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Comment on acp-2021-742

Anonymous Referee #2

Referee comment on "Measurement report: Observations of long-lived volatile organic compounds from the 2019–2020 Australian wildfires during the COALA campaign" by Asher P. Mouat et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-742-RC2>, 2021

Mouat et al. report on measurements of volatile organic compounds measured by a PTR-ToF-MS in New South Wales, Australia during the COALA campaign. They analyzed measurements during the night time on a particular day to construct emission factors for ~20 VOCs and compared these against previous field measurements in two different biomes (Australia and US). They find that the EFs in this work had mixed agreement with EFs from earlier work.

Biomass burning is an important source of VOCs to the atmosphere and are likely to play a vital role in influencing the atmospheric composition and its impacts. Hence, the work is well motivated. The manuscript is well written and I appreciated that the article was short. While the measurements are well described, the analysis and findings – as described – have gaps that need to be better described and discussed. My major and editorial comments are listed below. Based on these, I do not recommend publication of this manuscript in Atmospheric Chemistry and Physics at the moment.

Major comment:

Basis for analysis - I have several basic questions around the rationale and choice of the primary methods for the analysis. For example, I am not sure I fully followed why the sunset to sunrise time was selected for analysis. While the concentrations measured right before sunrise on Feb 4 are likely to be the least affected by O₃ and OH driven oxidation chemistry (assuming most of the emissions are picked up during transport over the previous night), it is unlikely that the samples measured at sunset on the previous day on Feb 3 can be assumed to be unoxidized. The opposite would be true for oxidation via NO₃ although species that are oxidized by all 3 radicals (i.e., O₃, OH, and NO₃) would suffer from several layers of confounding, since the oxidant exposures are not known. A case in point is that the change in the maleic anhydride to furan ratio (Figure 3 top panel) to a lower value coincides with the shift in where the air parcels are coming from, questioning

the appropriateness to use this ratio to determine the level of aging in that air parcel. In fact, the ratio decreases even further around 3 am on Feb 4 indicating that the air parcel at or after 3 am might represent the freshest plume possible. That the authors do not directly account for oxidation of the direct emissions of the species measured and production from the oxidation of their precursors, further adds to my concern. For instance, aren't furans oxidation products of aromatic oxidation chemistry too? How is this accounted for? Another objection with this analysis is that it seems impractical to analyze these specific species concentrations to construct EFs and emissions ratios (ERs), given that the air parcel may have picked up emissions over 100s of kilometers from fires at very different stages of burning and varying environmental conditions and the air parcel studied would have very well mixed with other air parcels arising from different source regions. The primary problem is that the measurement site is too far from the source of the fires. I am not convinced that this dataset can be used to infer EFs and ERs in a robust manner and the mixed agreement with previous measurements from the same region is hence not surprising.

Minor comments:

- Abstract: It would be good to describe the comparisons with earlier work quantitatively. That way the reader can understand the difference between 'mixed' and 'good'.
- Page 1, line 28: Is there a reference newer than Liu et al. (2010)?
- Page 2, lines 41-43: Is there a mechanistic reason for higher EFs for these species in Australia?
- Page 3, line 82: What is the latest understanding on sampling artifacts for VOCs using PTFE tubing as a function of volatility, functional group, etc.?
- Figure 1: Show Sydney and Melbourne too to orient the reader who may not be familiar with that part of the world?
- Page 5, lines 110-117: I am not convinced that one can use the maleic anhydride to furan ratio to quantify the absence of oxidation for two reasons. Gkatzelis et al. (2020) measured these ratios (i) much closer to the fire than this work and (ii) were representative of emissions from western US fuels. Can you arrive at the same conclusion if you use other ways to assess oxidation, e.g., MEK+MVK:isoprene, toluene:benzene? Note that these may not be the right VOC ratios to be used in this work.
- Page 5, Line 133: To me both acetonitrile and furan seem to go up around the same time at approximately 18:00 hours on Feb 3. So, I don't agree with this opening sentence. Why can't the base acetonitrile level between 17:00 and 18:00 on Feb 3 be background?
- Page 5, lines 118-143: I think I understand (but disagree; see above) the OH argument made here. But I am not sure I followed the NO₃ argument. To me, the m/z 85 to furan ratio is relatively constant over the entire period shown. As pointed out earlier for the maleic anhydride to furan ratio, the dip in the m/z 85 to furan ratio comes about at 3 am on Feb 4.
- Figure 4(a): The slopes are different and decreasing with time suggesting acrolein is produced in the samples measured earlier? This doesn't seem to have been discussed in Section 5.2 clearly.
- Figure 4: Are there examples of species where the correlations with CO are much more scattered or segregated with time than the species shown in the main text? This could be instructive on where this method fails. This information would also be useful to include in the SI for all species.
- Sections 5.2-5.3: To me, there needs to be a discussion of what the background

concentrations of these species are and its variability when the air parcel being sampled is not influenced by biomass burning. Also, why are the data not corrected for background concentrations?

- Table 1: Can these data be compared to laboratory studies and what could be learned from that comparison? Recent examples include Stockwell et al. (ACP, 2015), Hatch et al. (ACP, 2018), Koss et al. (ACP, 2018), and Sekimoto et al. (ACP, 2018). Can MCE explain differences in the EFs between this and earlier work? It would be good to also show these comparisons on a scatter or bar plot. Finally, could the dominant fuel be highlighted in this table across the different studies?
- Do the ERs between studies (compared in Table 1 and Section 5.3) align better if one used a different tracer instead of CO (e.g., acetonitrile)?
- Section 6: Do the effective EFs for the other more reactive species measured by the PTR-ToF-MS conclusively show the role of oxidation during day and night?