

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.

Anonymous Referee #2

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General Comments:

This is interesting work attempting to identify and quantify emissions specifically from the “pyrolysis process” preceding combustion from a prescribed fire. Trace gases were sampled using canisters and quantified offline by FTIR. Emission ratios and emission factors were calculated and compared to a few previous publications. The authors use Sekimoto et al. 2018’s ratio of ethyne to furan along with reporting higher ERs for several species compared to other studies as evidence that there was selective sampling of high-temperature pyrolysis emissions. Altogether, this is insufficient evidence that

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pyrolysis-only emissions were selectively captured by the custom sampling device. It is unclear how this body of work is useful to modelers as pyrolysis products are only part of the total fire emissions necessary to accurately model fire. While it does little to inform us about best practices for prescribed burn conditions, it is an interesting attempt to isolate pyrolysis compounds in an “uncontrolled” real-world setting, however, there are entire journals (e.g. Journal of Analytical and Applied Pyrolysis, Fuel, etc.) dedicated to identifying the chemical products from pyrolysis. There is insufficient motivation for why this data is useful and the authors have not made a strong case for publication. It is likely these partial fire results have a strong potential to mislead or confuse the casual reader.

Specific comments in no particular order:

(1) In the introduction, a lot of emphasis is placed on the importance of identifying and quantifying biomass burning emissions for model predictions, which guide best practices for prescribed burning conditions. Additionally, the authors highlight the complexities of fires and emission dependencies on fuel types, burn techniques, geometry, etc., however, there isn’t proper support/justification for why measurements of just the pyrolysis emissions is vital for these sorts of model predictions or for analyzing burn techniques. A more “realistic” set of emission factors is obtained following combustion as many of the products measured during “pyrolysis only” will likely be consumed and/or combusted in the flame at higher temperatures resulting in different chemical products.

(2) The introduction is quite long and needs to remain more focused. It covers everything including downwind formation measured by FTIR to a significant discussion of MCE. It may be useful to rearrange and focus the introduction on motivation and important background considerations of FTIR sampling and pyrolysis measurements and move MCE discussions later in the manuscript.

(3) P4 L 80 There is some discussion in the introduction about the importance of

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prescribed burning and here the authors reference the necessity to understand burn conditions to minimize gases released during prescribed burns. It may be persuasive to highlight Liu et al., 2017, which provides clear evidence that the PM emitted from a wildfire is much greater than that for a controlled prescribed burn. While the authors have steered clear of PM discussion, this still highlights some major differences observed between the two. It may also be useful to highlight some of the differences between a prescribed burn versus a wildfire in terms of fuel consumption as well as considerations on meteorological and fuel moisture conditions. Liu, X., et al. (2017), Airborne measurements of western U.S. wildfire emissions: Comparison with prescribed burning and air quality implications, *J. Geophys. Res. Atmos.*, 122, 6108–6129, doi:10.1002/2016JD026315

(4) P4 L 89 It is incorrectly stated that pyrolysis is the “first step” in the burning process. Initially there is evaporation of water and other gases absorbed to the solid fuel (distillation), then once the temperature gets high enough to break bonds in the solid fuel both organic aerosol and non-methane organic gases are given off (pyrolysis) and this flammable mixture serves as the airborne fuel that can be rapidly oxidized. Some of the pyrolysis products are processed in the flame to CO₂ and BC, however, much of it escapes unoxidized. Entrainments of unoxidized pyrolysis products in smoke naturally falls within definition of smoldering combustion (McKenzie et al., 1995). It might be useful to provide some detail and description of these various processes. It is also important to note that “smoldering” is a complex mixture of multiple processes. For instance, P16 L 308 the authors suggest they aren’t measuring products from smoldering combustion, however, distillation, glowing, and pyrolysis are often grouped into smoldering combustion, therefore where is the evidence you are measuring pyrolysis only? McKenzie, L. M., W. M. Hao, G. N. Richards, and D. E. Ward, Measurement and modeling of air toxins from smoldering combustion of biomass, *Environ. Sci. Technol.*, 29, 2047 – 2054, 1995.

