

Interactive comment on “Gas-Phase Pyrolysis Products Emitted by Prescribed Fires in Pine Forests with a Shrub Understory in the Southeastern United States” by Nicole K. Scharko et al.

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Responses to Referee Comments for ACP 2019 Referee #1 Referee Comments: In general I find this a well-written paper with no major issues. The methodology is appropriate and the data are presented in a well organised way. The analysis is straightforward. The paper adds to the body of work reporting VOC composition from fires in a non-laboratory setting, and should be especially useful to operators of FTIR. I have only a few comments and suggestions listed below. Supplementary materials were referenced in the manuscript but are not accessible online. The paper would benefit from

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a tighter definition of the specific fire process being targeted, especially the distinction between pyrolysis and the flaming stage. I don't have a good sense of how important the pre-flame pyrolysis emissions are compared to total emissions from a fire. Do the authors have a metric of what fraction of VOCs (or OH reactivity) is emitted in this process?

Author Comments: We thank the referee for their suggestions to improve the introduction of the paper, specifically the importance between pyrolysis and flaming stages. Also due to the suggestions of the 2nd referee, the introduction is now being heavily revised. We have made changes to the manuscript to reflect the distinction of the phases and the target fire process. With regards to the referee's comment about the supplemental section, the paper has been revised such that no supplemental material is called out in the body of the paper.

Referee Comments: Line 220: What is the OPAG CO detection limit?

Author Comments: We thank the referee for their inquiry of the OPAG's detection limit for CO. Unfortunately, the detection limit for CO measured at 2 cm⁻¹ resolution was approximately 100-500 ppm for a ca. one minute average in a non-optimized configuration. This was due to the moderate CO band strength coupled with interferences from N₂O and CO₂, but also due to alignment issues and light scattering due to smoke.

Referee Comments: Section 3.1: Since many VOCs were measured during this study, a more robust method of estimating high vs. low pyrolysis fraction could be to fit the entire VOC profiles in ppb provided in Sekimoto et al. 2018 to the measured species. It could also be helpful to compare the overall VOC profile measured here to the high-temperature pyrolysis profile.

Author Comments: We appreciate the referee's comments regarding VOC profiles and high temperature pyrolysis. However, while the IR technique described here identified five new compounds via IR for the first time, including five new VOCs, we believe the IR method provides neither a sufficient number of species nor an extended time profile so

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as to provide a broad enough data set from which high and low temperature fractions can be accurately estimated. We suggest combining the IR data with other techniques, e.g. GC and PTR-MS to derive a more expanded profile and more meaningful profile analysis. Such an analysis is beyond the scope of the present paper.

Referee Comments: Table 2: MCE is not reported in the table although it is in the table title.

Author Comments: Per the referee's suggestion, we have updated the table title accordingly.

Referee Comments: Figure 3: The reported mixing ratio (parts-per-thousand) seem excessively high, have similarly high mixing ratios ever been reported previously in the outdoor environment?

Author Comments: The reviewer is correct that most of the mixing ratios seen in Figure 3 are indeed high values, but only three of them actually achieve the parts-per-thousand level. Still, we agree the values are high but they are all for unoxidized hydrocarbon species and we think this is part of what makes this paper unique in that we have captured several hydrocarbon species whose high concentrations may be indicative of the early phases of burning, pyrolysis in particular.

Referee Comments: Figure 5: I'm not sure this figure adds anything to the paper and it could be removed. What do the colours indicate?

Author Comments: We thank the referee for this comment and are happy to clarify. The referee is completely correct in that the data in Figure 5 are somewhat redundant to the data in Table 2. Moreover, the color coded bars are basically superfluous but are added only for (gratuitous?) differentiation. However, we believe the figure does add value for the following reasons: (1) We think it wise to retain the figure to include the molecular structures of the effluents as many of the readers may be non-chemists and as such the structures could be useful; (2) To clearly show that it is the mostly the

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lighter alcohols and aldehydes that are predominant species found in the early stage (pyrolysis) emissions, vis-à-vis the aromatics and carboxylic acids which have lower emissions ratios, and (3) the visualization of the standard deviation does graphically emphasize the relatively large uncertainties.

Referee Comments: Line 484: What is meant by secondary reactions? Photolysis or reaction with OH? Or further pyrolysis reaction? Gilman et al. 2015 and Koss et al. 2018 are laboratory studies, so atmospheric reaction seems unlikely. What reaction could reduce the level of naphthalene a factor of 10 on the timescale of a laboratory study? Or is the reduction in ER an effect of elevated CO in the other studies?

Author Comments: We thank the referee for these comments. To clarify, what was meant here are not photolysis or OH-oxidation reactions, but rather additional ring-forming (Diels-Alder) type reactions that lead to larger polyaromatics e.g. anthracene and the like.

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