Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-702

Anonymous Referee #2

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-RC2, 2021

General Comments:

The manuscript by Lindsay et al. presents ground-based measurements of total peroxy radicals (XO2) within biomass burning smoke in McCall, Idaho in Aug 2018. The authors examined the diurnal profiles of radical concentration and ozone production rate in multiple smoke events with a unique set of measurements, and employed a 0D box model with different mechanisms to evaluate HOx radical chemistry. Overall, the paper presents useful results with detailed observational and model analysis, and are of interest to the atmospheric chemistry community. However, the paper would benefit from some additional model simulations and clarifications detailed below before it is acceptable for publication.

First, the authors find that the model was not able to reproduce the XO2 enhancement of 15 pptv during the Aug 17 smoke event, and suggested that HONO, which was not measured,may be the cause. This possibility is not really investigated in the paper. What magnitude of HONO would be needed to achieve the necessary production of XO2? It would be useful for the authors to verify their assumptions by conducting sensitivity analysis of the modeled HONO (perhaps by applying a scale factor to CO or NO2).

Second, there is an inadequate amount of discussion of how the modeled radical precursors compare to measurements. The authors showed significant model overestimates in XO2, P(ROx), and P(O3) across all model mechanisms used, but did not discuss in detail the possible causes of model discrepancies. More discussion on the cause of the model overprediction and what might be pursued to reconcile the problem would be useful. Are there inaccuracies in the recycling within XO2 species? What does the diurnal profile of model-obs discrepancy look like? What possible mechanisms could bridge the gap between measured and modelled total XO2? Is the modeled NOx close to observation? How is NOx constrained in the model (e.g., kept NO/NO2 ratio the same as observation or not)? This kind of analysis may help better understand where the model-measurement discrepancy arises from.

Last, the ozone analysis could be better utilized to reconcile the calculated rate of production with measurements. For example, the authors could show the changes in measured-to-modelled ratio of PO3 and XO2 with different parameters(e.g., NOx concentration), colored by different BB events, to find plausible explanations of the discrepancy.

Specific comments:

- How does the wind speed, RH, temperature vary each day? A brief description of meteorological conditions would be helpful. Or you could add a panel for that in Fig 2.
- It would be more clear if you move part of the key model description from the SI (Line S108-114) to the main text, mainly what and how the measurements were used to constrain the model and what values are used for unmeasured species.
- Line 376-377: Peng et al. showed HONO enhancement ratios decay to ~ 0.1 ppt/ppb instead of 1 ppt/ppb for aged (> 3h) plumes. What enhancement ratio is needed to resolve the model disagreement if you initialize the model with HONO that scales with CO (or NOx)?
- In line with the previous point, given the importance of HONO as an OH precursor, how does PO3 change after including HONO in the model? And how does that affect NOx? Is the estimation of the missing HONO different across different BB events?
- Figure 8: Why is the modeled P(ROx) almost a factor of 2 larger than observed? Line 481-482 suggests that the greatest HOx contributors in the carbonyls group are unmeasured carbonyls - how are they initialized in the model? How does each modeled radical precursor compare to the observation? Where are the sources of discrepancy in P(ROx)? It is important to mention how the uncertainty of the carbonyls input could affect the results and conclusions.
- Do XO2 measurements agree with the XO2 estimates derived from modified Leighton ratio calculated with measured ozone, NO and NO2 concentrations from the campaign? A scatter plot of derived XO2 versus ECHAMP observations could be made.

Minor Comments:

- Fig 2: How is smoke presence determined? There seems to be no text descriptions.
- Line 186: extra period and space
- Line 187: missing closing parenthesis
- Line 302, Extra space after “MCM-base”
- Line 357, sentence incomplete: “Clusters of data points at HCN concentrations ARE….”
- Figure 3: better have a legend for the bottom panel

- Figure 5. Add legend for model vs obs in panel a for convenience of the readers; also specify the analysis is for Aug 17 event in the caption
- Fig 6. Typo in the legend for the upper panel: ISOPO2 instead of Isoprene?
- Line 471-472: Did the decrease in OHR happen upon smoke arrival? From Fig 6 it seems to be upon smoke exit?
- Line 477-478: shall be "O(1D) reaction with H2O"
- SI Line 151: fix typo "GOES-Chem"
- Fig S10 and 11: fix caption placeholder (Fig X)