(5) The goal was to sample before the flame front, though it is likely that glowing com-

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bustion is also hot enough to drive pyrolysis. Additionally, the high heat release rate associated with flaming combustion likely pyrolyzes more fuels and there is often a peak in pyrolysis products before, during, or shortly after the peak in flaming product. Here the authors are likely probing only a portion of the pyrolysis products as sampling preceded the flame front only. There was no attempt to sample pyrolysis products escaping oxidation in the cool flame interiors or following the flame front. Thus, the “pyrolysis products” measured are likely biased/limited to products specifically sampled during the flame front sampling, and it has been shown in other work that pyrolysis mostly occurs after the flame front driven by the heat of glowing (Yokelson et al. 1996). For these reasons, how representative are the pyrolysis emissions measured here?

Yokelson, R. J., D. W. T. Griffith, and D. E. Ward, Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, *J. Geophys Res.*, 101, 21,067 – 21,080, 1996.

(6) It doesn’t appear as though there is any temperature data available, thus how can the authors distinguish between “low-temperature” and “high temperature” pyrolysis? The assignment is purely qualitative. Figure 1 only shows temperatures up to 170C. We’d expect in an oxygen-rich environment the biomass is readily ignited around 500-600C, therefore most “high temperature” pyrolysis experiments are performed in a N₂-atmosphere and more accurately report pyrolysis specific compounds. Determining and quantifying pyrolysis products across a range of temperatures and fuels would have been more useful by heating fuels in a laboratory where the FTIR could instead sample directly.

(7) There is some discussion about spectral regions used and MALT conditions, however, there is no discussion concerning the uncertainty and LODs of your measurements. While much of this may be discussed in Scharko et al. 2018, there still needs to be some information provided in this manuscript.

(8) The detection limits of 12 ppm for acetaldehyde described in the companion paper

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on this technique are not sensitive enough for most real-world smoke. Do the high LODs of other compounds prevent their detection in this work?

(9) Similar to whole air sampling canister-based measurements, there needs to be some discussion about the losses of compounds to the walls of the canister, compounds reacting away, as well as gases formed. Could this account for the higher ERs of alkenes such as ethyne? There is a brief mention of wall losses of NH₃, and I suspect this is the major reason no ammonia was measured in this study. The authors incorrectly state that the absence of NH₃ supports the fact that low-temperature pyrolysis and/or smoldering isn't measured in this study. It would be useful to cite other FTIR measurements and discussions of ammonia wall losses as well as the potential wall losses of other "sticky compounds" (Stockwell et al., 2014; Yokelson et al., 2003). Yokelson, R. J., Christian, T. J., Bertschi, I. T., and Hao, W. M.: Evaluation of adsorption effects 10 on measurements of ammonia, acetic acid, and methanol, *J. Geophys. Res.*, 108, 4649, doi:10.1029/2003JD003549, 2003.

(10) How useful is calculating an emission factor, considering the definition of EF is the amount of a compound emitted per unit of dry fuel consumed? If measurements only probe the beginning of the process before any combustion has occurred, then the fuel has not been completely consumed. Does this complicate the use of EFs and the assumptions about the amount of carbon consumed considered in the emission factor calculation?

(11) P13 L 249 – The authors mention the atmospheric chemistry effects of "total gases emitted during the burns" being the motivation for calculating OH reactivities, however, this is not really an accurate statement as this manuscript is only measuring pyrolysis products preceding combustion. More realistic EFs would be calculated from fire-integrated EFs. Is there other motivation for including a section in the manuscript on OH reactivity?

(12) Eqn 4: Sekimoto et al., 2018 hasn't shown how effective the use of these two

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proxies are for real-world fires and the equation was designed to predict total VOC emissions. Using this equation to justify sampling of "high temperature" pyrolysis is not supported. Additionally, in Figure 2 how have the authors decided to compare to these particular studies? Would it be more useful to compare to other field studies, instead of using so many laboratory fire-integrated emissions? It may be useful to focus on field studies with similar fuel types or similar burn conditions (e.g. Yokelson et al 2013, Akagi et al., 2013 "late EFs" calculated for smoldering combustions, Bertschi et al., 2003 samples residual smoldering combustion).

(13) How did the authors ensure they weren't getting flaming products from fire-driven flow? C₂H₂ has been observed to increase with increasing MCE (Burling et al., 2011; Yokelson et al 2008) and it's been noted as a "flaming" compound previously. I understand it can also be produced from smoldering combustion, but what makes the author's certain they are capturing pyrolysis produced C₂H₂?

(14) It is unclear how useful some of the tables and figures are. The comparisons to previous work seems arbitrary. Some justification for how studies were selected for comparisons are needed.

