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Comment on acp-2021-267

Anonymous Referee #2

Referee comment on "Nighttime and Daytime Dark Oxidation Chemistry in Wildfire Plumes: An Observation and Model Analysis of FIREX-AQ Aircraft Data" by Zachary C. J. Decker et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-267-RC2>, 2021

Decker et al. report based on a modeling study the fate of volatile organic compounds and NO_x in several wildfire plumes emitted in the western US. The focus of this modeling is on understanding the gas-phase evolution near and after sunset and elucidating complicated role of various oxidants in dark conditions. They find that the nitrate radical (NO₃) and phenolic emissions and their oxidation products (i.e., nitrophenolics) play an important role in dark wildfire plumes.

Fires are an important source of NO_x and organic carbon to the atmosphere and increasingly so in the western US. There are large uncertainties surrounding the oxidation chemistry of fire emissions and these uncertainties are even larger under dark conditions (i.e., optically thick plumes, nighttime). The manuscript addresses an important topic at the intersection of wildfire emissions and atmospheric chemistry. The methods and data analysis are appropriate although I will comment that the article is long and hard for the reader to comprehend in a single reading. I generally recommend publication of this article in ACP after the authors have had a chance to respond to the comments below.

Major comments:

- Length: The article is too long and I recommend that the authors try to summarize the key findings and arguments at the beginning of section 4 in a bulleted format. At the same time, they should also lay down the discrepancies discovered in the modeling as they wouldn't want the reader to assume that the model agreed with the measurements perfectly for all fires and instances. Researcher studying this topic will be more interested in the interpretation of the nuanced model-measurement comparison.
- VOC measurements: How did the individual BBVOCs as measured by the various gas-phase trace instruments compare against the time-resolved model predictions? It seems to me that several instruments in this list (<https://csl.noaa.gov/projects/firex-aq/dc8/payload.html>) could have easily measured the reduced and lightly-oxygenated VOCs described in this paper (alkanes, single-ring aromatics, alkenes, biogenic VOCs)? These comparisons, assuming if they are found to be reasonable, would provide

additional evidence for the oxidant-resolved decay of the VOCs driving the oxidation chemistry inside the plumes. A very related point is also why these same measurements were not used to initialize the BBVOCs. How do the lab measurements (e.g., during FIREX-2016) compare against these field measurements? Is it appropriate to use a lab-based emissions profile to initialize the model. Either these measurements need to be included in the analysis or a strong reason needs to be provided for why these were not included. I would consider this a major limitation of this study.

- Qualitative comparisons to day time: I mostly understand the novel contributions of this work in understanding the detailed nighttime evolution of BBVOCs and NO_x in wildfire plumes. However, this nighttime evolution needs to be placed in context of the global (i.e., day+night) evolution by comparing to the daytime evolution. How are the lifetimes of NO_x and BBVOCs different during the day versus night? What fraction of the total oxidation is happening between day and night? How important are daytime versus nighttime processes to the formation of certain oxidation products (e.g., nitrophenolics)? This day versus night perspective is missing to highlight the relative importance and uniqueness of nighttime chemistry to plume evolution. Perhaps this could be added to Section 4.

Minor comments:

- Line 206: Did the other fire cases not run into near-background levels if run for 12 hours?
- Line 209: How is the 'earliest smoke transect' define? Shouldn't this be at 't=0'?
- Line 282: An average of all outside-plume data for a given fire or was a transect-specific background used instead? If the former, it should be pointed out that the background would be evolving as well.
- Section 2.3.3: I anticipate that similar modeling exercises will be executed to study the gas/particle evolution in wildfire plumes given the data generated by FIREX-AQ and other similar field campaigns focused on fires (e.g., WE-CAN). The paper could benefit from a flowchart that explains the iterative process of constraining dilution and chemistry.
- Line 324-328: How does this reactive nitrogen evolution compare to observations during the WE-CAN campaign (Juncosa Calahorrano, JGR, 2020)?
- Figure 2, 3, and elsewhere: As most of the changes in the absolute concentrations and reactivity are being driven by dilution/mixing with background, it's hard to see the role of chemistry on the trace gas evolution. Wouldn't it be better to present these data with respect to a chemically-inert tracer (e.g., as a ratio to dCO or dAcetonitrile)?
- Line 446: NO₂?
- Line 528: This suggests that the lifetime of phenolics during the night are likely to be much longer than those during the day. This day versus night distinction needs to be provided to communicate and quantify that the nighttime/dark chemistry is much slower than during the day.
- General question: would it be more appropriate to refer to phenolics as oxygenated aromatics? I am not trained as a chemist so I don't know the answer to that question.
- Section 3.3.2: The nitrophenolic oxidation products are presumably semi-volatile so they should partition into the particle phase to some degree. How does this affect the model-measurement comparisons shown (SI Figures 5-10)?
- SI Figure 3: Why were early CO values for WF1 not included to model dilution? What's happening with the low CO values around 1 hour of age for WF2?
- Figure 11: Can similar comparisons be done for the various NO_z species (other than the nitrophenolics) as undertaken for CO, NO, NO₂, etc. in Figure 2 and phenolics in SI Figures 5-10? It looks like some of the NO_z species were measured as per SI Table 1.