Comment on acp-2021-929
Anonymous Referee #1

Referee comment on "Photochemical Evolution of the 2013 California Rim Fire: Synergistic Impacts of Reactive Hydrocarbons and Enhanced Oxidants" by Glenn M. Wolfe et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-929-RC1, 2021

The authors use a 0-D puff model to investigate emissions and chemistry in a biomass burning plume from the Rim Fire observed during the SEAC4RS campaign. The time evolution of normalized excess mixing ratios (NEMRs) is constrained by observations of \( \text{O}_3 \), \( \text{NO}_x \), a large number of \( \text{NO}_y \) species, and a large number of VOC which help constrain \( \text{RO}_x \) chemistry. Six model cases are investigated with a particular focus on HONO, 1) using only observed species, 2) adding unobserved VOC based on lab studies, 3) adding HONO as a primary emission, 4) adding HONO via particular nitrate photolysis, 5) adding HONO via heterogeneous reaction of \( \text{NO}_2 \), and 6) a combination of 2,3, and 4. Implications for the representation of the investigated chemistry in other models are briefly discussed.

The work is scientifically sound and valuable as a thorough investigation of a case study and is generally well presented. My general comments are to better contextualize the case study, and to provide additional detail on the expanded VOC reactivity and the lack of \( \text{NO}_y \) closure and how the latter relates to the HONO additions investigated. I elaborate below.

The investigation of the case study could benefit from some contextualization and summarization. While there is extensive literature available on the SEAC4RS campaign and this flight, certain details should be made available to the reader in this work, e.g. how did the Rim Fire compare to other fires investigated during SEAC4RS? A single background period is chosen, how does this background compare with other observations? What was the fuel mix for the Rim Fire? In a similar vein a number of changes in background are inferred for a variety of species many of which are likely related, e.g. an increase in biogenic background after 2 hours, these can be challenging to keep track of; I would recommend a timeline or concise summary of such changes as a single reference rather than the current references to a variety of sections above and below.

Realizing that once constructed the Lagrangian age is the time axis used, I would also encourage caution when referring to observed changes as a function of age which are
attributed to fire variability. In some instances, age is used to refer to the evolution or the fire which is a separate time axis from the aging of emissions from a given point in time.

Figure 4c shows the large fraction of OH reactivity which arises from unmeasured species particularly aromatics. What is not clear is what fractions of the secondary species arise from these additional species. While the authors make a compelling case that the amount of “missing” OH reactivity cannot be explained by measurement error, it is not clear whether there are additional bounds on this from the modeling results. Understanding that the secondary VOC also changes due to the change in OH and other oxidants, can the authors offer some estimate of what fraction of the OH reactivity from secondary species is due to the unmeasured VOC?

Figure 3 shows that the observed NO\(_y\), which is nominally a conserved family as defined here, is reduced markedly with increased Lagrangian age. As the authors discuss it is unlikely that any of the component observations are sufficiently far off to explain the discrepancy and major unmeasured components such as HONO, HO\(_2\)NO\(_2\), and CH\(_3\)O\(_2\)NO\(_2\) are also unlikely to fill the gap leaving open the possibility of unknown NO\(_y\) reservoirs. The HONO sensitivity studies introduce mechanisms converting observed NO\(_y\) to unobserved NO\(_y\) (although it is quickly returned), which provides a useful reference for flux out of observed NO\(_y\). How do these compare with the observed rate of loss?

Peng et al., 2020 observed a rapid decline in the HONO NEMR in the first two hours, while Theys et al., 2020 observed a decrease in the HONO/NO\(_2\) ratio on a similar time scale. These ratios are introduced in Sect. 2.4.2 in this work already. HONO time evolution seems to be broadly consistent with both works, but is the trend in either ratio reproduced in this work?

For the pNO\(_3\) photolysis case, without a process to covert NO\(_y\) back to pNO\(_3\) and with pNO\(_3\) constrained to observations is this an unbounded production of gas-phase NO\(_y\)? Given the dominance of PN as a fraction of observed NO\(_y\), is this the principal reason for the reproduction or is HONO chemically particularly well suited to accomplish this? As noted above, the text seems to indicate that there is evidence for unknown NO\(_y\) reservoirs, is the failure of closure across different criteria in Sect. 3.4 indicative of that or unrelated?

Technical comments:

Line 127: Can the authors provide details on the optimized lag-correlation. What was the method, what was the cost function?

Line 130: Why a single WAS sample for background? What statistics does this provide? How does this background compare with other measurements from SEAC4RS?
Line 146: It would be helpful for reproducibility to know which algorithm was used to compute the geometric median, and to what precision.

Line 149: I assume the authors mean here when the back trajectory first intersected the fire which would be when the trajectory last intersected the fire. I suggest rewording for clarity.

Line 152: When was the wind measurement for the transit time estimate taken? At observation or at time of emission? Does the 1h transit time generally comport with the back trajectories?

Line 178: “age-dependent” here should be substituted with “time-dependent” or something similar. If I understand correctly I would reserve “age” for the evolution of the trajectories and not to refer to different times of emission to avoid confusion.

Line 204: It is written “Heterogeneous chemistry is explicitly included.” I assume there is a “not” missing as this is a paragraph on limitations of the model.

Line 222: Why report the fuel composition if it is not assessed? Can the authors provide any information relating to this?

Line 235: Can the authors provide some assessment of the bulk characteristics converting compounds using this method? e.g. total carbon, average molecular elemental composition.

Line 252: How is the pNO$_3^-$ at the start of the puff constrained? If I understand correctly this is nominally the fire, which observations are taken to correspond to this?

Line 266: The linear relation is valid for the period of the observations, but J$_{NO_2}$ should not be linear with SZA as a general rule especially near twilight. The value of J$_{NO_2}$ at sunrise is negative using the equation. Is this relation extrapolated back in the puff model to the time of emission, if so what is the nominal SZA at emission?

Line 268: Should the values <10$^{-6}$ not be substituted by 1×10$^{-6}$ based on eq. 4? When multiplying the rate by 1000, is this lower limit similarly scaled?
Line 344: CH$_3$CHO is not subscripted here.

Line 395: I would move Text S2 to main text above to support this statement regarding oVOC production.

Line 402-03: I do not understand what the sentence “After 12 h, 32% of M1-simulated OH reactivity is comprised of nearly 2200 species, mostly oxygenated VOC.” Is seeking to communicate.

Line 496: This estimate is also substantially smaller than that in Theys et al., 2020 do the same reasons apply?

Line 507: Avoid Ar for Aromatic reserve for argon