymous Referee #1

Referee comment on "Ground-based investigation of $HO_x$ and ozone chemistry in biomass burning plumes in rural Idaho" by Andrew J. Lindsay et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-702-RC1, 2021

This manuscript presents measurements of XO2 (=RO2 + HO2) at a ground site influenced by biomass burning plumes. The measured XO2 is used to evaluate box modeling with different mechanisms. It is shown that model results are consistently greater than measured [XO2] by ~30%. The influence of biomass burning on ozone formation is also studied. The ozone formation is only slightly impacted by smoke because of low NOx, indicating the O3 chemistry is NOx-limited. Overall, the measurement is valuable and I recommend publication with major revisions noted.

Major Comments

- In the manuscript, the discrepancies between measured and modeled [XO2] are noted, but not fully explained. Namely, what causes the over-estimate of XO2 in models? Any recommendations to the chemical mechanisms? Or the difference is within the measurement uncertainty, which undermines the valuableness of the XO2 measurement? Looking at Figure 6, model sometimes is 50-60% higher than measurement. Why? The difference shown in Figure 6 seems larger than the 31% noted in the abstract. In fact, how is the "31%" calculated?
- The effect of HO2 heterogeneous uptake on the radical budget is likely over-stated. As the authors noted, the HO2 uptake coefficient is highly uncertain. A relatively large value (i.e., 0.2) is chosen. In dense BB plumes, organic aerosol is the dominant composition with mass fraction up to 80%. As discussed in Abbatt et al. 2012 and George et al., the HO2 uptake coefficient to solid organic particles is < 0.001 and to liquid organic particles is < 0.01. If applying the small gamma values, the HO2 heterogeneous is negligible even in dense BB plumes.
- Missing HONO as model input is invoked in several places as a possible reason for the model vs measurement difference, but this reasoning is questionable. First of all, the delta_HONO/delta_CO after 3hr aging of BB plume, as shown in Peng et al., is 0.1 ppt/ppb, rather than 1 ppt/ppb as quoted in the manuscript (Line 377). In addition, Peng et al. clearly stated that after 3hr the [HONO] is near or below the instrument detection limit and they refrain from interpreting what it implies in terms of potential HONO steady state in aged plumes. Lastly, HONO can be added to the box model (using delta_HONO/delta_CO = 0.1 ppt/ppb and measured CO), to directly test the

effect of missing HONO on the modeling results.

- Figure 5 is interesting and related discussions should be expanded. For example, what does the lack of correlation between P(O3) and NO when P(ROx) is small suggest. Does it suggest O3 formation is VOC-limited? More information can be distilled from the figure, or from the four variables in the figure (PO3, PROx, NO, and HCN).
- In the manuscript, some metrics are from direct measurement (e.g., [XO2]), some metrics are calculated from measures species (e.g., P(Ox) from Eqn. (3)), and some metrics are purely based on box model. These need to carefully worded in the discussion to avoid confusion. For example, Line 460 and others use the term "measured OH reactivity", which the reader believe is the calculated OH reactivity based on measured VOCs. Then, Line 477 refers to Eqn. (3) as measured P(ROx), which makes the reader confused for a bit, as it is calculated, not measured. Such subtleties hinder the readability of the manuscript.
- Line 482. Are there any constraints or independent verification on the contribution of photolysis of methyl glyoxal and glycoaldehyde to the P(ROX)? Their contributions seem much larger than expected, based on measurements of these two species in previous wildfire studies.

Minor Comments

- Line 26-28. The reader suggests to rephrase the sentence to "the model over-estimates the XO2 by 30%".
- Line 29-30. Suggest rephrasing to "likely due to the presence of an unmeasured HOx source that is not included in models". The whole sentence may need to be rewritten after investigating the role of HONO as mentioned above.
- Figure 5b. P(O3) is used in the y-axis, but P(Ox) is used in the figure caption. Be consistent.
- Line 387-397. The negative delta_O3/delta_CO on 8/16 is likely a result of inaccurate O3 background and mixing, rather than depletion. It is because as the authors noted, the [NO2] is much smaller than [O3], suggesting that [Ox] ~= [O3], which rules out the possibility of depletion.
- Be consistent with which model results are presented. For example, why is MCM-BBVOC-het presented in figure 8, but MCM-BBVOC in figure 6?