Technical corrections:

P2 L 39 Should be "biomass burning emissions"

P3 L 54 More up-to-date citations could be helpful here

P3 L 71 Similar to specific comment (2): There is some detailed discussion about the downwind changes in fire emissions measured by FTIR. It's not entirely clear why this is relevant in the discussion as no downwind smoke is measured in this study.

P4 L 84 & L 86 I don't think "hotter" and "cooler" is proper terminology. There is quite a range in temperatures in a fire, both in the flame itself and throughout the fuel bed, thus hotter/cooler are relative terms.

P4 L 86-87 It might be worth mentioning more OVOCs from smoldering combustion at

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lower MCE

P6 L 126 “attempts to ensure” Please change this phrasing, it is confusing.

P10 L 182 I don’t understand the “aliquots”- Does this mean samples in the same canister were all taken from different areas at different times?

P11 L 204 I’m confused about your H₂O and CO₂, this wording implies that you did not actually measure these species, though I’m assuming that instead the authors used different spectral regions that weren’t optically saturated as values are reported for these compounds later on?

P11 L 212- Instead of relative to any “known gas” it should be relative to a co-emitted, long-lived species. Some discussion to describe that CO and CO₂ can be generated during glowing, pyrolysis, and flaming would be useful.

P11 L 216- The background levels of both CO and CO₂ likely changed as fuels were burned in the area. I noticed several burns occurred in time fairly close together, but it is not clear whether the authors took into account the possibility of a changing background or if a constant background was assumed. I believe it is the latter, but this likely adds uncertainty to the ERs.

P11 L224- The authors state these are discrete ERs, however, it seems as though there are several samples in the same canister taken from various areas at various times, “aliquots” as they are described. Because of these sampling preferences, is this really a “discrete” sample and how comparable are these to other more traditional grab “snapshot” samples generally seen when sampling with canisters?

P12 L 230 also reference Ward and Radke, 1993 Ward, D. E., and L. F. Radke, Emissions measurements from vegetation fires: A comparative evaluation of methods and results, in *Fire in the Environment: The Ecological, Atmospheric and Climatic Importance of Vegetation Fires*, edited by P. J. Crutzen and J. G. Goldammer, pp. 53 – 76, John Wiley, New York, 1993

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P12 L 243- Stockwell et al. 2015 found these underestimates can be higher for certain fuel types Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 845–865, <https://doi.org/10.5194/acp-15845-2015>, 2015

P13 L 260 This first sentence is not entirely accurate. The combustion efficiency equation is designated to describe combustion chemistry and Sekimoto shows that MCE doesn’t necessarily describe their VOC emission profiles. It is true that MCE does not correlate with products as well for pure smoldering, especially for grab samples or in real time, because the same MCE may characterize different white smoke/glowing ratios. MCE is most useful when there is a range of flaming/smoldering as is common in most real-world fires, however, this is not the case in this manuscript.

P16 L308- The authors state: “the lower MCE values do not represent the fire burning in the smoldering stage” This is an unsupported claim and as I mentioned earlier smoldering is a grab bag for various processes that include distillation, glowing, and pyrolysis.

P16 L 311 This may be a good area to mention fire-driven flow

P17 Figure 2: where are the study average MCEs?

P18 L 336- What was the range of CO₂ emissions? If only a narrow spread, this might explain the lower correlation coefficients for something like C₂H₂ with CO₂.

Table 3. Stockwell et al 2015 has a more complete list of compounds measured including acetaldehyde, acetone, etc. Stockwell, C. E., Veres, P. R., Williams, J., and Yokelson, R. J.: Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution proton-transfer-reaction time-of-flight mass spectrometry, *Atmos. Chem. Phys.*, 15, 845-865, <https://doi.org/10.5194/acp-15-845-2015>, 2015.

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P29 L 531 The fuel type and N-composition certainly influences HCN emissions, however, it is random to highlight Indonesian peat here, this is a very unique fuel type and peat burns by smoldering combustion only, thus it follows that the fuel N is biased towards HCN rather than flaming products such as NO_x. Not sure it is worth mentioning in this manuscript.

P31 L 555 The authors argue NH₃ is only present in the smoldering phase. I'd argue you did measure some smoldering combustion and the most likely for no NH₃ detection is wall losses in the canisters as I discussed in specific comment (9).

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-174>, 2019.